DNC/HNC and N$_2$D$^+$/N$_2$H$^+$ ratios in high-mass star-forming cores

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ABSTRACT

Chemical models predict that the deuterated fraction (the column density ratio between a molecule containing D and its counterpart containing H) of N$_2$H$^+$, $D_{\text{frac}}$(N$_2$H$^+$), high in massive pre-protostellar cores, is expected to rapidly drop by an order of magnitude after the protostar birth, while that of HNC, $D_{\text{frac}}$(HNC), remains constant for much longer. We tested these predictions by deriving $D_{\text{frac}}$(HNC) in 22 high-mass star-forming cores divided in three different evolutionary stages, from high-mass starless core candidates (HMSCs, eight) to high-mass protostellar objects (HMPOs, seven) to ultracompact H ii regions (UCHIIs, seven). For all of them, $D_{\text{frac}}$(N$_2$H$^+$) was already determined through IRAM 30 m Telescope observations, which confirmed the theoretical rapid decrease of $D_{\text{frac}}$(N$_2$H$^+$) after protostellar birth. Therefore, our comparative study is not affected by biases introduced by the source selection. We have found average $D_{\text{frac}}$(HNC) of 0.012, 0.009 and 0.008 in HMSCs, HMPOs and UCHIIs, respectively, with no statistically significant differences among the three evolutionary groups. These findings confirm the predictions of the chemical models, and indicate that large values of $D_{\text{frac}}$(N$_2$H$^+$) are more suitable than large values of $D_{\text{frac}}$(HNC) to identify cores on the verge of forming high-mass stars, likewise what was found in the low-mass regime.

Key words: molecular data – stars: formation – ISM: molecules – radio lines: ISM – submillimetre: ISM

1 INTRODUCTION

The process of deuterium enrichment in molecules from HD, the main reservoir of deuterium in molecular clouds, is initiated by three exothermic ion–molecule reactions (e.g. Millar, Bennett & Herbst 1989):

\[ \text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 \ , \]
\[ \text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2 \ , \]
\[ \text{C}_2\text{H}_5^+ + \text{HD} \rightarrow \text{C}_2\text{HD}^+ + \text{H}_2 \ . \]

Since the backward reactions are endothermic by 232, 390 and 550 K, respectively, in cold environments [e.g. $T_{\text{kin}} \lesssim 20$ K for reaction (1)], they proceed very slowly, favouring the formation of deuterated ions. Moreover, the freeze-out of CO and other neutrals, particularly relevant in high-density gas ($n_{\text{H}_2} \gtrsim 10^6$ cm$^{-3}$), further boosts the deuteration process (e.g. Bacmann et al. 2003; Crapsi et al. 2005; Gerin et al. 2006). Therefore, in dense and cold cores, the deuterated fraction, $D_{\text{frac}}$, defined as the abundance ratio between a deuterated molecule and its hydrogenated counterpart, is expected to be much higher than the average [D/He] interstellar abundance (of the order of $10^{-5}$; Oliveira et al. 2003; Linsky et al. 2006). Because of the changes in physical and chemical properties of a star-forming core, its $D_{\text{frac}}$ is expected to change with the evolution too. Specifically, $D_{\text{frac}}$ is predicted to increase when a pre-protostellar core evolves towards the onset of gravitational collapse as the core density profile becomes more and more centrally peaked (due to the temperature decrease at core centre; e.g. Crapsi et al. 2007), and then it drops when the young stellar object formed at the core centre begins to heat its surroundings (see e.g. Caselli et al. 2002).

While this net drop in $D_{\text{frac}}$ before and after the protostellar birth in $D_{\text{frac}}$(N$_2$H$^+$) is clearly observed in both low-mass (Crapsi et al. 2005; Emprechtinger et al. 2009) and high-mass (Chen et al. 2011; Fontani et al. 2011) star-forming cores, other species show deviations from this general scenario. For example, DNC is produced in the gas from the same route reaction as N$_2$D$^+$, namely reaction (1), so that $D_{\text{frac}}$(HNC) and $D_{\text{frac}}$(N$_2$H$^+$) are expected to vary similarly with temperature (Turner 2001). However, Sakai et al. (2012) have measured $D_{\text{frac}}$(HNC) in a sample of 18 massive cores including both infrared-dark starless cores and cores harbouring high-mass protostellar objects (HMPOs), and found that $D_{\text{frac}}$(HNC) in the...
starless cores is only marginally higher than that measured in the protostellar cores. This ‘anomaly’ could be explained by the fact that the destruction processes of \( \text{N}_2\text{D}^+ \) are much faster than those of DNC: being an ion, \( \text{N}_2\text{D}^+ \) can recombine quickly (few years) with CO and/or electrons, while the neutral DNC has to be destroyed by ions (such as HCO\(^+\) and/or H\(^+\)) through much slower (10\(^5\)–10\(^6\) yr) chemical reactions (Sakai et al. 2012).

