The CN/C\textsuperscript{15}N isotopic ratio towards dark clouds\textsuperscript{*,**}

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ABSTRACT

Understanding the origin of the composition of solar system cosmon materials is a central question, not only in the cosmochemistry and astrochemistry fields, and requires various approaches to be combined. Measurements of isotopic ratios in cometary materials provide strong constraints on the content of the protosolar nebula. Their relation with the composition of the parental dark clouds is, however, still very elusive. In this paper, we bring new constraints based on the isotopic composition of nitrogen in dark clouds, with the aim of understanding the chemical processes that are responsible for the observed isotopic ratios. We have observed and detected the fundamental rotational transition of \textsuperscript{14}N\textsuperscript{2}N towards two starless dark clouds, L1544 and L1498. We were able to derive the column density ratio of \textsuperscript{14}N\textsuperscript{2}N over \textsuperscript{14}CN towards the same clouds and obtain the CN/C\textsuperscript{15}N isotopic ratios, which were found to be 500 ± 75 for both L1544 and L1498. These values are therefore marginally consistent with the protosolar value of 441. Moreover, this ratio is larger than the isotopic ratio of nitrogen measured in HCN. In addition, we present model calculations of the chemical fractionation of nitrogen in dark clouds, which make it possible to understand how CN can be deprived of \textsuperscript{15}N and HCN can simultaneously be enriched in heavy nitrogen. The non-fractionation of N\textsubscript{2}H\textsuperscript{+}, however, remains an open issue, and we propose some chemical way of alleviating the discrepancy between model predictions and the observed ratios.

Key words. ISM: abundances – ISM: clouds – ISM: general – ISM: molecules – astrochemistry

1. Introduction

Understanding the origin of the elements in the solar system is a crucial issue at the crossroads of astrophysics, cosmochemistry, and astrobiology. In this respect, comets play a particular role because they are considered the most ancient relics of the formation of the solar system from the protosolar nebula, 4.567 Gyr ago. If it is certain that all cometary material has an interstellar origin, what is unclear is whether there is any chemical species present in e.g. cometary ices that have remained unaltered since that time. The reduced spectra (in FITS format) are available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/557/A65

\textsuperscript{*} Appendices are available in electronic form at http://www.aanda.org

\textsuperscript{**} The reduced spectra (in FITS format) are available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/557/A65

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obtained by Gerin et al. (2009) in other cold dense cores using NH$_2$D, though with much larger uncertainties. These values contrast with the HCN measurements by Ikeda et al. (2002) and Lucas & Liszt (1998), who find ratios of 150 and 240 in dark and diffuse molecular gas respectively. More recently, Adande & Ziurys (2012) found similar values based on HCN and CN observations towards warm (T $>$ 25 K) molecular clouds, with ratios from 150 to 350. Even more recently, Hily-Blant et al. (2013, hereafter HB13) report HCN isotopic ratios between 140 and 360, where the range of values is shown to reflect genuine spatial variations of the ratio. HB13 also suggest that the large variations of the $^{14}$N/$^{15}$N ratio in cosmo-materials, in dark clouds, and in the more diffuse ISM may indeed be rooted in the interstellar nitrogen chemistry. The underlying idea is that there are two reservoirs of interstellar nitrogen characterized by different isotopic ratios: nitrile carriers (such as HCN) are systematically enriched in $^{15}$N with respect to the Sun’s value, whereas hydrides (such as ammonia) show values encompassing that measured in the Sun. The differential fractionation of these two reservoirs may originate in the interstellar chemistry of nitrogen. This is because nitriles essentially derive from atomic nitrogen, whereas hydrides derive from molecular nitrogen.

Because atomic and molecular nitrogen, which are presumably the main reservoirs of nitrogen, are not directly observable in the dense ISM, the determination of the bulk $^{14}$N/$^{15}$N is indirect and relies on the observation of minor N-bearing molecules. To which extent the abundance ratio of two isotopologues of a given molecule is representative of the elemental isotopic ratio depends on so-called fractionation processes: the stronger these processes, the larger the departure of the molecular abundance ratio from the elemental ratio. Fractionation processes are of two types: chemical and selective photodissociation effects. The latter effect can safely be ignored in dark clouds, which are dense and shielded regions. Chemical effects are potentially important in cold gas (Watson et al. 1976; Langer et al. 1984). Regarding nitrogen, Terzieva & Herbst (2000, hereafter TH00) investigated chemical fractionation in dense and cold clouds ($n_H = 2 \times 10^4$ cm$^{-3}$, $T = 10$ K), and found essentially no fractionation of any nitrogen-bearing molecule. This was further investigated by Charnley & Rodgers (2002), who showed, in contrast, that in situations where OH is strongly depleted from the gas-phase, there is more atomic nitrogen available for fractionation. Indeed, large fractionation levels are predicted, e.g. for NH$_3$, at early times in their calculations. However, these models also predict strong fractionation of N$_3$H$^+$, which is not observed. Therefore, none of the two available models of nitrogen fractionation in dark clouds are able to reproduce the observational constraints.

The CN radical plays a peculiar role in the nitrogen chemistry because it is a mediator of the atomic-to-molecular conversion (HB13). CN is also coupled with the dominant nitriles such as HCN and HNC, which derive from atomic nitrogen. Thus, the nitrogen fractionation level of CN potentially provides interesting constraints on the fractionation pathways. In this paper, we report the detection of $^{15}$C$^{15}$N towards two starless cores, L1544 and L1498. Put in conjunction with the N$_3$H$^+$ and HCN fractionation measurements available towards L1544, it is expected that these new observations will strongly constrain models.

