1. Introduction

Isotopologue abundance ratios are pivotal for tracing the origin and evolution of the molecular material in the process of star and planetary system formation. Stable isotopes can in fact be measured in star-forming regions as well as in the Solar System. Nitrogen has two stable isotopes, $^{14}\text{N}$ and $^{15}\text{N}$. The $^{14}\text{N}/^{15}\text{N}$ ratio varies greatly across the Solar System, depending on the material and molecular tracer. This ratio is $\sim 440$ in the solar wind and Jupiter (reflecting the composition of the protosolar nebula), $\sim 150$ on Earth (for molecular nitrogen), $\sim 150$ in comets (for CN, HCN, and NH$_3$), and $\sim 200$ in protoplanetary disks (for HCN) (Fauré & Marty 2015; Guzmán et al. 2015). The origins of the different $^{14}\text{N}/^{15}\text{N}$ ratios among Solar System bodies are not yet fully understood. However, given that nitrogen is generally enriched in $^{15}\text{N}$ in more pristine material such as comets, the different $^{14}\text{N}/^{15}\text{N}$ ratios that we observe are potentially inherited from the early phase in the formation of the Solar System. Furthermore, recent observations of different $^{14}\text{N}/^{15}\text{N}$ ratios in HCN and CN towards a protoplanetary disk point to the existence of multiple isotopic reservoirs of nitrogen for forming planets (Hily-Blant et al. 2019). In the dense interstellar medium (ISM), the $^{14}\text{N}/^{15}\text{N}$ ratio is inferred from N-bearing species and it is 300–500 for CN, HCN, and HNC (Hily-Blant et al. 2013a,b). The $^{14}\text{N}/^{15}\text{N}$ ratio in N$_2$H$^+$ instead varies from 180 to 1000 (Fontani et al. 2015; Bizzocchi et al. 2019). State-of-the-art reaction networks fail to reproduce the $^{14}\text{N}/^{15}\text{N}$ variation in N$_2$H$^+$ (Roueff et al. 2015; Wiström & Charnley 2018), although a faster recombination with electrons of the $^{15}\text{N}$ isotopologues in L1544 with respect to the normal species might explain the depletion of N$_2$H$^+$ in $^{15}\text{N}$ (Loison et al. 2019; Hily-Blant et al. 2020; Redaelli et al. 2020). The use of $^{13}\text{C}$ isotopologues to derive the column densities of CN, HCN, and HNC is suggested to be done with caution by Roueff et al. (2015) because of the possible depletion of $^{13}\text{C}$ with respect to the ISM $^{12}\text{C}/^{13}\text{C}$ ratio, and due to the interdependence of the $^{13}\text{C}$ and $^{15}\text{N}$ chemistry (Colzi et al. 2019).

Aside from local nuclear synthesis which causes an increasing excess of $^{15}\text{N}$ towards the Galactic centre (Adande & Ziurys 2012), two main mechanisms are responsible for the nitrogen fractionation in the ISM: isotope exchange at low temperatures and isotope-selective photodissociation. Isotope exchange is the
main chemical path to enrich molecules in deuterium towards the centre of pre-stellar cores (e.g., Caselli et al. 2003). In the case of HCN, as an example for nitrogen bearing species, the isotope exchange reaction is

\[
\text{H}^{14}\text{CN} + ^{15}\text{N} \rightarrow \text{HC}^{15}\text{N} + ^{14}\text{N} + 35 \text{ K},
\]

(1)

followed by the dissociative recombination of the cation with electrons. The isotope exchange reactions enrich molecules in the heavier isotope at a low temperature because of the lower zero-point energy of the heavier molecular species and the exothermicity of the reaction (Terzieva & Herbst 2000). The isotope exchange reactions involving nitrogen were later found to have barriers (Roueff et al. 2015), and hence they are not favourable to reproduce its fractionation (Wiström & Charnley 2018). Isotope-selective photodissociation favours the photodissociation of the $^{15}$N-bearing isotopologues of N$_2$. With $^{14}$N$_2$ being more abundant, it can self-shield better than $^{15}$N$_2$ and is consequently less affected by photodissociation (Heays et al. 2014; Visser et al. 2018). With $^{14}$N$_2$ being more photodissociated than $^{15}$N$_2$, the $^{15}$N available to form molecules increases. The effect of selective isotope-photodissociation on nitrogen fractionation has already been clearly observed in protoplanetary disks (Hily-Blant et al. 2019). The e-folding has already been clearly observed in protoplanetary disks (Hily-Blant et al. 2019).