The chemical models of Sakai et al. (2012) are able to partially reproduce the observational results obtained by Fontani et al. (2011) and Sakai et al. (2012). We have performed chemical calculations similar to those in Sakai et al. (2012) and obtained the consistent results (see Section 4.2 for the details of our chemical model): the \( \text{N}_2\text{D}^+ / \text{N}_2\text{H}^+ \) ratio approaches ~0.1 during the cold pre-protostellar phase and drops quickly to ~0.01 after the protostellar birth because it is very sensitive to temperature growth (Fig. 1, panel a), while the DNC/HNC ratio remains relatively high (above ~0.01) even after a rapid temperature rise and decreases in time-scales of several 10\(^3\) yr. On the other hand, the \( \text{N}_2\text{D}^+ / \text{N}_2\text{H}^+ \) drops much more quickly, in less than 100 yr (Fig. 1, panel b). However, the different criteria adopted by Fontani et al. (2011) and Sakai et al. (2012) to select the targets do not allow for a consistent observational comparison between the two deuterated fractions, as well as between models and data.

In this paper, we report observations performed with the Nobeyama 45 m Telescope in the DNC and \( \text{HN}^{13}\text{C}(1–0) \) rotational transitions towards 22 high-mass cores harbouring different stages of the high-mass star formation process, in which \( D_{\text{gas}}(\text{N}_2\text{H}^+) \) was already measured through observations of the IRAM 30 m Telescope (Fontani et al. 2011). In this way, our study is not affected by observational biases possibly introduced by the source selection. The main aim of the work is to test in the same sample of objects whether the \( \text{N}_2\text{D}^+ / \text{N}_2\text{H}^+ \) and DNC/HNC ratios trace differently the thermal history of high-mass cores despite the similar chemical origin, as predicted by Sakai et al. (2012). The sample, selected as explained in Fontani et al. (2011), is divided in eight high-mass starless cores (HMSCs), seven HMPDs and seven ultracompact \( \text{H} \uparrow \) regions (UCHIIs), so that all main evolutionary groups of the high-mass star formation process are almost equally represented. We stress that all HMSCs, except IR22134-B, have been previously classified as ‘quiescent’ by Fontani et al. (2011) to distinguish them from ‘perturbed’ cores, in which external phenomena (passage of outflows, shocks, nearby infrared objects) can have affected significantly the physical–chemical properties of the gas, as discussed in Fontani et al. (2011).

In Section 2, we give an overview of the technical details of the observations; Section 3 presents the main observational results, which are discussed in Section 4, including a detailed comparison with chemical models. A summary of the main findings of the paper is given in Section 5.

### 2 OBSERVATIONS

The \( \text{HN}^{13}\text{C}(1–0) \) and DNC(1–0) transitions were observed with the NRO 45 m Telescope in May 2012 towards 22 out of the 27 cores already observed by Fontani et al. (2011) in \( \text{N}_2\text{D}^+(2–1) \) and \( \text{N}_2\text{H}^+(3–2) \). The source coordinates, as well as some basic properties of the star-forming regions where they are embedded [local standard of rest (LSR) velocity of the parental core, distance to the Sun, bolometric luminosity, \( D_{\text{gas}}(\text{N}_2\text{H}^+) \) as measured by Fontani et al. (2011)] are listed in Table 1. The two transitions were observed simultaneously by using the sideband-separating superconductor–insulator–superconductor receiver, T100 (Nakajima et al. 2008).

Some important spectroscopic parameters of the lines observed and the main technical parameters are listed in Table 2. The half-power beam width is about 21 and 18 arcsec at 76 [DNC (1–0)] and 87 GHz [\( \text{HN}^{13}\text{C}(1–0) \)], respectively, similar to the beam width of the IRAM 30 m Telescope at the frequency of the \( \text{N}_2\text{D}^+(2–1) \) line (~15 arcsec; Fontani et al. 2011). The main beam efficiency (\( \eta_{\text{MB}} \)) is 0.53 and 0.43 at 76 and 87 GHz, respectively. We derived the main beam temperature (\( T_{\text{MB}} \)) from the antenna temperature (\( T_A^* \)) by using the relation \( T_{\text{MB}} = T_A^*/\eta_{\text{MB}} \), where \( \eta_{\text{MB}} \) is the main beam efficiency (see Table 2). For all the observations, we used digital backends SAM45 (bandwidth = 500 MHz, frequency resolution = 122.07 kHz). The telescope pointing was checked by observing nearby SiO maser source every one to two hours and was maintained to be better than 5 arcsec. The line intensities were calibrated by the chopper wheel method. All the observations were carried out with the position switching mode.
Table 1. List of the observed sources. Columns 4–6 show the velocity at which we centred the spectra (corresponding to the systemic velocity), the source distance and bolometric luminosity of the associated star-forming region, respectively. The latter is a very rough first approximation of the core luminosity because it is based on infrared measurements having poor angular resolution. We adopt as source names those adopted by Fontani et al. (2011), who took them from the reference papers listed in column 7. For completeness, $D_{\text{IRC}}$(N$_2$H$^+$) derived by Fontani et al. (2011) for each core is given in column 8.