The paper is structured as follows. In Sect. 2, we present the observations and column density derivation. In Sect. 3, we present our fractionation model, to which we compare the $^{14}$N/$^{15}$N measured in CN and other molecules. The discussion is the subject of Sect. 4.

### 2. Observations

The $N = 1$–0 rotational spectrum of $^{15}$C$^{15}$N is split into fine and hyperfine structures, which arise from the electron spin and the $I = 1/2$ nuclear spin of the $^{15}$N atom. There are two groups of lines due to the fine structure, which are distant by 300 MHz (see Table 1). The strongest hyperfine component is the $(N, J, F) = (1, 1, 2) \rightarrow (0, 0, 1)$ transition at 110024.590 MHz, with a relative intensity of 0.417 (Saleck et al. 1994). The next strongest transitions have relative intensities of 17%, with frequencies 109689.610 and 110023.540 MHz. All six hyperfine components were observed simultaneously towards L1498 and L1544 at the IRAM 30m telescope in May 2012 ($\approx 16$ h per source) under good weather conditions. The VESPA autocorrelator was used as a spectrometer to provide us with high-resolution spectra, namely, 20 kHz or 0.054 km s$^{-1}$ at 110 GHz. The typical receiver temperature achieved with the EMIR detectors (Carter et al. 2012) was $\approx 40$ K, resulting in system temperatures $\approx 120$ K. Amplitude calibration was performed using the three-phase IRAM method typically every 10 min. Pointing and focus sessions using strong continuum sources were repeated every one and two hours respectively. The wobbler-switching mode (140° throw) was used to provide us with high-quality baselines, such that residual bandpass calibration effects could be handled.

Table 1. Spectroscopic properties of the observed species and transitions.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$B^a$ (MHz)</th>
<th>$\mu_a^b$ (Debye)</th>
<th>Transition$^c$</th>
<th>Frequency$^d$ (MHz)</th>
<th>$A_{uu}^e$ (s$^{-1}$)</th>
<th>$g_u^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$CN</td>
<td>54353.130</td>
<td>1.45</td>
<td>1 3/2 2 3 $\rightarrow$ 0 1/2 1 2</td>
<td>108780.201</td>
<td>1.05 $\times 10^{-5}$</td>
<td>7</td>
</tr>
<tr>
<td>C$^{15}$N</td>
<td>54958.510</td>
<td>1.45</td>
<td>1 3/2 2 $\rightarrow$ 0 1/2 1</td>
<td>110024.590</td>
<td>1.09 $\times 10^{-5}$</td>
<td>5</td>
</tr>
</tbody>
</table>

Notes. (a) Rotational constant. (b) Dipole moment. (c) For $^{15}$N, the quantum numbers are $NJF$ with $J = N + S$ and $F = J + I$, where $S$ is the electronic spin and $I$ is the nuclear spin of $^{15}$N. For $^{13}$C, we follow the CDMS convention (which differs from Bogey et al. 1984), where the quantum numbers are $NJF_1F_2$ with $F_1 = J + I_1$, $F = F_1 + I_2$ where $I_1 = 1/2$ and $I_2$ are the nuclear spin of C$^{12}$ and C$^{13}$ respectively. (d) For resolved hyperfine structures, frequency of a given hyperfine component. (e) Einstein coefficient for spontaneous decay. (f) Total degeneracy of the upper level.
with first-order polynomial fitting. The HC$^{15}$N(1–0) data reported in this paper are taken from Hily-Blant et al. (2010b). The $^{13}$CN(1–0) rotational spectrum also presents fine and hyperfine structures, which are described in Bogey et al. (1984). For the present analysis, we use only the brightest hyperfine component, at 108780.201 (Hily-Blant et al. 2008). The spectroscopic properties of both species and observed transitions are summarized in Table 1. Towards L1544, the $^{13}$CN spectrum is taken from Hily-Blant et al. (2010b), and towards L1498, it is taken from unpublished spectra of Padovani et al. (2011). Data reduction was done using the CLASS software (Hily-Blant et al. 2005). All plots were done in the GILDAS environment provided by IRAM (Pety 2005). The J2000 coordinates for L1498 and L1544 are $\alpha$, $\delta$ $=$ 04:10:51.50, 25:09:58.0 and 05:04:16.90, 25:10:47.0 respectively.

### 3. Results

Among the three brightest C$^{15}$N lines, only the strongest, with a relative intensity of 42%, is clearly detected towards both sources. The line properties, which are derived from Gaussian fits, are summarized in Table 2. We also give the properties of the $^{13}$CN(1–0) line obtained in a similar fashion. We note a 0.1 km s$^{-1}$ discrepancy between the velocities of the $^{13}$CN and C$^{15}$N lines towards L1498, which could not be ascribed to any obvious technical issue. We note, however, that the uncertainty on the rest frequency reported in the Cologne Database for Molecular Spectroscopy (Müller et al. 2005) is 0.1 MHz, or 0.25 km s$^{-1}$, which could account for the observed shift. New observation of the $^{13}$CN(1–0) towards L1498 should be performed to check this discrepancy. We are, however, most confident that the detected lines are $^{13}$CN and C$^{15}$N, since we searched for other lines at those frequencies in public databases and could not find any likely candidate. There is a marginal detection of the 110023.540 MHz line towards L1544, which has a peak intensity of 20 mK. This intensity well matches what would be expected from the relative intensities (17% that of the strongest line), which suggests that the lines are optically thin. This secondary component is not detected towards L1498, though there is some emission at the expected velocity (within the 0.1 MHz uncertainty), with an upper limit that is consistent with the relative intensities of these two components. The analysis below is based solely on the strongest C$^{15}$N line at 110024.590 MHz.

