Depletion of $^{15}$N in the center of L1544: Early transition from atomic to molecular nitrogen?

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ABSTRACT

We performed sensitive observations of the N$^{15}$ND$^-$ (1–0) and $^{15}$NND$^-$ (1–0) lines toward the prestellar core L1544 using the IRAM 30 m telescope. The lines are not detected down to 3σ levels in 0.2 km s$^{-1}$ channels of $\sim$6 mK. The non-detection provides the lower limit of the $^{14}$N/$^{15}$N ratio for N$_2$D$^+$ of $\sim$700–800, which is much higher than the elemental abundance ratio in the local interstellar medium of $\sim$200–300. The result indicates that N$_2$ is depleted in $^{15}$N in the central part of L1544, because N$_2$D$^+$ preferentially traces the cold dense gas, and because it is a daughter molecule of N$_2$. In situ chemistry is probably not responsible for the $^{15}$N depletion in N$_2$: neither low-temperature gas phase chemistry nor isotope selective photodissociation of N$_2$ explains the $^{15}$N depletion; the former prefers transferring $^{15}$N to N$_2$, while the latter requires the penetration of interstellar far-ultraviolet (FUV) photons into the core center. The most likely explanation is that $^{15}$N is preferentially partitioned into ices compared to $^{14}$N via the combination of isotope selective photodissociation of N$_2$ and grain surface chemistry in the parent cloud of L1544 or in the outer regions of L1544, which are not fully shielded from the interstellar FUV radiation. The mechanism is most efficient at the chemical transition from atomic to molecular nitrogen. In other words, our result suggests that the gas in the central part of L1544 has previously gone through the transition from atomic to molecular nitrogen in the earlier evolutionary stage, and that N$_2$ is currently the primary form of gas-phase nitrogen.

Key words. astrochemistry – ISM: clouds – ISM: molecules – ISM: individual objects: L1544

1. Introduction

Nitrogen is the fifth most abundant element in the universe. Our understanding of nitrogen chemistry in star-forming regions is limited compared to other volatile elements, such as carbon and oxygen. The dominant form of gaseous nitrogen in star-forming regions is unclear (e.g., Bergin & Tafalla 2007), while it is theoretically expected to be either atomic N or N$_2$ (e.g., Aikawa et al. 2005; Le Gal et al. 2014). One of the main limiting factors is that neither atomic N nor N$_2$ is directly observable in the cold and dense gas of star-forming regions. However, the N$_2$ abundance can be constrained indirectly by observing a proxy molecule N$_2$H$^+$ (e.g., Maret et al. 2006).

The observational and theoretical studies of nitrogen isotope fractionation in star-forming regions can help to constrain nitrogen chemistry. Nitrogen has two stable isotopes, $^{14}$N and $^{15}$N. The elemental abundance ratio [$^{14}$N/$^{15}$N]$_{elem}$ in the local interstellar medium (ISM) has been estimated to be $\sim$200–300 from the absorption line observations of N-bearing molecules toward diffuse clouds (Lucas & Liszt 1998; Ritchey et al. 2015). L1544 is a prototypical prestellar core located in the Taurus molecular cloud complex. In L1544, the $^{14}$N/$^{15}$N ratio of several different molecules has been measured: $^{14}$N$_2$H$^+$/N$^{15}$NH$^+$ $\approx$ 920–300$^a$, $^{14}$N$_2$H$^+$/[NNH$^+$] $\approx$ 1000$^b$–240$^b$, $^{14}$NH$_3$/[NH$_2$H$^+$] $\approx$ 700$^b$ (Gérin et al. 2009), CN/$^{15}$N $\approx$ 500 ± 75 (Hily-Blant et al. 2013b), and HCN/H$^{15}$N = 257 (Hily-Blant et al. 2013a). Among the measurements, the significant depletion of $^{15}$N in NH$_2$H$^+$ is the most challenging for the theory of $^{15}$N fractionation. In general, molecules formed at low temperatures are enriched in $^{15}$N through gas-phase chemistry triggered by isotope exchange reactions (e.g., Terzieva & Herbst 2000). A $^{15}$N-bearing molecule has a slightly lower zero-point energy than the corresponding $^{14}$N isotopolog. This results in endothermicity for the exchange of $^{15}$N for $^{14}$N, which inhibits this exchange at low temperature enabling the concentration of $^{15}$N in molecules. Astrochemical models for prestellar cores, which consider a set of nitrogen isotope exchange reactions, have indeed predicted that atomic N is depleted in $^{15}$N, while N$_2$ (and thus N$_2$H$^+$) is enriched in $^{15}$N (e.g., Charnley & Rodgers 2002). The model prediction clearly contradicts the observation of the N$_2$H$^+$ isotopologs in L1544. The $^{15}$N depletion in N$_2$H$^+$ was recently found in other prestellar cores as well, such as L183, L429, and L694-2 (Redaelli et al. 2018). Furthermore, Roueff et al. (2015) recently pointed out the presence of activation barriers for some key nitrogen isotope exchange reactions, based on their quantum chemical calculations. Then $^{15}$N fractionation
triggered by isotope exchange reactions may be much less efficient than previously thought (Roueff et al. 2015, but see also Wirstöm & Charnley 2018).