| Source | RA(J2000) ($^h$ $^m$ $^s$) | Dec.(J2000) ($^\circ$ $^\prime$ $^\prime\prime$) | $V_{\text{LSR}}$ (km s$^{-1}$) | $d$ (kpc) | $L_{\text{bol}}$ | Ref. | $D_{\text{IRC}}$(N$_2$H$^+$) |
|--------|--------------------------|-----------------------------|-----------------|--------|----------------|-----|----------------|
|        |                          |                             |                 |        |                |     |                 |
| HMSC   |                          |                             |                 |        |                |     |                 |
| I00117-MM2 $^a$ | 00:14:26.3 | +64:28:28 | $-$36.3 | 1.8 | $10^{3.1}$ | (1) | 0.32 |
| G034-G2(MM2) $^a$ | 18:56:50.0 | +01:23:08 | $+$43.6 | 2.9 | $10^{1.6}$ | (2) | 0.7 |
| G034-F2(MM7) $^a$ | 18:53:19.1 | +01:26:53 | $+$57.7 | 3.7 | $10^{1.9}$ | (2) | 0.43 |
| G034-F1(MM8) $^a$ | 18:53:16.5 | +01:26:10 | $+$57.7 | 3.7 | $-$ | (2) | 0.4 |
| G028-C1(MM9) $^a$ | 18:42:46.9 | $-$04:04:08 | $+$78.3 | 5.0 | $-$ | (2) | 0.38 |
| I20293-WC $^a$ | 20:31:10.7 | +40:03:28 | $+$6.3 | 2.0 | $10^{3.6}$ | (3) | 0.19 |
| I22134-G $^b$ $^a$ | 22:15:10.5 | $+$58:48:59 | $-$18.3 | 2.6 | $10^{4.1}$ | (5) | 0.023 |
| I22134-B $^b$ | 22:15:05.8 | $+$58:48:59 | $-$18.3 | 2.6 | $10^{4.1}$ | (5) | 0.09 |

| Source | RA(J2000) ($^h$ $^m$ $^s$) | Dec.(J2000) ($^\circ$ $^\prime$ $^\prime\prime$) | $V_{\text{LSR}}$ (km s$^{-1}$) | $d$ (kpc) | $L_{\text{bol}}$ | Ref. | $D_{\text{IRC}}$(N$_2$H$^+$) |
|--------|--------------------------|-----------------------------|-----------------|--------|----------------|-----|----------------|
|        |                          |                             |                 |        |                |     |                 |
| HMPO   |                          |                             |                 |        |                |     |                 |
| I00117-MM1 $^a$ | 00:14:26.1 | +64:28:44 | $-$36.3 | 1.8 | $10^{3.1}$ | (1) | $\leq$0.04 |
| I0809−1732 $^b$ | 18:11:51.4 | $-$17:31:28 | $+$32.7 | 3.6 | $10^{4.5}$ | (7) | 0.031 |
| 18517+0437 $^b$ | 18:54:14.2 | $+$04:41:41 | $+$43.7 | 2.9 | $10^{4.1}$ | (8) | 0.026 |
| G75-core $^a$ | 20:21:44.0 | +37:26:38 | $+$0.2 | 3.8 | $10^{8.8}$ | (9,10,18) | $\leq$0.02 |
| I20293-MM1 $^a$ | 20:31:12.8 | +40:03:23 | $+$6.3 | 2.0 | $10^{3.6}$ | (3) | 0.07 |
| I21307 $^a$ | 21:32:30.6 | +51:02:16 | $-$46.7 | 3.2 | $10^{3.6}$ | (11) | $\leq$0.03 |
| I23385 $^a$ | 23:40:54.5 | $+$61:10:28 | $-$50.5 | 4.9 | $10^{3.2}$ | (12) | 0.028 |