Line intensities towards L1544 are stronger than towards L1498 and are also broader by a factor $\approx 2$. This is likely due to the L1544 lines presenting two closely velocity components (Hily-Blant et al. 2010b), which are not resolved in the C$^{15}$N spectrum. These two velocity components may be related to the collapse signature recently evidenced by the inverse P-Cygni profile of a water line (Caselli et al. 2012). To derive column densities from the emission lines, we performed radiative transfer calculations with the RADEX code (van der Tak et al. 2007), using the large velocity gradient (LVG) approximation for an expanding sphere. The hyperfine rate coefficients for C$^{15}$N and $^{13}$CN were derived from the rate coefficients computed by Kalugina et al. (2012) for CN+H$_2$ using the infinite-order-sudden approximation (see Appendix C). We assumed that the source has a constant density and temperature and that it uniformly fills the telescope beam. The line width was held fixed at 0.2 km s$^{-1}$ for L1498 and at 0.4 km s$^{-1}$ for L1544. The intensity of the observed $^{13}$CN(1–0) transition was computed for varying $^{13}$CN column density (N($^{13}$CN)), H$_2$ density ($n$(H$_2$)), and kinetic temperatures (T). The kinetic temperatures considered span the range 7 to 12 K by steps of 1 K. Figure B.1 shows the resulting line intensity for a kinetic temperature of 10 K. A continuum range of solutions matches the observation constraints summarized in Table 2, with densities $n$(H$_2$) $=$ 10$^6$ to a few 10$^7$ cm$^{-3}$ and associated $^{13}$CN column densities from 6 $\times$ 10$^{11}$ to 2.5 $\times$ 10$^{12}$ cm$^{-2}$. Refined calculations were then performed across this range for both $^{13}$CN and C$^{15}$N. For C$^{15}$N, a similar ensemble of solutions was found. Even though the density and column density are degenerate, the $^{13}$CN and C$^{15}$N solutions are characterized by a constant $^{13}$CN/C$^{15}$N column density ratio across the full range of solutions. Finally, refined calculations were done in which the C$^{15}$N column density was such that 6 $\leq$ N($^{13}$CN)/N(C$^{15}$N) $\leq$ 9. The $^{13}$CN/C$^{15}$N column density ratios are 7.5 and 7 for L1544 and L1498 respectively. Although the density and column density are degenerate, equal excitation temperatures (within 0.1 K) of 3–5 K are found for the $^{13}$CN and C$^{15}$N, across the full range of solutions. The $^{13}$CN line is found to be only marginally thin, with an opacity close to unity, whilst the C$^{15}$N line can safely be assumed to be thin. It is of interest to note that LTE calculations using excitation temperatures in the range 3–4 K provide abundance ratios which agree reasonably well with the above LVG calculations.

On chemical grounds, both species follow similar formation and destruction routes and are thus expected to coexist spatially. The above column density ratios are representative of their abundance ratios. If we now assume that $^{12}$CN/^{13}CN = $^{12}$C/$^{13}$C and adopt for the latter the value of 68 from Milam et al. (2005), we derive an isotopic ratio CN/C$^{15}$N = 476 $\pm$ 70 in L1498 and CN/C$^{15}$N = 510 $\pm$ 70 in L1544, where conservative uncertainties are applied (see Table 2). Altogether, these values give CN/C$^{15}$N $=$ 500 $\pm$ 75.

The $^{13}$CN column density may also be compared with the H$^{13}$CN column density, which is 1.8 $\times$ 10$^{12}$ cm$^{-2}$ towards L1498 (Padovani et al. 2011) and 4.6 $\times$ 10$^{12}$ cm$^{-2}$ towards L1544 (HB13). The $^{13}$CN/H$^{13}$CN ratios are thus 0.6 and 1.7 for L1498 and L1544 respectively, which are in harmony with ratios found by Hily-Blant et al. (2010b) towards several starless cores.

### Table 2. Line properties towards L1544 and L1498 and associated column density ratios from LVG calculations.

<table>
<thead>
<tr>
<th>Source</th>
<th>$^{13}$CN$^a$</th>
<th>C$^{15}$N$^a$</th>
<th>$^{13}$CN/C$^{15}$N$^b$</th>
<th>C$^{14}$N/C$^{15}$N$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$W$ (mK km s$^{-1}$)</td>
<td>$T_0$ (mK)</td>
<td>$v_0$ (km s$^{-1}$)</td>
<td>FWHM (km s$^{-1}$)</td>
</tr>
<tr>
<td>L1498</td>
<td>28(2)</td>
<td>114(14)</td>
<td>7.84(0.01)</td>
<td>0.23(0.02)</td>
</tr>
<tr>
<td>L1544</td>
<td>73(4)</td>
<td>166(15)</td>
<td>7.17(0.02)</td>
<td>0.44(0.03)</td>
</tr>
</tbody>
</table>

