

ISOTOPIC ANOMALIES IN PRIMITIVE SOLAR SYSTEM MATTER: SPIN-STATE-DEPENDENT FRACTIONATION OF NITROGEN AND DEUTERIUM IN INTERSTELLAR CLOUDS

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ABSTRACT

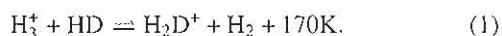
Organic material found in meteorites and interplanetary dust particles is enriched in D and ¹⁵N. This is consistent with the idea that the functional groups carrying these isotopic anomalies, nitriles and amines, were formed by ion–molecule chemistry in the protosolar nebula. Theoretical models of interstellar fractionation at low temperatures predict large enrichments in both D and ¹⁵N and can account for the largest isotopic enrichments measured in carbonaceous meteorites. However, more recent measurements have shown that, in some primitive samples, a large ¹⁵N enrichment does not correlate with one in D, and that some D-enriched primitive material displays little, if any, ¹⁵N enrichment. By considering the spin-state dependence in ion–molecule reactions involving the ortho and para forms of H₂, we show that ammonia and related molecules can exhibit such a wide range of fractionation for both ¹⁵N and D in dense cloud cores. We also show that while the nitriles, HCN and HNC, contain the greatest ¹⁵N enrichment, this is not expected to correlate with extreme D enrichment. These calculations therefore support the view that solar system ¹⁵N and D isotopic anomalies have an interstellar heritage. We also compare our results to existing astronomical observations and briefly discuss future tests of this model.

Key words: astrochemistry – ISM: clouds – ISM: molecules – meteorites, meteors, meteoroids – molecular processes – planets and satellites: formation

1. INTRODUCTION

The isotopic enrichments measured in the primitive organic matter found in comets, interplanetary dust particles and meteorites (Remusat et al. 2006; Floss et al. 2006; Aléon 2010), probably had their chemical origin in a low-temperature environment that facilitated ion–molecule isotopic exchange reactions, such as the dense interstellar medium (ISM) or the outer protosolar nebula (Mumma & Charnley 2011; Messenger et al. 2003).

The enhanced D/H ratios seen in some primitive material (Messenger 2000; Robert 2003; Messenger et al. 2003; Keller et al. 2004; Hartogh et al. 2011) almost certainly originated in low-temperature environments. Deuterium enhancement is initiated by the exothermic ion–molecule exchange reaction (Millar et al. 1989) going to the right



In dense cores where CO and other heavy molecules have condensed as ices on to dust grains (i.e., become depleted), H₂D⁺ molecules can continue to react with HD, producing HD₂⁺ and D₃⁺ (Roberts et al. 2003). This produces very high levels of deuteration in the remaining gaseous species as well as, through the resulting high atomic D/H ratios, in molecular ice mantles (e.g., Ceccarelli et al. 2007). A similar D fractionation chemistry can also occur in the cold regions of protoplanetary disks (Willacy 2007).

In both Jupiter Family and Oort Cloud comets, ¹⁴N/¹⁵N ratios are measured (~130–170) for both CN and HCN (Hutsemékers et al. 2008; Bockelée-Morvan et al. 2008) that are significantly lower than both the terrestrial and protosolar values (272 and 440, respectively; Marty 2012). Primitive materials can exhibit large bulk ¹⁵N enhancements (¹⁴N/¹⁵N ~ 180–300), and high

spatial resolution measurements further show that they also contain distinct “hotspots” which exhibit the greatest D and ¹⁵N enhancements known (¹⁴N/¹⁵N < 100) (Messenger 2000; Aleon et al. 2003; Floss et al. 2006; Busemann et al. 2006; Briani et al. 2009a; Aléon 2010).