| Source | RA(J2000) ($^h$ $^m$ $^s$) | Dec.(J2000) ($^\circ$ $^\prime$ $^\prime\prime$) | $V_{\text{LSR}}$ (km s$^{-1}$) | $d$ (kpc) | $L_{\text{bol}}$ | Ref. | $D_{\text{IRC}}$(N$_2$H$^+$) |
|--------|--------------------------|-----------------------------|-----------------|--------|----------------|-----|----------------|
|        |                          |                             |                 |        |                |     |                 |
| UCHII  |                          |                             |                 |        |                |     |                 |
| G5.89-0.39 $^b$ | 18:00:30.5 | $-$24:04:01 | $+$9.0 | 1.28 | $10^{5.1}$ | (13,14) | 0.018 |
| I19035-0517 $^b$ | 19:00:01.5 | $+$06:46:35 | $+$32.4 | 2.2 | $10^{3.9}$ | (9) | 0.04 |
| 19410+2363 $^a$ | 19:43:11.4 | $+$23:44:06 | $+$22.4 | 2.1 | $10^{4.0}$ | (15) | 0.047 |
| ON1 $^a$ | 20:10:09.1 | $+$31:31:36 | $+$12.0 | 2.5 | $10^{3.3}$ | (16,17) | 0.017 |
| I22134-VLA1 $^a$ | 22:15:09.2 | $+$58:49:08 | $-$18.3 | 2.6 | $10^{3.1}$ | (9) | 0.08 |
| 23033+5951 $^a$ | 23:05:24.6 | +60:08:09 | $-$53.0 | 3.5 | $10^{4.0}$ | (15) | 0.08 |
| NGC 7538-IR5 $^a$ | 23:14:01.8 | +61:27:20 | $-$57.0 | 2.8 | $10^{4.6}$ | (6) | 0.030 |

| Transition | Rest frequency (GHz) | $E_u/k$ (K) | $\mu_0$ (D) | BW (MHz) | $\Delta v$ (kHz) | HPBW (arcsec) | $\eta_{MB}$ | $T_{sys}$ (K) |
|------------|---------------------|-------------|------------|--------|-----------------|---------------|----------|-------------|
| DNC (1−0)  | 76.305 727          | 3.66        | 3.05       | 40     | 37              | 21            | 0.53     | 0.25        |
| HN13C (1−0) | 87.090 850          | 4.18        | 3.05       | 40     | 37              | 18            | 0.43     | 0.15        |

3 RESULTS

3.1 Detection rates and line profiles

We have detected DNC (1−0) emission in: six out of eight HMSCs, three out of seven HMPOs and five out of seven UCHIIs. HN13C (1−0) has been detected towards all cores detected in DNC, except I00117-MM2, undetected in HN13C but detected in DNC (although a faint line at $-2.5\sigma$ rms level is possibly present in the spectrum). Therefore, the detection rate follows a trend with core evolution similar to the one observed in N$_2$D$^+$ by Fontani et al. (2011): its maximum is in the HMSC phase, then it decreases in the HMPO phase but does not decrease further in the later stage of UCHIIs. In Appendix A, available online, we show all spectra (Figs A1–A6). They have been analysed with the CLASS program, which is part of the GILDAS software$^1$ developed at the IRAM and the Observatoire de Grenoble.

$^1$ The GILDAS software is available at http://www.iram.fr/IRAMFR/GILDAS.
Both transitions have a hyperfine structure due to electric quadrupole interactions of nitrogen and deuterium nuclei. We tried to fit the observed spectral line profiles by considering these components through the command ‘method hfs’ into CLASS. However, given that the maximum separation between the components is 1.28 km s\(^{-1}\), the method failed. Due to this, and because the observed spectra typically show single-peaked profiles, the lines have been fitted with Gaussian functions. In Tables 3 and 4, we give the main parameters of the lines derived through Gaussian fits: integrated area \((\text{pk})\), full width at half-maximum \((\Delta v)\), peak temperature \((T_{pk})\) and 1σ rms of the spectrum.

Asymmetric profiles and hints of non-Gaussian high-velocity sources in the (1–0) line of the G034-F2, G028-C1, and G034-G2 are evident, while the (2–1) line seems Gaussian. In a systematic way, we see that many HMSCs have HN\(^{13}\)C(1–0) line widths in between 2 and 3 km s\(^{-1}\), i.e. almost twice the corresponding DNC(1–0) line widths. However, the low signal-to-noise ratio in the spectra, and the fact that the kinematics in the targets may be complex and due to the superimposition of several velocity components (as suggested by the deviations from the Gaussian line shape, see Section 3.1), could explain the different line widths of DNC and HN\(^{13}\)C in these sources.

A similar comparison between the DNC(1–0) line widths and those of the N\(_2\)D\(^{13}\)(2–1) transition detected by Fontani et al. (2011). Globally, DNC and HN\(^{13}\)C(1–0) have comparable line widths (left-hand panel in Fig. 2) regardless of the evolutionary stage of the cores. This global trend confirms that the two transitions arise from gas with similar turbulence, as already found in the massive star-forming cores studied by Sakai et al. (2012). Incidentally, we note that four HMSCs have HN\(^{13}\)C(1–0) line widths in between 2 and 3 km s\(^{-1}\), i.e. almost twice the corresponding DNC(1–0) line widths. However, the low signal-to-noise ratio in the spectra, and the fact that the kinematics in the targets may be complex and due to the superimposition of several velocity components (as suggested by the deviations from the Gaussian line shape, see Section 3.1), could explain the different line widths of DNC and HN\(^{13}\)C in these sources.