Notes. $^{a)}$ From Gaussian fits. Statistical uncertainties at the 1σ are in parenthesis for a velocity resolution of 0.05 km s$^{-1}$ at 110 GHz. $^{b)}$ Adopting FWHM of 0.20 and 0.40 km s$^{-1}$ for L1498 and L1544 respectively. Conservative uncertainties based on $\chi^2$ minimization. $^{c)}$ Adopting $^{12}$C/$^{13}$C = 68 (Milam et al. 2005).
4. Comparison to model predictions

4.1. Fractionation of nitriles and hydrides

The CN/C15N abundance ratios inferred in the two starless cores are thus only slightly larger than the protosolar value of 14N/15N = 441, but significantly larger the HCN/HC15N ratio derived by HB13 towards L183 and L1544, which are smaller than the protosolar ratio. In contrast, the CN/C15N ratio is similar to that measured in hydrides (NH3, N2H+) towards dark clouds by Bizzocchi et al. (2010), Gerin et al. (2009), and Lis et al. (2010).

At first glance, this is at odds with the suggestion that hydrides and nitriles present different fractionation degrees (HB13), because one would have expected CN to behave more like HCN than like NH3. Yet, it must be recognized that CN plays a particular role in the chemistry of nitrogen: though it is a nitrile, it reacts directly with N to form N2, from which hydrides derive. Hence, the non-fractionation of CN may not be in contradiction with the chemical picture proposed in by HB13.

4.2. Model calculations

We thus wish to understand how the CN radical gets deprived in 15N and at the same time HCN is enriched in 15N. To this aim, we implemented the fractionation reactions of TH00 in a dark cloud chemical network based on Flower & Pineau des Forêts (2003), in which the nitrogen chemistry has been fully revised. The most important changes regard the dissociative recombinations of ions such as NH++, NH+, and NH+, which are critical for the production of hydrides. Following Dislaire et al. (2012), the dissociative recombination of N2H+ possesses a channel producing NH with a branching ratio of ≈5% (Vigren et al. 2012).

The gas phase ortho-to-para conversion of H2 through proton exchange reactions has also been fully updated (Rist et al. 2013, and references therein) since the rate of the key reaction N++ + H depends critically on the ortho-to-para ratio of H2 (Dislaire et al. 2012). Other important reactions have been updated, based on the recent laboratory work of Daranlot et al. (2012). In a first approach, the updated chemical network of Le Gal was simplified by ignoring the ortho- and para- forms of H2, H3+, and other nitrogen-bearing molecules. This means that the rate of the reaction N++ + H2 was held fixed at a value corresponding to an ortho:para ratio of H2, of 10^-3, in a similar fashion as in Dislaire et al. (2012).

The chemical fractionation reactions considered by TH00 are ion-neutral reactions, because they are the fastest and are hence expected to be the most efficient. These reactions consist in forward and backward reactions,

\[ A^+ + B \xrightarrow{k_f} C^+ + D + \Delta E, \]

where \( \Delta E \) is the zero-point energy difference between the products and reactants, such that \( \Delta E > 0 \) if the reaction is exothermic. The rates of the forward and backward reactions are related through

\[ k_f/k_c = f(B,m) \exp[\Delta E/kT], \]

where \( f(B,m) \) is a factor that depends on the masses and partition functions of the reactants and products. The values of \( \Delta E \) and \( f(B,m) \) are taken from the work of TH00 and are listed in Table A.2. At temperatures smaller than \( 10^4 \), the forward reaction proceeds much faster than the backward reaction, thus shifting the steady-state abundances towards the reactants. In implementing the fractionation reactions of TH00 in our network, we adopted a single Langevin rate of \( 10^{-9} \) cm^3 s^-1 for all forward reactions. The remaining reactions involving nitrogen atoms in our network have been duplicated to include their 15N analogue. The total number of species and reactions are 144 and 870 respectively. We do not consider freeze-out of any species in these models. We follow the time evolution of the chemical state of a parcel of gas of density \( n_H = 10^6 \) cm^-3 and kinetic temperature of 10 K, which was exposed to a cosmic-ray ionisation rate \( \zeta = 1.3 \times 10^{-17} \) s^-1 and shielded from the ambient UV field by 20 mag of visual extinction, such that external UV photons do not play any significant role. However, secondary photons, which result from the fluorescence of H2 molecules excited by collisions with the electrons produced by cosmic-rays are explicitly taken into account and are responsible for a significant fraction of the ionisation. The initial abundances are given in Table A.1, where an elemental isotopic ratio of nitrogen \( R_0 = 440 \) was adopted (Marty et al. 2011).

4.3. Chemical considerations

The resulting abundances and abundance ratios of selected species are shown in Fig. 1. As is evident, all species reach a steady state after typically 5 Myrs, similar to what was found by Flower et al. (2006). This timescale is comparable to the lifetime of molecular clouds (Tassis & Mouschovias 2004) but is larger than the free-fall timescale and slightly larger than the ambipolar diffusion one (e.g. Walmsley et al. 2004). Those dynamical timescales are mostly relevant for the inner and dense parts of dark clouds and are not directly applicable to the rather low density material modelled here. It is possible, but not certain, that the nitrogen-bearing species have reached steady-state. In any case, it must be recognized that the chemical timescale depends strongly on the initial abundances adopted.