Theoretical models of nitrogen isotopic chemistry in molecular cloud cores, where gaseous molecules are being depleted by accretion on to dust grains, can reproduce the range of ¹⁴N/¹⁵N ratios found in primitive matter (~50–280; Aléon 2010) through exchange reactions between ¹⁵N atoms and molecular ions such as ¹⁴N₂H⁺ and HC¹⁴NH⁺ (Charnley & Rodgers 2002; Rodgers & Charnley 2008a, 2008b). These models predict that N₂, NH₃, HCN, CN, and HNC molecules should possess the greatest ¹⁵N enrichments. There are two ¹⁵N-fractionating pathways (Rodgers & Charnley 2008b): a slow one to N₂ and ammonia (~10⁶ years) and more rapid one to HCN and other nitriles (~10⁵ years).

Recent, albeit sparse, astronomical observations of starless cores indicate that interstellar NH₃ and N₂ are not as enriched as predicted for the ISM or as measured in the solar system: ¹⁴NH₃/¹⁵NH₃ ≈ 334 (Lis et al. 2010) and ¹⁴N₂H⁺/¹⁴N¹⁵NH⁺ ≈ 446 (Bizzocchi et al. 2010). On the other hand, preliminary measurements indicate that interstellar HCN and HNC are highly enriched in ¹⁵N (Milam & Charnley 2012). These discrepancies are potentially related to different fractionating pathways and timescales.

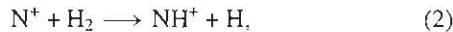
However, the most pressing problem for a direct ISM–solar system isotopic connection concerns the fact that, while ¹⁵N and D meteoritic hotspots do seem to correlate in some samples (e.g., Aleon et al. 2003), they clearly do not in others (e.g., Busemann et al. 2006; Gourier et al. 2008). Yet, as has been noted by several authors (Alexander et al. 2008; Briani et al. 2009b; Bonal et al. 2010; Aléon 2010), the low-temperature interstellar environments most conducive to producing large ¹⁵N enrichments, should also produce concomitantly enormous molecular D/H ratios (e.g., in ammonia or HCN). Thus, one would expect ¹⁵N and D hotspots to *always* be spatially

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correlated, contrary to what is seen. This presents a serious challenge for ion–molecule fractionation chemistry.

In cold interstellar environments, nuclear spin states can be an important factor in determining chemical reaction rates (e.g., Flower et al. 2006). The major interstellar collision partner, molecular hydrogen, has a 170.5 K difference in zero-point energy between the *para* (antiparallel spins) and the *ortho* (aligned nuclear spins) forms; this allows some endoergic reactions to proceed, even at low temperatures, if a substantial fraction of the H_2 is in the higher energy form, *o*- H_2 . Pagani et al. (2011) demonstrated that a high H_2 *ortho*-to-*para* ratio (OPR) therefore inhibits (“poisons”) the production of H_2D^+ in reaction (1), suppressing the overall deuteration.

The fractionation of ^{15}N may also be influenced by the OPR of H_2 . Ammonia formation is initiated by the production of N^+ from N_2 by He^+ , which then reacts in



followed by a sequence of ion–molecule reactions with H_2 through to NH_4^+ and a final electron dissociative recombination. Reaction (2) has an activation energy of $\lesssim 200$ K (Gerlich 1993) which, at low temperatures, can be overcome by the internal energy of *o*- H_2 (Le Boulton 1991). Thus, ammonia formation in dark clouds is dependent on the H_2 OPR, a distinction not made in earlier fractionation models (e.g., Rodgers & Charnley 2008b). A recent re-assessment of the OPR dependence in the original experimental data by Dislaire et al. (2012) indicates that previous work has overestimated the low-temperature rate coefficient for reaction (2), involving *o*- H_2 , by almost three orders of magnitude (cf. Le Boulton 1991). Thus, the precise abundance of *o*- H_2 could play a pivotal role in producing a diverse range of D- ^{15}N fractionation in interstellar precursor molecules.

In this Letter, we quantify the effect the H_2 OPR has on interstellar ^{15}N fractionation and demonstrate that this can account for the isotopic anomalies observed in primitive solar system materials.