Another mechanism that can cause $^{15}\text{N}$ fractionation is photodissociation of $N_2$ (Heays et al. 2014). $N_2$ photodissociation is prone to self-shielding. Because $^{14}\text{N}^{15}\text{N}$ is much less abundant than $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ needs a higher column density of the ISM gas for self-shielding. This makes $N_2$ photodissociation an isotope-selective process. As a result, $N_2$ is depleted in $^{15}\text{N}$, which is consistent with the observation of the $N_2^+H^+$ isotopolog in L1544. Isotope-selective photodissociation of $N_2$ is efficient only for limited regions where the interstellar UV radiation field is not significantly attenuated, however (Heays et al. 2014; Furuya & Aikawa 2018). The prestellar core L1544 has high density and $AV$ (>10 mag for a millimeter-dust continuum peak). Detection of carbon chain species, such as C$_2$H$_2$, however, may indicate that the interstellar UV radiation penetrates to moderate depth in L1544 (Spezzano et al. 2016). Then it is unclear how it affects depth in L1544 (Spezzano et al. 2016). It is then unclear whether the isotope-selective photodissociation of $N_2$ is at work in L1544, and how it affects the measurement of the $^{15}\text{N}/^{14}\text{N}$ ratio of $N_2^+$.

In order to test the selective photodissociation scenario, we observed $^{15}\text{N}$ isotopologs of $N_2D^+$ toward prestellar core L1544. Compared with $N_3H^+$, $N_3D^+$ selectively traces colder and denser regions (i.e., core center) (Caselli et al. 2002a), where the attenuation of the interstellar UV radiation field is more significant. If the isotope-selective photodissociation of $N_2$ by the penetrating UV radiation is the cause of the $^{15}\text{N}$ depletion in $N_3H^+$, the $^{15}\text{N}/^{14}\text{N}$ ratio of $N_2D^+$ should be lower than that of $N_2H^+$ and be close to $[^{14}\text{N}^{15}\text{N}]_{\text{elem}}$. Moreover, $N_2D^+$ is less optically thick than $N_3H^+$, which allows us to accurately evaluate the column density of the $^{14}\text{N}$ isotopolog and thus the $^{15}\text{N}/^{14}\text{N}$ ratio, although more sensitive observations are required for the detection of the $^{15}\text{N}$ isotopologs of $N_2D^+$ than those of $N_2H^+$.

2. Observations

We observed the $N^{15}\text{ND}^+(1–0)$, $^{15}\text{NND}^+(1–0)$, and $N_2D^+(1–0)$ transitions toward the prestellar core L1544 with the IRAM 30 m telescope at Pico Veleta on 2017 December 22–24. We tracked the L1544 continuum dust emission peak at 1.3 mm, where $^{15}\text{N}$ isotopologs of $N_2H^+$ were previously detected (Bizzocchi et al. 2010, 2013). The observed position is $(\alpha_{2000}, \delta_{2000}) = (05^h04^m17^s21, 25^\circ10'42"8)$ (Caselli et al. 2002a). The telescope pointing was checked every two hours by observing the continuum source 0439+360 near the target position and was ensured to be better than $\pm3\arcsec$. The half-beam power width was $32\arcsec$–$33\arcsec$.