In our calculations, the steady state is characterized by an N:N2 abundance ratio close to unity, suggesting near equipartition between these two reservoir species. This is in sharp contrast to the calculations of Hily-Blant et al. (2010a), who found N3 to be 30–40 times more abundant than N. Unfortunately, the use of different chemical networks, namely OSU 2009 in the latter case, impedes any direct comparison but undoubtedly calls for further investigation. Still, our predicted ratio is similar to that determined by Flower et al. (2006) with an older version of our chemical network. Another characteristic is the HNC:HCN = 1 ratio. We also see that NH3 is the most abundant of the three hydrides, with an abundance of 1.2 × 10^-8, when NH and NH2 have abundances of 3.5 × 10^-9 and 4.3 × 10^-8 respectively. The predicted abundance of ammonia is close to its value of 1.5–5.0 × 10^-8 in the cold envelope of IRAS 16293-2422. The latter estimate is a revision of the value published in Hily-Blant et al. (2010a). It is based on non-LTE radiative transfer calculations using the publicly available RATRAN and LTE codes, and taking into account all the observed ammonia lines, including the 572 GHz fundamental line (Hogerheijde & van der Tak 2000; Brinch & Hogerheijde 2010). These calculations will be detailed elsewhere. There is also a good agreement for the abundances of NH and NH2. The predicted CN:HCN abundance ratio of 0.2 is smaller than the observed value, a discrepancy already noted by Hily-Blant et al. (2010b).

We now examine the predicted fractionation degree, that is, the enrichment or depletion in 15N with respect to the elemental ratio, of several nitrogen-bearing species, which is our main concern. The right panel of Fig. 1 shows the abundance ratios of nitrogen-bearing isotopologues as a function of time. Probably
the main result is that our model does predict large variations of the isotopic ratio in several species, contrary to the calculations of TH00, who found very small fractionation for all species. Our model predicts that the isotopic ratio of N, which we note $R(N)$, is $\approx 630$, and that $R(N_2) \approx 400$ (see Table 3). Since these species are also the reservoirs of nitrogen, this implies that most of the nitrogen is fractionated, either enriched or deprived in $^{15}N$ and any enrichment/depletion of N in $^{15}N$ implies depletion/enrichment of $N_2$. Another striking feature is that until a few $10^6$ Myrs, isotopic ratios remain close to the initial value of 440. Beyond this time, three types of behaviour may be emphasized: species that are enriched in $^{15}N$, those that are deprived in $^{15}N$, and those that are not fractionated. The latter group includes $NH_3$ and $NHCO$. The positively fractionated molecules are $HCN$, $HNC$, and $NH$, for which the steady-state isotopic ratio is $\approx 330$, and the depleted ones are $N$, $NO$, and $CN$. (see Table 3). The latter exhibits an isotopic ratio of $\approx 550$.

For $^{15}NO$, the main formation channel is through reaction with $^{15}N$, whilst the destruction channel is through reaction with N. Hence the steady-state abundances of NO and $^{15}NO$ are given respectively by

$$[NO] = \frac{f_1}{d_1} \times [OH]$$

and

$$[^{15}NO] = \frac{f_1}{d_1} \times [^{15}N][OH]/[N].$$

leading to an isotopic ratio $NO/^{15}NO = N/^{15}N$. The situation is similar for CN, but as already noted, the isotopic ratio of CN is lower than that of N (and NO). This is because $^{12}C_2N^+$ and $^{12}H_2CN^+$ are efficiently fractionated by the ion-neutral reactions of TH00 (see Table A.2), such that their isotopic ratios become smaller than $R_0$. The dissociative recombination of these ions, which are normally negligible in producing CN, contributes to about 10% to the formation of $^{15}CN$. As a result, $^{15}CN$ does not strictly follow the same behaviour as N and NO. Because HCN and HNC are primarily formed through the dissociative recombination of $H_2CN^+$, their isotopic ratios are similar to that of $H_2CN^+$.

We now turn our attention to nitrogen hydrides. To understand the different behaviour of $NH$ on the one hand and $NH_2$ and $NH_3$ on the other hand, we first need to understand what determines the relative abundances of $^{15}N^+$ and $N^+$. The $N^+$ ion is mostly produced by the reaction of $N_2$ with $He^+$. This is also true for $^{15}N^+$, but the fractionation reaction

$$^{15}N^+ + N_2 \rightarrow N^+ + ^{15}N_2$$

presents an exothermicity of 28 K. The forward process leading to $N^{15}N^+$ is therefore enhanced at low temperature with respect to the reverse process, and this is why $R(N_2) < R(N^+)$. As $N_2^+$ is a daughter molecule of $N_2$, this also explains how
\( \delta = 100 \times (\text{R}_{\text{obs}}/\text{R}_{\text{calc}} - 1) \)

\( [X^n] = \frac{n(X^n)}{n(X^{15}N)} \) for species containing two nitrogen atoms, the ratio is normalized to the protololar value \( ^{14}N/^{15}N = 440 \) from Marty et al. (2011). (d) Depletion factor \( \delta_{15N} = 1000 \times (\text{R}_{\text{obs}}/\text{R}_{\text{calc}} - 1) \), where the reference value \( \text{R}_{\text{obs}} = 272 \) is the isotopic ratio of the Earth atmosphere.