2. MODEL

We consider the chemical evolution of the central regions of a static prestellar core (Charnley & Rodgers 2002) with a gas density $n(H_2) = 10^6 \text{ cm}^{-3}$, a temperature of 10 K and a visual extinction of $A_V > 10$ mag. Cosmic-ray ionization occurs at a rate of $\zeta = 3 \times 10^{-17} \text{ s}^{-1}$. The chemical model used here is based on Rodgers & Charnley (2008a, 2008b)² and Figure 1 shows the most important reactions for ^{15}N fractionation. Helium, carbon, oxygen, and nitrogen are included at elemental abundances given by Savage & Sembach (1996). We are interested in cores that are just about to form protostars and so we assume that all carbon is initially bound up in CO, with the remaining oxygen in atomic form, and the nitrogen is partly atomic with 50% in molecular and atomic forms, respectively.³ The elemental $^{14}N/^{15}N$ ratio is assumed to be 440, with the same fraction of ^{15}N in atomic form initially, $^{15}N/^{15}N^{14}N = 1$.

The gas–grain interaction is modeled according to Charnley (1997): all neutral gas-phase species, except H_2 , He, N, and N_2 , stick and freezeout onto grains upon collision. No grain surface chemistry or desorption is considered, except for sticking of

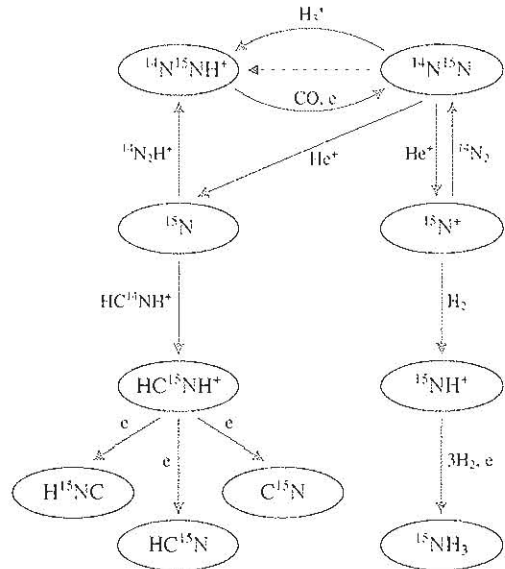


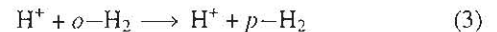
Figure 1. Chemical network showing the main reactions responsible for ^{15}N enhancement in nitriles and ammonia.

H atoms (with an efficiency of 0.6) followed by reaction to produce H_2 molecules which are ejected upon formation (see Section 2.1).

2.1. Inclusion of Spin-state Reactions

The reaction network has been expanded to contain *ortho* and *para* forms of H_2 , H_2^+ , and H_3^+ , and couples 279 gas-phase species by 4420 reactions. Both spin types have been considered equally likely to react with a given species, with the exception of reaction (2), where new rates of Dislaire et al. (2012) for *ortho* and *para* H_2 , $k_{2,o} = 4.20 \times 10^{-10} (T/300)^{-0.17} \exp(-44.5/T) \text{ cm}^3 \text{ s}^{-1}$ and $k_{2,p} = 8.35 \times 10^{-10} \exp(-168.5/T) \text{ cm}^3 \text{ s}^{-1}$, respectively, have been adopted. Other temperature-dependent H_2 reactions have energy barriers that are too high for the ground-state energy difference between the spin types to have a significant effect at 10 K.