We employed Eight Mixer Receiver (EMIR) E090 with dual polarization mode. The system noise temperatures were typically from 70 K to 130 K during the observation run. The $N^{15}\text{ND}^+(1–0)$ and $^{15}\text{NND}^+(1–0)$ transitions were observed simultaneously (Set 1), while the $N_2D^+(1–0)$ transition was observed with a different frequency setting (Set 2). The hyperfine components and their relative intensities of the $N^{15}\text{ND}^+(1–0)$ and $^{15}\text{NND}^+(1–0)$ transitions were experimentally studied by Dore et al. (2009), and they are listed in Table A.1. A frequency-switching mode was employed with a frequency offset of 7.35 MHz. We used eight Fourier transform spectrometer (FTS) autocorrelators with a bandwidth of 1820 MHz. The frequency resolution of 50 kHz corresponds to 0.2 km s$^{-1}$ at 75 GHz. We integrated the spectrum for a total on-source time of 5.2 h for Set 1 and 0.4 h for Set 2. Two orthogonal polarizations were simultaneously observed, and are averaged together to produce the final spectrum. The main-beam temperature ($T_{MB}$) is derived by $T_B/T_{eff}$, where $T_B$ is the antenna temperature, $T_{eff}$ is the forward efficiency (95%), and $B_{eff}$ is the main-beam efficiency (74%). The final rms noise is 2.3 mK in $T_{MB}$ for $N^{15}\text{ND}^+(1–0)$, 2.1 mK for $^{15}\text{NND}^+(1–0)$, and 11 mK for $N_2D^+(1–0)$. The $^{15}\text{NHH}^+(1–0)$ and $^{15}\text{NNH}^+(1–0)$ transitions were also observed in Set 1. Both transitions were detected, and the obtained spectra are similar to those obtained in the framework of ASAI IRAM 30 m large program (De Simone et al. 2018; Lefloch et al. 2018), which observed the same object and the same position with the same velocity resolution, but employing wobbler-switching mode. We do not discuss the observations of the $^{15}\text{N}$ isotopologs of $N_3H^+$ in this work because they have been studied in detail in previous work (Bizzocchi et al. 2010, 2013; De Simone et al. 2018).

### Table 1. Derived column density and $^{14}\text{N}/^{15}\text{N}$ ratio.

| Species       | $N_{tot}$ (cm$^{-2}$) | $^{14}\text{N}/^{15}\text{N}$ |
|---------------|----------------------|-------------------------------|
| $N_2D^+$      | $(5.4 \pm 0.3) \times 10^{12}$ | –                             |
| $N^{15}\text{ND}^+$ | $<7.0 \times 10^9$ | $>730$                         |
| $^{15}\text{NND}^+$ | $<6.5 \times 10^9$ | $>780$                         |

3. Results

The data were processed using the GILDAS software (Pety et al. 2005). The $N_2D^+(1–0)$ transition was clearly detected, while $N^{15}\text{ND}^+(1–0)$ and $^{15}\text{NND}^+(1–0)$ were not detected, as shown in Fig. 1. Line parameters for $N_2D^+(1–0)$ were estimated using the HFS routine implemented in CLASS. The derived total optical depth of the lines and the FWHM line width are 3.08 $\pm$ 0.19 and 0.406 $\pm$ 0.003 km s$^{-1}$, respectively. The main component of the $N_2D^+(1–0)$ transition (77.1096162 GHz), which has a fraction of 7/27 of the total line strength, is marginally optically thick ($\sim0.8$). We derived the total column density of $N_2D^+$ using Eq. (A1) of Caselli et al. (2002b), which is valid for optically thick emission. For the column density calculation, the excitation temperature ($T_{ex}$) was set to be 5 K, which was previously derived from $N_3H^+(1–0)$ and $N_2D^+(2–1)$ observations toward the same object and the same position (Caselli et al. 2002a; Crapsi et al. 2005). The parameters of the observed transitions were taken from the Cologne Database for Molecular Spectroscopy (Müller et al. 2001, 2005). The total column density of $N_2D^+$ ($N_{tot}(N_2D^+)$) is evaluated to be $(5.4 \pm 0.3) \times 10^{12}$ cm$^{-2}$. The error on $N_{tot}(N_2D^+)$ is given by propagating the errors on the total optical depth and the FWHM line width. Our $N_{tot}(N_2D^+)$ is very close to that obtained by Crapsi et al. (2005) ($4.3 \pm 0.6) \times 10^{12}$ cm$^{-2}$), who derived it from the $N_2D^+(2–1)$ data.