A similar comparison between the DNC(1–0) line widths and those of the N\(_2\)D\(^{13}\)(2–1) transition is shown in the right-hand panel of Fig. 2, for which a strong correlation is found (correlation coefficient \(r = 0.52\)). This time the DNC lines show a systematically smaller broadening not only in the HMSC group but also in the groups containing the more evolved objects. In this case, however, the reason could be also attributed to the fact that the two transitions require different excitation conditions: the (1–0) line traces gas colder, and hence more quiescent, than that associated with the emission of the (2–1) line.
3.3 Deuterated fraction of HNC

To derive \( D_{\text{frac}}(\text{HNC}) \) from the line parameters, we have adopted the same approach as in Sakai et al. (2012). First, we assume that the lines are optically thin. This is justified by both the shape of the lines (which do not have the flat-topped shape typical of high optical-depth transitions) and by the findings of Sakai et al. (2012) in similar objects. Secondly, given the similar critical density of the two transitions \((\sim 0.5 \times 10^9 \text{ cm}^{-3})\), we assume that their excitation temperatures and emitting regions, and thus the filling factors, are the same. Under these hypotheses, the column density ratio is given by (see Sakai et al. 2012)

\[
\frac{N(\text{DNC})}{N(\text{HN}^{13}\text{C})} \simeq 1.30 \exp \left( -\frac{0.52}{T_{\text{ex}}} \right) \frac{A_{\text{DNC}}}{A_{\text{HN}^{13}\text{C}}},
\]

where \( T_{\text{ex}} \) is the excitation temperature and \( A \) is the integrated area of the line (in \( T_{\text{MB}} \) units).

The method adopted to fit the lines does not allow us to derive directly \( T_{\text{ex}} \), for which a good fit to the hyperfine structure is needed. Therefore, in equation (4), as \( T_{\text{ex}} \) we have taken the kinetic temperatures given in Fontani et al. (2011, see their table 3) assuming that the lines are thermalized. These have been derived either directly from the \( \text{N}_2\text{H}^+ \) (3–2) transition or from NH\(_3\) measurements, and then extrapolated to \( T_k \) following Tafalla et al. (2004). In principle, the excitation temperature derived from \( \text{N}_2\text{H}^+ \) or NH\(_3\) can be different from that of the DNC and HN\(^{13}\text{C} \) (1–0) lines, but we stress that equation (4) shows that the column density ratio is little sensitive even to changes of an order of magnitude in \( T_{\text{ex}} \) (see also Sakai et al. 2012).

We have then converted \( N(\text{DNC})/N(\text{HN}^{13}\text{C}) \) into \( N(\text{DNC})/N(\text{HN}^{12}\text{C}) = D_{\text{frac}}(\text{HNC}) \) by calculating the \(^{13}\text{C}/^{12}\text{C} \) abundance ratio from the relation: \(^{13}\text{C}/^{12}\text{C} = 1/(7.5 \times D_{\text{frac}} + 7.6)\) (Wilson & Rood 1994), where \( D_{\text{frac}} \) is the source Galactocentric distance in kpc, and multiplying equation (4) by this correction factor. In Table 5, we list the column density ratio \( D_{\text{frac}}(\text{HNC}) \) for the cores observed and the physical parameters used to derive it as explained above: Galactic coordinates (longitude \( l \), latitude \( b \)), Galactocentric distance \((D_g)\), isotopic abundance ratio \(^{13}\text{C}/^{12}\text{C} \), \( A_{\text{DNC}} \), \( A_{\text{HN}^{13}\text{C}} \) and \( T_{\text{ex}} \).

4 DISCUSSION

4.1 \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) versus \( D_{\text{frac}}(\text{HNC}) \)

Table 5 shows that the HMSC group has the highest average \( D_{\text{frac}}(\text{HNC}) \) (mean value \( \sim 0.012 \), \( \sim 0.019 \) if one includes the lower limit on I00117-MM2). The HMPOs and UCHII groups have very similar average \( D_{\text{frac}}(\text{HNC}) \) (\( \sim 0.009 \) and \( \sim 0.008 \), respectively), but given the dispersion and the poor statistics, there are no significant statistical differences between the three groups. By comparing the observational data of this work and those of Fontani et al. (2011), we clearly note a different behaviour of \( D_{\text{frac}}(\text{HNC}) \) and \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) in high-mass star-forming cores: \( D_{\text{frac}}(\text{HNC}) \) does not change significantly going from the pre-protostellar phase to subsequent phases of active star formation, while \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) is smaller by an order of magnitude in the evolved phases (HMPOs and UCHIIIs) than in the pre-protostellar phase (HMSCs), and the latter evolutionary group is undoubtedly statistically separated from the other two (Fontani et al. 2011). We stress once more that these results, obtained towards the same clumps and with comparable telescope beam sizes, are not affected by possible biases introduced by the source selection.