### 4.4. Comparisons to the observations

The present model predictions are now compared to the CN and HCN isotopic ratios observed in L1544 and L1498 (right panel of Fig. 1). The isotopic ratio of HCN are \( \text{R}(\text{HCN}) = 230 \pm 350 \) and 190–280 towards the central positions of L1544 towards L183 respectively (HB13). This value is not available in the case of L1498. For CN, we take the values determined in Sect. 3. As is evident, the model predictions agree well with all the observational constraints. In particular, the isotopic ratios of CN and HCN estimated in L1544 are well reproduced by our model calculations.

More problematic is the case of \( N_2H^+ \). The constraints on \( N_2H^+/N_2^{15}N^+ \) from Bizzocchi et al. (2010), who found \( 446 \pm 71 \), are plotted in Fig. 1. Our model predicts a significant enrichment for \( N_2H^+ \), with \( \text{R}(N_2H^+) = 280 \). The fractionation of \( N_2H^+ \) is associated with the reaction of \( N_2H^+ \) with \( \text{N}^+ \) and \( \text{H}^+ \) starts to dominate the formation \( \text{N}^+ \) and \( \text{H}^+ \) drops and the reaction \( \text{NH}^+ + \text{H}^+ \) becomes closer to that of \( \text{NH} \). Apart from this moderate change affecting \( \text{NH} \) and \( \text{N}_2 \), we conclude that the above results do not depend on the assumed value of \( \text{R}(\text{H}^+) \).
or an N–N bond. In the latter case, the reaction likely requires a strong activation energy. If we artificially switch off these two reactions, we note that the fractionations of $^{15}NH_3^+$ and $^{13}NH_3^+$ become equal, as expected, with a isotopic ratio of 340. Yet, this value is only slightly larger than the value in Table 3 and is still outside the permitted value from Bizzocchi et al. (2010) by a small factor. The same argument may apply even more likely to the fractionation reactions $N + N^+_3$, which proceeds through N–N bond breaking. Suppressing the latter reactions has a much stronger effect on the fractionation picture because these reactions are responsible for the fractionation of atomic nitrogen (see the discussion above). In particular, NH becomes less fractionated and CN and $N_2^+$ have similar isotopic ratios $\approx 400$, whereas HCN fractionation remains unaffected. This further illustrates the dichotomy suggested by HB13. Observations of $^{15}NNH_3^+$ would enable the first suggestion to be tested.

The models presented here have a C/O abundance ratio of 0.50, which falls in between the low–metal-abundance value of 0.41 from Wakelam & Herbst (2008) and the value of 0.67 from Flower & Pineau des Forêts (2003). We also performed model calculations with C/O = 0.40, for which all the above reasoning applies equally, though predicting a smaller $R(CN)$ whilst maintaining a fractionation of HCN close to the case C/O = 0.50. We thus found a better agreement with the calculations having C/O = 0.50. Exploring the effects of the initial abundances is an important area of investigation. However, it is beyond the scope of the present work and is deferred to a subsequent paper.

5. Conclusions and perspectives

Combining observations of $^{15}$N and $^{13}$CN and assuming a CN:$^{13}$CN isotopic ratio, we have estimated the CN:$^{15}$N ratio towards two dark clouds. In both cases, the CN molecule appears slightly depleted in $^{15}$N with respect to the solar wind elemental ratio, with a CN:$^{13}$N ratio $\approx 500 \pm 75$ or depletion values $\delta_{15} = [272/R(CN)] - 1 = -527$ to $-360\%$. Towards L1544, additional constraints are provided by the HCN:HC$^{15}$N ratio. We performed chemical model calculations, which include ion-neutral fractionation reactions for nitrogen-bearing species. Our gas-phase model predicts significant fractionation of many species. This is in sharp contrast to the former predictions of Terzieva & Herbst (2000). Even though the model of Charnley & Reger (2012) produces many species as possible is most welcome. However, $^{15}$N detection is time demanding, and further progress may rather benefit from observations of HC$^{15}$N and H$^{13}$NC towards a larger sample of sources. In addition, observations of $^{15}$NH$_3$ would bring extremely interesting constraints, but the discrepancy between the results of Lis et al. (2010) and Gerin et al. (2009) suggests that the interpretation of such observations may not be straightforward. Observations of $^{15}$NO would also be most valuable. However, this molecule presents both fine and hyperfine splittings such that the intensity may be diluted within too many components, making this species particularly difficult to detect. The hypothesis of Hily-Blant et al. (2013) could also be pushed forward by observing isotopologues of more complex nitriles, such as HC$_3$N and beyond.

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References

Chasseron, S., & Gounelle, M. 2007, Comptes Rendus Geoscience, 339, 872
Table A.1. Elemental abundances (taken from Flower & Pineau des Forêts 2003), except for O. Numbers in parentheses are powers of 10.

<table>
<thead>
<tr>
<th>Species</th>
<th>$n(X)/n_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.1</td>
</tr>
<tr>
<td>N</td>
<td>6.4(−5)</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>1.5(−7)</td>
</tr>
<tr>
<td>O</td>
<td>2.1(−4)</td>
</tr>
<tr>
<td>C$^+$</td>
<td>8.3(−5)</td>
</tr>
<tr>
<td>S$^+$</td>
<td>1.9(−6)</td>
</tr>
<tr>
<td>Fe$^+$</td>
<td>3.0(−9)</td>
</tr>
</tbody>
</table>

Notes. $n_H = n(H) + 2n(H_2)$.