Upper limits to $N_{tot}(N^{15}\text{ND}^+)$ and $N_{tot}(^{15}\text{NND}^+)$ were obtained from the $3\sigma$ upper limits to the integrated intensity $3\sigma\sqrt{\Delta v\nu}$ of the transitions, where $\sigma$ is the rms noise of the spectra, $\Delta v$ is the FWHM line width of the spectra, assumed to be the same as that of $N_2D^+(1–0)$, and $\nu$ is the velocity resolution. Assuming local thermal equilibrium, the $3\sigma$ intensity upper limits were converted into the column density upper limits using Eq. (A4) of Caselli et al. (2002b), which is valid for optically thin emission. $T_{ex}$ is assumed to be 5 K. We obtain $N_{tot}(N^{15}\text{ND}^+) < 7.0 \times 10^9$ cm$^{-2}$ and $N_{tot}(^{15}\text{NND}^+) < 6.5 \times 10^9$ cm$^{-2}$.


**Fig. 1.** Spectra of the N$_2$D$^+$$(1–0)$ transition (top panel), the N$^{13}$ND$^+$(1–0) transition (middle panel), and the $^1$NND$^+$(1–0) transition (bottom panel) observed toward L1544. The intensity scale is the main-beam temperature. In the top panel, the red curve depicts the result of the HFS fit. The N$^{13}$ND$^+$(1–0) transition and the $^1$NND$^+$(1–0) transition were not detected down to 3σ levels in 0.2 km s$^{-1}$ channels of 6.9 mK and 6.3 mK, respectively. The vertical blue lines indicate the positions of the expected hyperfine components.

4. Discussion and conclusion

From the column densities of the N$_2$D$^+$ isotopologs, we obtain the lower limits of the $^{14}$N/$^{15}$N ratios of 730 for N$^{13}$ND$^+$ and 780 for $^1$NND$^+$. These lower limits are significantly higher than $^{14}$N/$^{15}$N$_{elem}$ in the local ISM (~200–300; Lucas & Liszt 1998; Ritchey et al. 2015). It is reasonable to consider the $^{14}$N/$^{15}$N$_{elem}$ ratios of N$_2$D$^+$ as the ratio of N$_2$, because N$_2$D$^+$ primary forms by N$_2$ + X$^3$D$, where X is H or D. Then our observations indicate that N$_2$ is significantly depleted in $^{15}$N in the central part of L1544. If we assume $T_{\text{ex}}$ of 4.5 K (5.5 K) in the column density evaluation, the lower limits of the $^{14}$N/$^{15}$N ratios become 600 (950) for N$^{13}$ND$^+$ and 640 (1010) for $^1$NND$^+$. Our qualitative conclusion is thus robust against the assumed value of $T_{\text{ex}}$. Colzi et al. (2018) recently derived the $^{14}$N/$^{15}$N$_{elem}$ ratio in the local ISM of ~400 from the observations of HCN isotopologs toward a sample of 66 cores in massive star-forming regions. Even when this higher elemental abundance ratio is adopted, our qualitative conclusion does not change.

As described in Sect. 1, nitrogen isotope exchange reactions make N$_2$ enriched in $^{15}$N; they are thus not relevant to the observed fractionation. Isotope-selective photodissociation of N$_2$ by penetrating interstellar FUV photons is also ruled out as the cause of the $^{15}$N depletion because the penetration would be negligible in the central part of L1544, where N$_2$D$^+$ emission arises. Our lower limits of the $^{14}$N/$^{15}$N ratios for N$_2$D$^+$ are consistent with those of N$_2$H$^+$ (~1000) obtained by Bizzocchi et al. (2013), which also supports that isotope-selective photodissociation of N$_2$ is not responsible for the $^{15}$N depletion in Sect. 1. We note that cosmic-ray induced photodissociation of N$_2$ does not cause $^{15}$N fractionation because the destruction of N$_2$ by He$^+$ is much faster (Heays et al. 2014; Furuya & Aikawa 2018). Therefore, in situ chemistry is probably not responsible for the $^{15}$N depletion in N$_2$ in the central part of L1544.