In Fig. 3, we compare \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) and \( D_{\text{frac}}(\text{HNC}) \) measured in the cores observed in both \( \text{N}_2\text{D}^+ \) (Fontani et al. 2011) and DNC. As one can see, the sources with the largest \( D_{\text{frac}}(\text{N}_2\text{H}^+) \) tend to also have the largest \( D_{\text{frac}}(\text{HNC}) \), despite the different absolute magnitude especially in the HMSC group. In fact, the two parameters are slightly correlated, with a Kendall’s \( \tau \) rank correlation coefficient of \( \sim 0.36 \) (excluding lower and upper limits, which tend to reinforce the possible correlation though).

Figure 2. Left-hand panel: comparison between the line widths (full width at half-maximum derived from Gaussian fits) for DNC(1–0) and HN\(^{13}\text{C}(1–0)\). Only the sources detected in both lines are shown. Circles indicate HMSCs, squares HMPOs and triangles UCHIIIs. Right-hand panel: same as left-hand panel but the comparison is between DNC(1–0) and \( \text{N}_2\text{D}^+ \)(2–1).
The deuteration of both molecules increases similarly with time: this is due to the fact that the deuterium fractionation is initiated in both species by the same route reaction (i.e. H\(^+\)\(\rightarrow\)D\(^+\) + e\(^-\)).

4.2 \(D_{\text{frac}}(N_2H^+)\) and \(D_{\text{frac}}(HNC)\) versus chemical models

The results presented in Section 4.1 are consistent overall with the scenario proposed by the chemical models of Sakai et al. (2012): the N\(_2\)D\(^+\)/N\(_2\)H\(^+\) abundance ratio sharply decreases after the protostellar birth, while the DNC/HNC abundance ratio decreases more gradually and maintains for longer the high deuteration of the earliest evolutionary stages of the core. In this subsection, we compare the observational results with the model predictions in detail. We have solved the chemical rate equations with the state-of-the-art gas–grain reaction network of Aikawa et al. (2012). The model includes gas-phase reactions, interaction between gas and grains and grain surface reactions. The parameters for chemical processes are essentially the same as in Sakai et al. (2012), except for the binding energy of HCN and HNC; we adopt a binding energy of 4170 K for HCN (Yamamoto, Nakagawa & Fukui 1983), while a smaller value of 2050 K was used for those species in Sakai et al. (2012). We assume the binding energy of HNC to be the same as that of HCN. Species are initially assumed to be atoms (either neutrals or ions), except for hydrogen and deuterium, which are in molecular form. The elemental abundance of deuterium is set to \(3\times10^{-5}\) and \(13\)K, while those of HCN and HNC are essentially the same as in Sakai et al. (2012). We assume that the deuterated fractions of the HMSCs must be comparable to the time-scale of high-mass starless phase (3.7–10\(^5\) yr) estimated by the statistical study of Chambers et al. (2009), while Parsons, Thompson & Chrysostomou (2009) estimated it to be a few 10\(^{–5}\)–10\(^5\) yr.

A comparison between model predictions and observational results is illustrated in Fig. 4. In our model, in the pre-protostellar stage \((T\approx 15\ \text{K})\), the deuteration of both molecules increases similarly with time: this is due to the fact that the deuterium fractionation is initiated in both species by the same route reaction (i.e. H\(^+\)\(\rightarrow\)D\(^+\) + e\(^-\)), as mentioned in Section 1. On the other hand, if we assume that the deuterated fractions of the HMSCs must be compared with the model predictions before the temperature rise, i.e. before \(T\approx 10^5\) K, the measured \(D_{\text{frac}}(\text{HNC})\) and \(D_{\text{frac}}(N_2H^+)\) cannot be reproduced simultaneously in a single model: \(D_{\text{frac}}(\text{HNC})\) can be well reproduced with \(n_{\text{H}_2} = 10^5\ \text{cm}^{-3}\), while \(D_{\text{frac}}(N_2H^+)\) is reproduced with \(n_{\text{H}_2} = 10^5\ \text{cm}^{-3}\). This discrepancy could indicate

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**Table 5.** Parameters used to derive the deuterated fraction, \(D_{\text{frac}}(\text{HNC})\), as explained in Section 3.3.