## 2. Observations

The emission maps of the 1-0 transition of the $^{13}$C and $^{15}$N isotopologues of CN, HCN, and HNC towards L1544 were obtained using the IRAM 30 m telescope (Pico Veleta, Spain) in two different observing runs in 2013 and 2015. We performed a 2.5′×2.5′ on-the-fly (OTF) map centred on the source dust emission peak ($\tau_{2200} = 0.5^{+0.6}_{-0.0}$) of L1544, which was the case. The emission maps were done using the GILDAS software (Pety 2005). The emission maps have a beam size of 30.1′′, and were gridded to a pixel size of 6′′ with the CLASS software in the GILDAS package, which corresponds to a typical system temperature of $T_{\text{sys}} \approx 90$–150 K. The data processing was done using the GILDAS software (Pety 2005). The emission maps have a beam size of 30.1′′, and were gridded to a pixel size of 6′′ with the CLASS software in the GILDAS package, which corresponds to a typical system temperature of $T_{\text{sys}} \approx 90$–150 K.

## 3. Analysis

The spectrum of the 1-0 transition of H$^{13}$CN observed towards the dust peak of L1544 was extracted from the centre of the map shown in Fig. 1 and fit with the HyperFine Structure (HFS) tool in CLASS using frequencies measured in the laboratory (Fuchs et al. 2004) with the assumption of the same excitation temperature of the hyperfine components. We derived $T_{\text{ex}} = 3.5$ K and an optical depth of 0.4, 2, and 1.2 for the $J = 1-0$ $F = 1-1$, 2-2, and 0-0 components, respectively. We repeated the same exercise towards a sample of four other positions in the mapped area, so as to test whether we could assume a constant 3.5 K $T_{\text{ex}}$ across L1544, which was the case. The integrated intensity maps shown in Fig. 1 were used to compute the column density maps of H$^{13}$CN and HC$^{15}$N, assuming...
to-noise ratio that allows for the computation of the 14N/15N ratio larger than 5.

The emission maps of 13CN and C15N do not have a signal-to-noise ratio that allows for the computation of the 14N/15N ratio map. To check whether the same trend observed in HCN is also present in 13CN and C15N, we averaged the C15N 1-0 transition and one of the hyperfine components of the 13CN 1-0 transition towards several positions across the core. In the left panel of Fig. 3, the regions where the spectra of 15N and 13CN have been averaged are marked as black circles on the H2 column density map of L1544. The size of the areas has been optimised to have a signal-to-noise ratio of at least 3. The black crosses mark the centre of each region, and their offsets with respect to the centre of the map (i.e., the dust peak of L1544) are reported in the respective spectra shown in the right panel. The right panel of Fig. 3 shows the averaged spectra from each region.

The hyperfine structure of the 1-0 transition of HN13C could not be resolved with the 6 kHz resolution of the VESPA spectra. The line shape that we observe deviates from previous observations towards other starless cores, for example those from van der Tak et al. (2009) and Padovani et al. (2011), suggesting that some of the hyperfine transitions might be self-absorbed.