Initially, the H_2 OPR is set to the high-temperature statistical equilibrium value of 3. Measurements in the diffuse ISM by Crabtree et al. (2011) are consistent with an H_2 OPR around 1; we find adopting this lower value has little effect on our results. The reaction



is exothermic by 170.5 K and so *o*- H_2 is efficiently converted into *p*- H_2 at low temperatures. We assume that the H_2 formed and ejected from grains has an OPR of 3; this ensures a steady-state OPR is reached. Reaction rates for conversion between *ortho* and *para* species, as well as for their interaction with electrons and cosmic rays, have been implemented from Walmsley et al. (2004). Branching ratios for *o/p*- H_3^+ formation from H_2^+ and H_2 , and rates for H_3^+ interaction with CO and N_2 , are taken from Pagani et al. (2009). Furthermore, all reactions involving proton transfer from H_3^+ to neutral molecules have been assigned branching ratios according to Oka (2004) and no spin conversion is assumed to take place in reactions involving electron transfer to H_2^+ . Apart from these special cases, reactions are assumed to produce *ortho* and *para* versions of H_2 , H_2^+ , and H_3^+ with equal probability.

² We do not consider the neutral–neutral isotope exchange reactions proposed by Rodgers & Charnley (2008b).

³ The effect of different N/N_2 ratios on this chemistry is discussed in detail by Rodgers & Charnley (2008a).

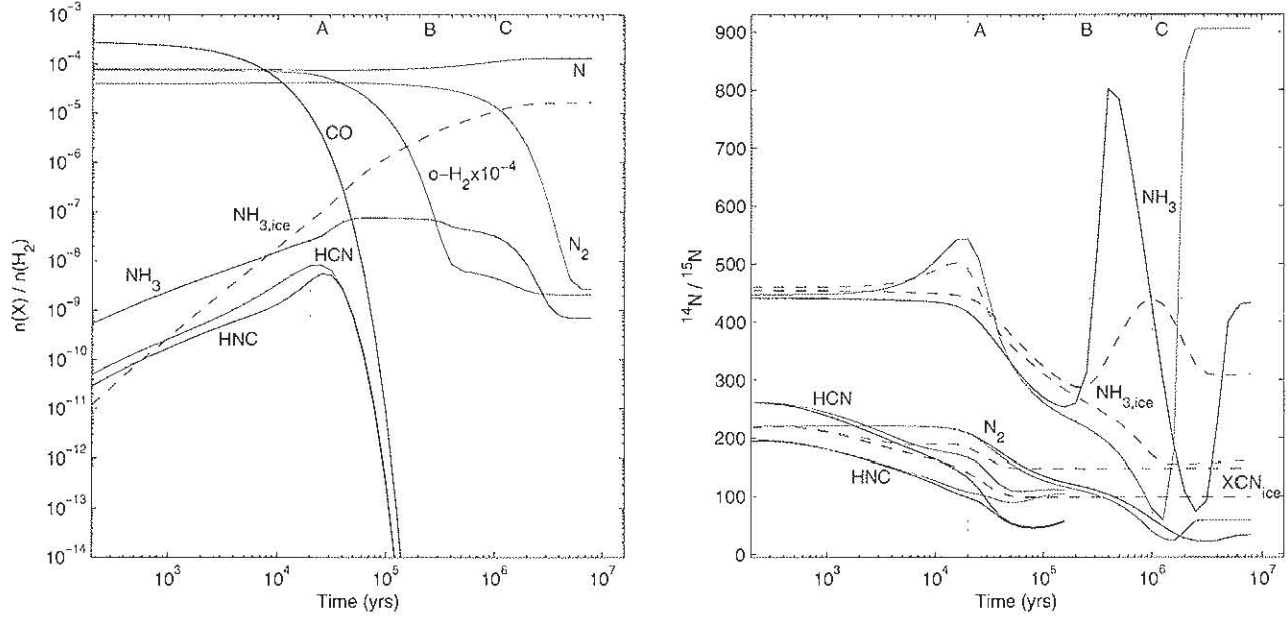
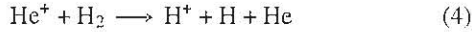


Figure 2. Left panel: time evolution of the nitrogen chemistry in dense cores, compared to CO and *o*-H₂. Crucial times for the ¹⁵N fractionation in nitrogen hydrides are marked by vertical dotted lines, labeled A, B, and C. Right panel: evolution of the ¹⁴N/¹⁵N ratio in gas-phase molecules and bulk of ammonia and nitrile ices. Black curves represent the current model, while red curves show the corresponding isotopic ratios in the model of Rodgers & Charnley (2008a). The assumed elemental value of 440 is marked by a dotted horizontal line. Values for gas-phase nitriles are omitted after $\sim 2 \times 10^5$ years when abundances for both isotopologues are essentially zero due to freezeout. Dashed curves represent ice-phase species.