The most likely explanation is that the $^{15}$N depletion is inherited from more diffuse gas, as recently proposed by Furuya & Aikawa (2018), based on their astrochemical models in forming and evolving molecular clouds. They found that during the evolution of molecular clouds, the nitrogen isotopes can be differentially partitioned between gas and ice, making $^{15}$N-depleted gas and $^{15}$N-enriched ice. In the molecular cloud, where the external UV radiation field is not fully shielded, $^{14}$N$^{15}$N is selectively photodissociated with respect to $^{14}$N$_2$, which results in the enrichment of $^{15}$N in the photodissociation product, atomic N. Atomic N is adsorbed onto grain surfaces and converted into NH$_3$ ice by surface reactions, while adsorbed N$_2$ does not react with other species, including atomic H. As long as the nonthermal desorption (especially photodesorption in their models) of NH$_3$ ice is less efficient than that of N$_2$ ice, the net effect is the loss of $^{15}$N from the gas phase, producing $^{15}$N-depleted gas and $^{15}$N-enriched ice. When the external UV radiation field is sufficiently shielded, $^{15}$N depletion does no longer proceed, but is largely conserved unless a significant amount of NH$_3$ ice is sublimated.

As noted by Furuya & Aikawa (2018), the mechanism is the most efficient around the chemical transition from atomic N to N$_2$, where the self-shielding of $^{14}$N$_2$ becomes important. Before the transition, both $^{14}$N$_2$ and $^{14}$N$^{15}$N are efficiently photodissociated, while after the transition, the abundance of atomic N is too low to affect the bulk gas isotopic composition. Therefore, if the mechanism proposed by Furuya & Aikawa (2018) was at work in the parent cloud of L1544 or the outer regions of L1544, it means that the transition from atomic to molecular nitrogen should have occurred there as well.

Nitrogen chemistry mainly consists of three competing processes: (i) the conversion of atomic N to N$_2$ in the gas phase, (ii) destruction of N$_2$, for instance, via photodissociation and reaction with He$^+$, and (iii) freeze-out of atomic N and N$_2$ onto dust grains followed by surface reactions (e.g., Daranlot et al. 2012; Li et al. 2013). The conversion of atomic N into N$_2$ has been proposed to occur by slow neutral-neutral reactions, such as NO + N and CN + N (Herbst & Klemperer 1973; Daranlot et al. 2012). According to the pseudo-time-dependent gas-phase
astrochemical model under dense cloud conditions (10^5 cm^{-3}, 10 K, 10 mag) by Le Gal et al. (2014), the conversion of atomic N into N_2 takes an order of Myr, depending on elemental abundances. In the gas-ice model of Daranlot et al. (2012), under the similar physical conditions, the conversion of atomic N to N_2 takes ~5×10^3 yr, and it occurs after the significant fraction of nitrogen is frozen out. On the other hand, N_2 mainly forms via the reactions NH_3 + N and NH + N around the transition from atomic to molecular nitrogen in the models of Furuya & Aikawa (2018) and Furuya & Persson (2018), in which the dynamical evolution of molecular clouds is considered. NH_2 and NH are mainly formed via photodesorption of NH_3 ice, followed by photodissociation in the gas phase. In this case, the formation rate of N_2 from atomic N is, roughly speaking, similar to the freeze-out rate of atomic N. Considering that interstellar ices, at least water ice, are already abundant in molecular clouds with relatively low line-of-sight visual extinction (e.g., ~3 mag for the Taurus dark clouds, Whittet 1993), it may not be surprising that the transition from atomic to molecular nitrogen occurs in the parent cloud of L1544 or in the outer regions of L1544. It should be noted that the N_2-dominated region could be larger than the regions traced by NH_3 and HN_3 emission, since their abundances are controlled not only by N_2, but also by CO; the catastrophic CO freeze-out, which occurs in the late stage of the interstellar ice formation at high densities (>10^10 cm^{-3}; e.g., Pontoppidan 2006), causes their abundances to be enhanced (e.g., Aikawa et al. 2005).