We used the four effective hyperfine transitions described in van der Tak et al. (2009) and derived the optical depth of each component using the HFS tool in CLASS. The resulting $\tau$ are 1.7, 3.1, 1.9, and 0.1 for the four lines ordered by increasing velocity. Given that the weakest hfs component, at 87090.67 MHz, is optically thin towards the dust peak, we performed a Gaussian fit with four components for all pixels in our map with the aim of isolating the thin component and using it to compute the column density map. Unfortunately, the resulting integrated intensity map is observed at 3$\sigma$ only in the central 30'' of the map. We

![Fig. 1. Integrated intensity maps of the 1-0 transitions of H13CN and HC15N towards the inner 2' x 2' of L1544. The 30'' beam of the 30m telescope is shown at the bottom left of each map. The solid white contours are 30%, 60%, and 90% of the peak intensity of the N(H2) map of L1544 computed from Herschel/SPIRE data (Spezzano et al. 2016). The dashed black contours indicate the 10$\sigma$ integrated emission with steps of 10$\sigma$ for H13CN, and 5$\sigma$ with steps of 5$\sigma$ for HC15N (rmsH13CN = 6 mK km s$^{-1}$, rmsHC15N = 7 mK km s$^{-1}$).](image1.png)

![Fig. 2. 14N/15N ratio map of HCN towards L1544. The map was computed only in the pixels where the integrated emission of both H13CN and HC15N was detected with a signal-to-noise ratio larger than 5. The IRAM 30 m beam of 30'' (~5000 au) is shown in the bottom right of the map. The solid white contours are 30%, 60%, and 90% of the peak intensity of the N(H2) map of L1544 computed from Herschel/SPIRE data (Spezzano et al. 2016). The column density of HCN was computed from the column density of H13CN assuming the 12C/13C ratio of 68 (Milam et al. 2005). The corresponding error is shown in Fig. A.3.](image2.png)
extracted the spectra of HN\(^{13}\)C and H\(^{15}\)NC towards the same positions used for the CN isotopologues in Fig. 3 (see Fig. A.1). To make a direct comparison with HCN as well, we extracted the spectra of the \(^{13}\)C and \(^{15}\)N isotopologues of HCN towards the same regions (see Fig. A.2).

### 4. Results and discussion

The \(^{14}\)N/\(^{15}\)N ratio map of HCN in the left panel of Fig. 2 shows a clear decrease towards the south-east of L1544. The HC\(^{14}\)N/HC\(^{15}\)N in the north-west of the core is 367 ± 54, while in the south-east it is 187 ± 34. Towards the dust peak, the HC\(^{14}\)N/HC\(^{15}\)N is 437 ± 63, similar to the \(^{14}\)N/\(^{15}\)N ratio reported for HC\(_3\)N in Hily-Blant et al. (2018). The pre-stellar core L1544 is located at the end of a filament in the eastern edge of the Taurus Molecular Cloud. Because of its location and its structure, the southern part of L1544 is more efficiently illuminated by the interstellar radiation field (ISRF) than the northern part, and this has already been shown to have an impact on the chemical differentiation within the core (Spezzano et al. 2016). The \(^{14}\)N/\(^{15}\)N ratio map of HCN towards L1544 in this work suggests that the uneven illumination from the ISRF on L1544 has an impact on the \(^{15}\)N fractionation. As the largest \(^{15}\)N fractionation is observed towards the southern part of L1544, which is the most illuminated by the ISRF, we conclude that the dominant fractionation process is the isotope-selective photodissociation of N\(_2\) (Heays et al. 2014, Guzmán et al. 2017) tentatively observed the effect of isotope-selective photodissociation towards the protoplanetary disk V4046 Sgr. This result was later confirmed by Hily-Blant et al. (2019) towards the disk orbiting the T Tauri star TW Hya. The \(^{14}\)N/\(^{15}\)N ratio in HCN increases towards the dust peak of L1544 because we are looking through the densest regions of L1544, where the high density reduces the efficiency of the photodissociation, and consequently the enrichment of \(^{15}\)N in molecular species.

While we cannot compute the \(^{14}\)N/\(^{15}\)N ratio maps for CN, the spectra extracted towards four positions across the core in Fig. 3 strongly suggest that also for CN the nitrogen fractionation is affected by the ISRF. In boldface in each spectrum, the \(^{14}\)N/\(^{15}\)N ratio for CN derived in the corresponding region is reported. In green we report the \(^{14}\)N/\(^{15}\)N derived using the \(^{12}\)CN column density directly from the spectra shown in Fig. B.1. The values in boldface in green report the \(^{14}\)N/\(^{15}\)N ratio computed from the column density of \(^{13}\)CN using the \(^{12}\)C/\(^{13}\)C ratio of 68 (Milam et al. 2005).