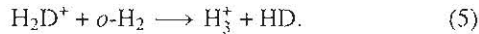
2.2. Other Reactions

Since nitrogen fractionation is initiated by He⁺ reactions (see Figure 1), the He⁺ chemistry dictates the timescale of fractionation. In particular, the rate for the reaction



has previously been assigned widely different values at 10 K, ranging from $1.1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (Rodgers & Charnley 2008b) to $2.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (Walmsley et al. 2004). We have adopted the measured low-temperature rate $k_4 = 3.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (Schauer et al. 1989).

In order to qualitatively compare the temporal patterns in ¹⁵N fractionation to the expected levels of deuteration during core evolution, we also include the chemistry for *ortho* and *para* H₂D⁺ in the model since *o*-H₂ can overcome the barrier for the reverse of reaction (1), i.e.,



The most important reactions for spin-state-dependent *o/p*-H₂D⁺ formation and destruction are adapted from Walmsley et al. (2004), and we assume a deuterium abundance corresponding to HD = 1.5×10^{-5} relative to elemental hydrogen.

3. RESULTS

Figure 2 shows the evolution of the major chemical species. The ammonia abundance builds up to about 10^{-7} with respect to H₂ around a core age of 10^5 years (left panel), which is comparable to what is typically observed (Hotzel et al. 2004). Similarly, the peak HCN and HNC agree well with values observed in dense cores (Padovani et al. 2011). At this time the CO is depleted by a factor of $> 10^3$. A steady-state H₂ OPR

of 2.3×10^{-5} , consistent with attempts to quantify the OPR in the cold dark cloud B68 (Troscompt et al. 2009), is reached after about 10^6 years.

The right panel of Figure 2 shows the evolution of the molecular ¹⁴N/¹⁵N ratios in the current model, compared to the corresponding results from the Rodgers & Charnley (2008a) model. As expected (see, e.g., Figure 1), the inclusion of a spin-state dependence does not significantly affect the evolution of fractionation in the nitriles: the ¹⁵N enhancement starts to build up from the initial pool of atomic ¹⁵N early on, and continues to increase until gas-phase abundances have dropped to below 10^{-13} . The ¹⁴N/¹⁵N ratios in gas-phase HCN and HNC lie in the range ≈ 50 –260. When all nitriles are frozen out, the ¹⁵N enhancement in the bulk of nitrile ices (CN, HCN, HNC, and H₃CN) is ~ 5 .

The inclusion of spin-state dependence does however have a dramatic effect on the ¹⁵N fractionation in ammonia. The relative delay in the timing of the late enhancement peak in the current model, as compared to Rodgers & Charnley (2008a), stems from the higher rate ($\sim 3\times$) of reaction (4) (see Section 2.2). However, the main difference is that the NH₃ enrichment is not monotonic in time. The sharp decrease starting around 2×10^5 years (time B) (i.e., an increase in ¹⁴NH₃/¹⁵NH₃), is caused by the inefficiency of reaction (2) as the *o*-H₂ abundance drops (see Figure 2).