| Core                  | \(l\) (°) | \(b\) (°) | \(D_{\text{frac}}\) (kpc) | \(^{13}\text{C}^{12}\text{C}\) | \(A_{\text{DNC}}\) (K km s\(^{-1}\)) | \(A_{\text{HNC}}\) (K km s\(^{-1}\)) | \(T_{\text{exc}}\) (K) | \(D_{\text{frac}}(\text{HNC})\) |
|-----------------------|------------|------------|-----------------------------|-------------------------------|--------------------------------------|--------------------------------------|--------------------------|-------------------------------|
| HMSC                  |            |            |                             |                               |                                      |                                      |                          |                               |
| I00117-MM2            | 2.082      | 0.037 06   | 9.5                         | 79                            | 0.20                                 | \(\leq 0.14\)                       | 14                       | 0.008                         |
| G034-F2(MM7)          | 0.6071     | 0.005 093  | 5.9                         | 52                            | 0.38                                 | 1.05                                | 17                       | 0.009                         |
| G034-F1(MM8)          | 0.6068     | 0.005 021  | 5.9                         | 52                            | 0.23                                 | 0.52                                | 17                       | 0.011                         |
| G034-G2(MM2)          | 0.6132     | 0.0192     | 6.4                         | 55                            | 0.53                                 | 0.87                                | 17                       | 0.014                         |
| G028-C1(MM9)          | 0.5004     | 0.008 629  | 4.8                         | 43                            | 0.58                                 | 1.69                                | 17                       | 0.010                         |
| I20293-WC             | 1.384      | 0.003 144  | 8.4                         | 70                            | 0.47                                 | 0.42                                | 17                       | 0.02                          |
| I22134-B              | 1.819      | 0.033 83   | 9.5                         | 79                            | \(\leq 0.14\)                       | 0.09                                | 17                       | \(\leq 0.025\)                |
| I22134-G              | 1.819      | 0.033 73   | 9.5                         | 79                            | \(\leq 0.14\)                       | 0.35                                | 25                       | \(\leq 0.006\)                |
| HMPO                  |            |            |                             |                               |                                      |                                      |                          |                               |
| G5.89−1732            | 0.231      | 0.001 963  | 5.1                         | 46                            | 0.43                                 | 1.96                                | 38                       | 0.006                         |
| 18517+0437            | 0.6592     | 0.017 45   | 6.5                         | 56                            | 0.43                                 | 0.79                                | 43                       | 0.0125                        |
| G7-core               | 1.329      | 0.002 301  | 8.4                         | 71                            | \(\leq 0.19\)                       | 0.43                                | 96                       | \(\leq 0.008\)                |
| I20293-MM1            | 1.385      | 0.003 035  | 8.4                         | 70                            | 0.21                                 | 0.52                                | 43                       | 0.008                         |
| I23385                | 2.005      | 0.006 124  | 11.5                        | 94                            | \(\leq 0.19\)                       | 0.15                                | 43                       | \(\leq 0.017\)                |
| UCHII                 |            |            |                             |                               |                                      |                                      |                          |                               |
| G5.89−1732            | 0.1088     | 0.017 43   | 7.2                         | 62                            | 0.72                                 | 4.64                                | 26                       | 0.003                         |
| I19035-VLA1           | 0.7151     | 0.011 13   | 7.0                         | 60                            | 0.29                                 | 0.54                                | 39                       | 0.011                         |
| 19410+2336            | 1.05       | 0.005 147  | 7.7                         | 65                            | 0.36                                 | 0.90                                | 21                       | 0.008                         |
| ON1                   | 1.22       | 0.021 77   | 8.0                         | 68                            | 0.40                                 | 1.37                                | 26                       | 0.006                         |
| I22134-VLA1           | 1.819      | 0.033 83   | 9.5                         | 79                            | \(\leq 0.16\)                       | 0.18                                | 47                       | \(\leq 0.014\)                |
| 20303+5951            | 1.928      | 0.001 401  | 10.3                        | 85                            | 0.39                                 | 0.54                                | 25                       | 0.011                         |
| NGC 7538-IRS 9        | 1.953      | 0.015 93   | 9.9                         | 82                            | \(\leq 0.16\)                       | 0.57                                | 26                       | \(\leq 0.004\)                |

\(a\) assumed equal to the gas kinetic temperature listed in Table A.3 of Fontani et al. (2011).
that the observed lines of DNC (and HN\textsuperscript{13}C) arise from regions that, on average, are less dense than those responsible for the emission of N\textsubscript{2}D\textsuperscript{+} (and N\textsubscript{2}H\textsuperscript{+}). In fact, the observational parameters are averaged values measured over slightly different angular regions (∼21 arcsec for DNC and ∼16 arcsec for N\textsubscript{2}D\textsuperscript{+}), so that the emission seen in DNC could be more affected than that seen in N\textsubscript{2}D\textsuperscript{+} by the contribution from the low-density envelope surrounding the dense cores, where the deuterium fractionation is expected to be less important. This can explain why the model with lower average gas density can reproduce \(D_{\text{frac}}(\text{HNC})\), but not \(D_{\text{frac}}(\text{N}_2\text{H}^+)\), for which a higher average gas density is needed. Another possibility is that we are missing something in the current chemical model. For example, we do not consider the ortho state of hydrogen molecules in this work. The presence of ortho-H\textsubscript{2} suppresses the deuteration process of molecules, since the internal energy of ortho-H\textsubscript{2} helps to overcome the endothermicity of reaction (1) in the backward direction (Flower, Pineau des Forêts & Walmsley 2006). If we consider ortho-H\textsubscript{2}, however, both the DNC/HNC and N\textsubscript{2}D\textsuperscript{+}/N\textsubscript{2}H\textsuperscript{+} abundance ratios would be lowered.