![Fig. 3. \(^{14}\)N/\(^{15}\)N ratio of CN in 4 positions across L1544. Left panel: H\(_2\) column density map of L1544 computed from Herschel/SPIRE observations (Spezzano et al. 2016). The black crosses show the centre of the areas where the spectra shown in the right panel have been extracted. The black circles show the regions where the spectra shown in the right panel have been averaged. Right panel: spectra of \(^{13}\)CN (J, F\(_{J} \pm 1 \, 3/2 \, 2-0 \, 1/2 \, 1/2 \, 2)\) in black and C\(^{13}\)N (N, J, F\(_{J} \pm 1 \, 3/2 \, 2-0 \, 1/2 \, 1\) in red, extracted towards the offsets marked in the left panel. The values in boldface in blue report the \(^{14}\)N/\(^{15}\)N ratio in CN for each set of spectra derived using the \(^{12}\)CN column density directly from the spectra shown in Fig. B.1. The values in boldface in green report the \(^{14}\)N/\(^{15}\)N ratio computed from the column density of \(^{13}\)CN using the \(^{12}\)C/\(^{13}\)C ratio of 68 (Milam et al. 2005).](image-url)

Figure A.1 shows the spectra of the 1-0 transitions of HN\(^{13}\)C and H\(^{15}\)NC in the left panel and the 1-0 transitions of HN\(^{13}\)C and H\(^{15}\)NC in the right panel, respectively. The spectra in the left panel are extracted towards four positions across the core in Fig. 3. The spectra in the right panel are extracted towards the offsets marked in the left panel. The values in boldface in blue report the \(^{14}\)N/\(^{15}\)N ratio in CN for each set of spectra derived using the \(^{12}\)CN column density directly from the spectra shown in Fig. B.1. The values in boldface in green report the \(^{14}\)N/\(^{15}\)N ratio computed from the column density of \(^{13}\)CN using the \(^{12}\)C/\(^{13}\)C ratio of 68 (Milam et al. 2005).
in Roueff et al. (2015) shows that their $^{14}$N/$^{15}$N abundance ratio profiles can differ, especially between 10$^5$ and 10$^6$ yr. Nevertheless, the $^{14}$N/$^{15}$N ratios in HCN, CN, and HNC shown in Fig. 8 of Roueff et al. (2015) only range between 390 and 450, while we observe ratios that vary from 150 to 450. Non-local thermodynamic equilibrium (non-LTE) modelling is necessary to confirm our results, in particular for the $^{13}$C/$^{12}$C line where an isolated hyperfine component is not present.

5. Conclusions

Our $^{14}$N/$^{15}$N ratio map of HCN towards L1544 shows, for the first time, that the fractionation of nitrogen presents significant variations across a pre-stellar core. The $^{14}$N/$^{15}$N ratio in HCN decreases towards the south-east of the core, the region of L1544 that corresponds to a steeper drop in H$_2$ column density and is consequently more efficiently illuminated by the ISRF. This was already shown in previous observations of carbon-chain molecules, which in fact peak towards the region L1544 which is more exposed to the ISRF, where a significant fraction of carbon is maintained in atomic form (Spezzano et al. 2016). The same trend is also observed for CN and the opposite trend is observed for HNC. Our results indicate that isotope-selective photodissociation plays an important role in the fractionation of nitrogen in L1544. We note that $^{14}$N$^3$N photodissociates more efficiently than $^{14}$N$_2$ because it is not abundant enough to self-shield. The photodissociation of $^{14}$N$^3$N is expected to be more efficient towards the more illuminated southern part of the core, where more atomic $^{14}$N will be available to form cyanides such as HCN and CN. Furthermore, HNC shows the opposite behaviour with respect to HCN and CN. Further studies are necessary to understand the underlying cause.