Table A.2. Fractionation reactions and rate coefficients ($k(T) = \alpha(T/300)^\beta \exp(-\Delta E/T)$ cm$^3$ s$^{-1}$) implemented in our chemical network (from TH00).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Delta E$</th>
<th>$k(10^9)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{15}$N + H$_2$ $\rightarrow$ N$_2 + ^{15}$NH$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N$_2 + ^{15}$NH$^+$ $\rightarrow$ $^{15}$NN + H$_2^+$</td>
<td>2.0</td>
<td>0.0</td>
<td>10.7</td>
<td>6.9(−10)</td>
</tr>
<tr>
<td>$^{15}$NN + $^2$H$_2$ $\rightarrow$ N$_2 + ^{15}$NNH$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>$^{15}$N + $^{15}$NNH$^+$ $\rightarrow$ N$_2 + ^{15}$N$_2^+$</td>
<td>2.0</td>
<td>0.0</td>
<td>2.3</td>
<td>1.6(−9)</td>
</tr>
<tr>
<td>$^{15}$N + N$_2^+$ $\rightarrow$ $^{15}$NNH$^+$ + N</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N$_2 + ^{15}$NNH$^+$ $\rightarrow$ N$_2 + ^{15}$NH$_2$</td>
<td>1.0</td>
<td>0.0</td>
<td>36.1</td>
<td>2.7(−11)</td>
</tr>
<tr>
<td>$^{15}$N + N$_2^+$ $\rightarrow$ N$_2 + ^{15}$NH$_2$</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N$_2 + ^{15}$NNH$^+$ $\rightarrow$ N$_2 + ^{15}$N$_2^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>27.7</td>
<td>6.3(−11)</td>
</tr>
<tr>
<td>$^{15}$N + N$_2$ $\rightarrow$ N$_2 + ^{15}$NN</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N$^+$ + $^{15}$NN $\rightarrow$ N$^+$ + N$_2$</td>
<td>0.5</td>
<td>0.0</td>
<td>28.3</td>
<td>3.0(−11)</td>
</tr>
<tr>
<td>$^{15}$N$^+$ + NO $\rightarrow$ N$^+$ + $^{15}$NO</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N$^+$ + $^{15}$NO $\rightarrow$ N$^+$ + NO</td>
<td>1.0</td>
<td>0.0</td>
<td>24.3</td>
<td>8.8(−11)</td>
</tr>
<tr>
<td>$^{15}$N + H$_2$C$^+$ $\rightarrow$ N + H$_2$C$^{15}$N$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N + H$_2$C$^{15}$N$^+$ $\rightarrow$ $^{15}$N + H$_2$C$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>35.9</td>
<td>2.8(−11)</td>
</tr>
<tr>
<td>$^{15}$N + H$_2$NC$^+$ $\rightarrow$ N + H$_2$C$^{15}$N$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0(−9)</td>
</tr>
<tr>
<td>N + H$_2$C$^{15}$N$^+$ $\rightarrow$ $^{15}$N + H$_2$NC$^+$</td>
<td>1.0</td>
<td>0.0</td>
<td>35.9</td>
<td>2.8(−11)</td>
</tr>
</tbody>
</table>

The $^{13}$C (with nuclear spin $I = 1/2$) and $^{15}$N ($I = 1/2$) substitutions in CN (in which $^{14}$N has a nuclear spin $I = 1$) significantly modify the hyperfine structure of the molecule. The fine-structure rate coefficients can be considered nearly identical for the three isotopologues. To derive the $^{13}$CN and $^{15}$N hyperfine rate coefficients, we used the infinite-order-sudden (IOS) approximation applied to the CN fine-structure rate coefficients of Kalugina et al. (2012). Within this approximation, where the fine-structure energy spacings are ignored compared to the collision energy, the rate coefficients between fine-structure levels ($k_{N_j \rightarrow N'_j}(T)$ for a $^{15}$N state molecule) can be obtained directly from the “fundamental” fine-structure rate coefficients (those out of the lowest $N = 0$ level) as follows:

$$k_{N_j \rightarrow N'_j}(T) = (2j' + 1) \sum_{L} \frac{\epsilon L}{2} \left( \frac{j'}{2} \frac{L}{2} \frac{j}{2} \right)^2 \left( \frac{1}{1} \frac{1}{2} \frac{1}{2} \frac{1}{2} \right)^2 \times \frac{1}{2} \left( 1 + \epsilon (1)^{j' + F} \right)^{2} k_{N_j \rightarrow N'_j}(T),$$

(B.1)

where $\epsilon$ is equal to $+1$ if the parity of initial and final rotational $N_j$ level is the same or $-1$ if the parity of initial and final rotational $N_j$ level differ.