Inspection of Fig. 4 also shows that an average \(D_{\text{frac}}(\text{N}_2\text{H}^+) \geq 0.2\) in a starless core with \(n_{\text{H}_2} = 10^4\ \text{cm}^{-3}\) is reached at a time close to ∼10\textsuperscript{5} yr. Assuming this as the time necessary for the starless core to collapse, as suggested by Chambers et al. (2009), this means that only cores relatively close to the onset of gravitational collapse, i.e. the so-called pre-stellar cores, can give rise to the observed high values of \(D_{\text{frac}}(\text{N}_2\text{H}^+)\). This behaviour is in agreement with the predictions of chemical models including also the spin states of the H\textsubscript{2} and H\textsubscript{3} isotopologues (Kong et al. 2013), in which levels of \(D_{\text{frac}}(\text{N}_2\text{H}^+)\) larger than 0.1 are possible only in cores older than ∼10\textsuperscript{5} yr. Models with higher average density (∼10\textsuperscript{6} cm\textsuperscript{-3}) can reproduce such high deuterated fractions in shorter times, but these average densities are not realistic to represent regions with angular sizes of ∼16 arcsec, like those that we have observed.

In the protostellar stage (\(T = 40\) K), the N\textsubscript{2}D\textsuperscript{+}/N\textsubscript{2}H\textsuperscript{+} abundance ratio sharply decreases in time-scale of ∼10\textsuperscript{2} yr, while the DNC/HNC abundance ratio decreases in ∼10\textsuperscript{4} yr both in the model with \(n_{\text{H}_2} = 10^4\ \text{cm}^{-3}\) and in that with \(10^5\ \text{cm}^{-3}\). Again,
the measured $D_{\text{frac}}(\text{HNC})$ is better reproduced by the model with $n_{\text{H}_2} = 10^4 \text{ cm}^{-3}$ after $10^4-10^5 \text{ yr}$ from a temperature rise, while our model slightly underestimates $D_{\text{frac}}(N_2H^+)$, regardless of the average gas density, unless the protostellar cores are extremely young (i.e. age shorter than $10^2 \text{ yr}$). It should be noted that once the gas temperature rises, not only the N$_2$D$^+$/N$_2$H$^+$ ratio, but also the N$_2$H$^+$ abundance decreases significantly in models. Also, according to models of spherical star-forming cores (Lee, Bergin & Evans 2004; Aikawa et al. 2012), the central warm gas is still surrounded by a spherical shell of cold and dense gas during the early stages of collapse, in which both N$_2$D$^+$ and N$_2$H$^+$ are still abundant. This is not taken into account for simplicity in our one-box model. However, such residual emission from the cold envelope could explain the higher N$_2$D$^+$/$N_2$H$^+$ ratio still apparent after the sudden temperature rise.

5 CONCLUSIONS

We have observed the DNC and HN$^{13}$C(1-0) rotational transitions towards 22 massive star-forming cores in different evolutionary stages, towards which $D_{\text{frac}}(N_2H^+)$ was already measured by Fontani et al. (2011). The aim of the work was to compare $D_{\text{frac}}(\text{HNC})$ to $D_{\text{frac}}(N_2H^+)$ in the same sample of sources and with similar telescope beams, so that the comparison should not suffer from possible inconsistencies due to different sample selection criteria. The main observational result of this work confirms the predictions of the models of Sakai et al. (2012), namely that $D_{\text{frac}}(\text{HNC})$ is less sensitive than $D_{\text{frac}}(N_2H^+)$ to a sudden temperature rise, and hence it should keep more than $D_{\text{frac}}(N_2H^+)$ of the thermal history of the cores, despite the chemical processes leading to the deuteration of the two species are similar. Therefore, our work clearly indicates that $D_{\text{frac}}(N_2H^+)$ is more suitable than $D_{\text{frac}}(\text{HNC})$ to identify HMSCs. Based on the predictions of our chemical models, the starless cores studied in this work having $D_{\text{frac}}(N_2H^+)$ around 0.2–0.3 are very good candidate massive ‘pre-stellar’ cores, because only relatively ‘evolved’ starless cores can be associated with such high values of $D_{\text{frac}}(N_2H^+)$. Several results require follow-up high-angular resolution observations to map the emitting region of DNC and N$_2$D$^+$, as well as DNC and HN$^{13}$C, and test if these are slightly different as the present low-angular resolution data seem to suggest. Observations of higher excitation HN$^{13}$C and DNC lines (3–2 or 4–3) may be also important to constrain better the excitation conditions.

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Additional Supporting Information may be found in the online version of this article:

Appendix. Spectra (http://mnras.oxfordjournals.org/lookup/suppl/doi:10.1093/mnras/stu298/-/DC1).

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