The effect of isotope-selective photodissociation in nitrogen fractionation has already been observed towards a protoplanetary disk where the irradiation from UV photons in the inner part of the disk transmits into a lower $^{14}$N/$^{15}$N ratio in HCN (Hily-Blant et al. 2019). With our work we show that the uneven illumination from the ISRF onto a pre-stellar core has an effect on the $^{14}$N/$^{15}$N ratio through the isotope-selective photodissociation. With the $^{14}$N/$^{15}$N ratio in atomic nitrogen decreasing towards the southern part of L1544, the $^{14}$N$_2$/$^{14}$N$^3$N ratio will have the opposite behaviour and increase towards the south of L1544 because the $^{14}$N$_2$ is expected to be less affected by photodissociation. As a consequence, we expect the $^{14}$N/$^{15}$N ratio in molecules that are formed from molecular nitrogen, such as N$_2$H$^+$, to show the opposite behaviour with respect to HCN and CN. This trend has already been observed towards the high-mass star-forming region IRAS 05358+3543 in Colzi et al. (2019). Future maps of $^{14}$N$_2$H$^+$/^{14}$N$^3$NH$^+$ or $^{14}$N$_2$H$^+$/^{14}$N$^3$NH$^+$ towards L1544 are needed to confirm this point for low-mass star-forming regions.

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S. Spezzano et al.: Nitrogen fractionation towards a pre-stellar core traces isotope-selective photodissociation
Appendix A: Observed spectra

Figures A.1 and A.2 show the spectra of the $^{13}$C and $^{15}$N isotopologues of HCN and HNC towards the positions shown in the left panel of Figure 3 (where the spectra of $^{13}$CN and C$^{15}$N were extracted). A sharp decrease can be seen towards the south in the lines of the $^{13}$C isotopologues, while the intensities of the lines of the $^{15}$N isotopologues are almost constant across the core.

The spectra shown in Figures A.1 and A.2, as well as in Figure 3 show a small shift in velocity across the core. Such a shift is predicted by the model from Ciolek & Basu (2000) shown in Fig. 6 in Caselli et al. (2002), and it has already been observed in L1544 (see for example Figure B.1 in Spezzano et al. (2016)). Figure A.3 shows the error map on the HC$^{14}$N/HC$^{15}$N column density ratio map, and it is calculated by propagating the errors on the column density maps of H$^{13}$CN and HC$^{15}$N, which include the rms of the spectra as well as a 10% calibration error.

Fig. A.1. Spectra of HN$^{13}$C ($N = 1$-0) in black and H$^{15}$NC ($N = 1$-0) in red extracted in the regions shown as black circles in the left panel in Figure 3. The values in boldface report the $^{14}$N/$^{15}$N ratio in HNC for each set of spectra derived using the $^{13}$C/$^{12}$C ratio of 68 (Milam et al. 2005).
Fig. A.2. Spectra of $^{13}$CN ($J, F = 1 \times 0$) in black and HC$^{15}$N ($N = 1-0$) in red extracted in the regions shown as black circles in the left panel in Figure 3. The values in boldface report the $^{14}$N/$^{15}$N ratio in HCN for each set of spectra derived using the $^{12}$C/$^{13}$C ratio of 68 (Milam et al. 2005). We note the sharp decrease in the $^{13}$CN line towards the south, when compared to the almost constant HC$^{15}$N.

Fig. A.3. Error map of $^{14}$N/$^{15}$N ratio of HCN towards L1544. The map was computed only in the pixels where the integrated emission of both H$^{13}$CN and HC$^{15}$N was detected with a signal-to-noise ratio larger than 5. The IRAM 30m beam of $30''$ (∼5000 au) is shown in the bottom right of the map. The solid white contours are 30%, 60%, and 90% of the peak intensity of the N($H_2$) map of L1544 computed from Herschel/SPIRE data (Spezzano et al. 2016).
Appendix B: Effect of the $^{12}$C/$^{13}$C fractionation