It may be interesting to estimate the partitioning of elemental nitrogen between gas and ice. The abundance of gaseous N_2 in dense prestellar cores was previously estimated from the comparison of N-chemistry models with the observations of N_2H^+ and other relevant species. Maret et al. (2006) inferred that gaseous N_2 contains only a few percent of the overall elemental nitrogen (N/H = 6 × 10^{-5} in the local ISM; Przybilla et al. 2008) in the dense cloud B68. Paganini et al. (2012) also inferred that gaseous N_2 contains ≤1% of elemental nitrogen in the prestellar core L183. While Maret et al. (2006) suggested that atomic N is the primary form of elemental nitrogen in B68 to account for this low gaseous N_2 abundance, their model predicts that NH_3 ice is the primary nitrogen reservoir (see also Daranlot et al. 2012; Furuya & Persson 2018). The gas-ice astrochemical model by Ruaud et al. (2016), on the other hand, predicts that the HCN ice is more abundant than NH_3 ice. Figure 2 shows the fraction of elemental nitrogen in the form of ice as functions of the 14N/15N ratio of the bulk ice. In the figure, the 14N/15N ratio of the bulk gas (i.e., that of N_2) is assumed to be 1000. If NH_3 and HCN ices are the primary forms of elemental nitrogen in L1544, as predicted by the astrochemical models, the 14N/15N ratio of the icy species should be close to but slightly lower than [14N/15N]_{elem}.

Gérin et al. (2009) found that the 14N/15N ratio of gaseous NH_3D is >700 in L1544. The 14N/15N ratios of gaseous NH_3 in the cold gas of dense molecular clouds were derived to be 334 ± 50 in Barnard 1 and 340 ± 150 in NGC 1333 (Lis et al. 2010). These measurements indicate that gaseous NH_3 in the cold gas is not significantly enriched in 15N. It should be noted, however, that the origin of gaseous NH_3 in the cold gas, that is, whether it is formed by gas-phase reactions or released from ices via nonthermal desorption, remains unclear. The 14N/15N ratio of icosic species in star-forming regions could be constrained by measuring the molecular 14N/15N ratios in the warm (>100 K) gas surrounding protostars. This type of observations is crucial for better understanding the nitrogen partitioning.

Finally, observations of comets have found that cometary NH_3 and HCN are enriched in 15N by a factor of around three (Mumma & Charnley 2011; Shinnaka et al. 2016) compared to the Sun (~150 versus 441; Marty et al. 2011). The ammonia abundance with respect to water in cometary ices (0.4–1.4%) is lower than that in interstellar ices (typically ~5%) (Mumma & Charnley 2011; Öberg et al. 2011). These (possible) differences between the N-bearing species in cometary and interstellar ices might indicate a primordial variation in the ice formation environments or ice processing in the solar nebula (e.g., Lyons et al. 2009; Furuya & Aikawa 2014).

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Fig. 2. Estimated fraction of elemental nitrogen in ices as functions of the 14N/15N ratio of the ices. The estimated fractions with different 14N/15N_{elem} are shown by different colors. In all cases, the 14N/15N ratio of the bulk gas is assumed to be 1000.
Appendix A: Additional table

| Species | F′–F | Frequency (GHz) | Relative intensity |
|---------|------|----------------|-------------------|
| $^{15}$ND$^+$ | 1–1 | 76.0168733 | 1.000 |
|         | 2–1 | 76.0185970 | 1.667 |
|         | 0–1 | 76.0211239 | 0.333 |
| $^{15}$NND$^+$ | 1–1 | 74.7605619 | 1.000 |
|         | 2–1 | 74.7609788 | 1.667 |
|         | 0–1 | 74.7615650 | 0.333 |

Note: Frequencies and relative intensities for transitions of $^{15}$ND$^+$ and $^{15}$NND$^+$ are taken from Dore et al. (2009).