For $^{15}$N, which possesses a single non-zero nuclear spin, the IOS rate coefficients among hyperfine-structure levels can be obtained from the $k_{N_j \rightarrow N'_j}(T)$ rate coefficients as:

$$k_{N_j \rightarrow N'_j}(T) = (2j + 1)(2j' + 1)(2F' + 1) \sum_{L} \frac{2L + 1}{L + 1} \times \left( \frac{j'}{2} \frac{L}{2} \frac{j}{2} \right)^2 \left( \frac{F'}{F} \frac{L}{L} \right)^2 \times \frac{1}{2} [1 + \epsilon (1)^{j' + F} + 1] k_{N_j \rightarrow N'_j}(T),$$

(B.2)

where $I = 1/2$ is the nuclear-spin of $^{15}$N. In practice, the CN fine-structure energy spacings are not negligibly small and the IOS approximation is expected to fail at low temperature ($T < 100$ K). However, since it correctly predicts the relative rates among hyperfine levels (because the propensity rules are properly included through the Wigner coefficients), a simple method to correct the low temperature results is to scale the IOS results, as originally suggested by Neufeld & Green (1994):

$$k_{N_j \rightarrow N'_j}(T) = \frac{k_{N_j \rightarrow N'_j}(T)}{k_{N_j \rightarrow N'_j}(T)} k_{N_j \rightarrow N'_j}(T).$$

(B.3)

In this approach the CC rate coefficients $k_{N_j \rightarrow N'_j}(T)$ and $k_{N_j \rightarrow N'_j}(T)$ must be employed as the IOS fundamental rates in both Eqns. (B.1) and (B.2). The scaling procedure thus ensures that:

$$\sum_{F} k_{N_j \rightarrow N'_j}(T) = k_{N_j \rightarrow N'_j}(T).$$

(B.4)

It should be noted that the propensity rule $\Delta j = \Delta F$ predicted by the recoupling approach is also properly reproduced by IOS approximation, as discussed in Faure & Lique (2012). We note that for CN there is also a strong propensity for transitions with even $\Delta N$ Kalugina et al. (2012). In practice, the first 22 hyperfine levels of $^{15}$N were considered, corresponding to rate coefficients for all 210 transitions among levels with $N \leq 5$.

1 Note that there is a typo regarding the sign of $\epsilon$ in Eq. (7) of Faure & Lique (2012).

Appendix A: Chemical model

We implemented the fractionation reactions of TH00, assuming a symmetry factor $f(B, m)$ of unity for all reactions, unless $N_2$ appears as a reactant or as a product. In these cases, $f(B, m) = 0.5$ or 1 respectively. A constant Langevin rate of $10^{-9}$ cm$^3$ s$^{-1}$ was adopted for these ion-neutral reactions. The zero-point energy differences are taken from TH00. The reactions and their rate coefficients are listed in Table A.2.

Appendix B: Collisional rate coefficients

The hyperfine rate coefficients for $^{13}$CN+H$_2$ and $^{15}$N+H$_2$ were derived from the fine-structure rate coefficients computed by Kalugina et al. (2012) for CN+H$_2$. The latter coefficients were determined from fully quantum close-coupling (CC) calculations based on a highly correlated potential energy surface. Rate coefficients were deduced for temperatures ranging from 5 to 100 K. Full details can be found in Kalugina et al. (2012).
For $^{13}$CN, which possesses two non-zero nuclear spins, the IOS rate coefficients among hyperfine structure levels can be obtained similarly, including an additional coupling:

$$\begin{align*}
&k_{\text{IOS}}^{N_j F_1 F \rightarrow N'_{j'} F'_{1'} F'}(T) = (2j+1)(2j'+1)(2F_1+1)(2F'+1)(2F''+1) \\
&\times \sum_{L} \frac{2L+1}{L+1} \left( \begin{array}{c}
\jmath' \\
-1/2
\end{array} \right)^2 \left( \begin{array}{c}
\jmath \\
1/2
\end{array} \right)^2 \left( \begin{array}{c}
F'_1 \\
F_1
\end{array} \right)^2 \left( \begin{array}{c}
F'_1 \\
F_1
\end{array} \right)^2 \left( \begin{array}{c}
F'' \\
F
\end{array} \right)^2 \left( \begin{array}{c}
I_1 \\
I
\end{array} \right)^2 \left( \begin{array}{c}
I_1 \\
I
\end{array} \right)^2 \\
&\times \frac{1}{2} \left[ 1 - \epsilon(-1)^{j+j'+j'} \right] k_{0,1/2 \rightarrow L,1/2}(T),
\end{align*}$$

where $I_1 = 1/2$ and $I_2 = 1$ are the nuclear spins of $^{13}$C and $^{14}$N respectively. The propensity rule is in this case $\Delta j = \Delta F_1 = \Delta F$ and the scaling formula writes

$$\begin{align*}
k_{\text{INF}}^{N_j F_1 F \rightarrow N'_{j'} F'_{1'} F'}(T) &= \frac{k_{\text{IOS}}^{N_j F_1 F \rightarrow N'_{j'} F'_{1'} F'}(T)}{k_{\text{CC}}^{N_j \rightarrow N' F_1 F'}(T)} k_{\text{CC}}^{N_j \rightarrow N' F_1 F'}(T).
\end{align*}$$

(B.6)

In practice, the first 62 hyperfine levels of $^{13}$CN were considered, corresponding to rate coefficients for all 1676 transitions among levels with $N \leq 5$. 

**Fig. B.1.** LVG predictions at $T = 10$ K towards L1544 (left) and L1498 (right). In each panel, the grey scale shows the predicted intensity of the 110024.590 MHz component of the C$_{15}$N(1–0) hyperfine multiplet. The boxes (full line) delineate the solutions for the C$_{15}$N (cyan) and the $^{13}$CN lines (white). The dashed box shows the C$_{15}$N solutions when the C$_{15}$N column density is multiplied by factors of 7.5 and 7 for L1544 and L1498 respectively.