We extracted the spectra of the $N = 1-0$ $J = 3/2-1/2$ $F_1 = 2-1$ $F = 3-2$ transition of $^{13}$CN and the $N = 1-0$ $J = 1/2-1/2$ $F = 1-1$ of CN towards the four positions marked in the left panel in Figure 3 and derived the $^{12}$CN/$^{13}$CN (see Figure B.1). We used the map of the weakest hyperfine component of the 1-0 transition of the main isotopologue, which is only slightly optically thick, with $\tau$ ranging from 1.1 to 1.4 across the map, and it does not show signs of self-absorption in our spectra with 50 kHz resolution. In contrast to the spectra shown in Figures A.2 and A.1, where the lines of the $^{12}$C and $^{13}$N isotopologues do not decrease at the same pace towards the south of L1544, the intensity variations of the lines of $^{12}$CN and $^{13}$CN do not show a substantial difference. We computed the column density for $^{12}$CN and $^{13}$CN from the spectra shown in Figure B.1, assuming optically thick emission, and $T_e = 4.2$ K. The excitation temperature and optical depth were derived by modelling the observed line of $^{12}$CN with RADEX, assuming a kinetic temperature of 8 K and a volume density of $1 \times 10^5$ cm$^{-3}$, and it is consistent with the excitation temperature previously derived for $^{13}$CN and C$^{15}$N in Hily-Blant et al. (2013a). Please note that the choice of volume density has an impact on the resulting excitation temperature, and consequently on the optical depth of the $^{12}$CN line and the resulting column density. For example, if we assume a volume density of $5 \times 10^5$ cm$^{-3}$, the corresponding excitation temperature is 5 K, which reduces the optical depth of the $^{12}$CN line by almost a factor of two, and in turn decreases the $^{12}$CN/$^{13}$CN ratios in the central and northern offset, where the $^{12}$CN line is brighter. The $^{12}$CN/$^{13}$CN ratio derived in this work (193±10 towards the dust peak) is larger than the values derived in B1b, where $^{12}$CN/$^{13}$CN = 50$^{15}$ (Daniel et al. 2013). However, the chemical models presented in Colzi et al. (2020) can reproduce values of $^{12}$CN/$^{13}$CN larger than 68 (the isotopic ratio for the local ISM, Milam et al. 2005), as seen in Figure 7 of Colzi et al. (2020). The variation of the $^{12}$CN/$^{13}$CN ratio with density and time in the models is mainly connected to the competition between the enrichment of carbon monoxide in $^{13}$C and the availability of $^{13}$C. Our results for CN indicate that the effect of the illumination on the nitrogen fractionation across the core is not affected by the fractionation of carbon. Consequently, we can assume that the $^{12}$N/$^{13}$N ratio map of HCN in the left panel of Figure 2 might need to be corrected by an offset (i.e. a different $^{12}$C/$^{13}$C ratio), but it will not change its trend substantially because of the carbon fractionation. Chemical modelling for the combined fractionation of carbon and nitrogen is currently underway and is beyond the scope of this Letter. It is however important to note that the ratio between the $^{13}$C and $^{15}$N isotopologues for CN and HCN is the same towards the dust peak of L1544, ~6, and it drops for both molecules to ~3 towards the south-west of the core, strongly suggesting that both molecules undergo the same chemical paths for the fractionation of nitrogen. While the normal isotopologues trace the core and the cloud where the core is embedded, it is safe to assume that the $^{13}$C and $^{15}$N isotopologues only trace the core. Therefore, it might be more appropriate to compare the $^{12}$C and $^{13}$N isotopologue ratios instead of the ratios involving the main isotopologue, even when it is possible to derive a direct measurement.

![Fig. B.1. Spectra of $^{13}$CN (N = 1-0 J = 3/2-1/2 F_1 = 2-1 F = 3-2) in black and CN (N = 1-0 J = 1/2-1/2 F = 1-1) in red extracted in the regions shown as black circles in the left panel in Figure 3. The $^{12}$CN/$^{13}$CN column density ratio derived towards the four offsets is written in boldface in each spectrum.](image-url)