To understand what causes the fractionation patterns, we compare abundances to isotopologue ratios at crucial times in the evolution, marked by vertical lines A, B, and C in Figure 2. Initially, the limiting reaction for fractionation is the production of ¹⁵N⁺, and the ¹⁴N/¹⁵N ratio in ammonia is simply double that of ¹⁴N₂/¹⁴N¹⁵N. As gas-phase CO gets depleted after $\sim 10^4$ years (A), more He⁺ becomes available to produce ¹⁵N⁺, which starts to enrich the nitrogen hydrides beyond that of N₂. However, after $\sim 10^5$ years, the H₂ OPR drops below 2×10^{-7}

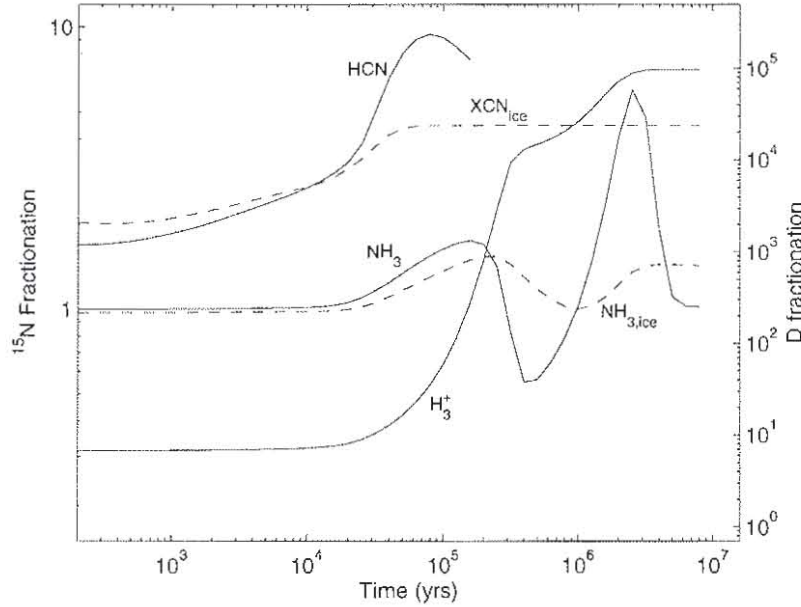
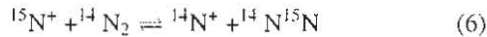


Figure 3. Nitrogen fractionation in ammonia and HCN, both gas-phase (solid) and bulk ice (dashed) in blue curves according to left-hand axis, compared to deuterium fractionation in $\text{H}_2\text{D}^+/\text{H}_3^+$ (green curve and scale on right-hand axis). ^{15}N enhancements are given relative to the elemental $^{15}\text{N}/^{14}\text{N}$ ratio of 1/440, while D enhancements are relative to elemental $\text{D}/\text{H} = 1.5 \times 10^{-5}$.

(B), reaction (2) becomes less efficient, and more $^{15}\text{N}^+$ is instead circulated back into molecular nitrogen by



(Terzieva & Herbst 2000), lowering the ^{15}N fraction in ammonia to less than half the elemental fraction. The reason for ammonia to subsequently become ^{15}N enriched after 10^6 years (C) is that the molecular nitrogen fraction decrease substantially. This both reduces the fraction of $^{15}\text{N}^+$ converted back into molecular form (Figure 1) and decreases the amount of $^{14}\text{N}^+$ available to produce $^{14}\text{NH}_3$.

Fractionation changes in the bulk of amine ices follows the pattern of gas-phase fractionation, but with a time lag and not as pronounced extreme values. While the bulk of amine ices on grains has ^{15}N fractions within 30% of the elemental fraction, at any given time the fractionation in the outer monolayer may show much larger variations (Rodgers & Charnley 2008a).

In Figure 3 the calculated deuterium fractionation in H_3^+ is plotted together with the molecular ^{15}N fractionation. The D/H ratios in other gas-phase molecules, in atoms, and therefore also in the accreted molecular ices, will closely follow that of H_3^+ . The increase in deuteration follows very closely the drop in $\sigma\text{-H}_2$ abundance, and after 2×10^5 years (time B), ratios of $\text{D}/\text{H} > 1\%$ are predicted. These trends in both deuteration and OPR evolution agree well with previous investigations (Pagani et al. 2011; Flower et al. 2006).

Figure 3 shows that gas-phase chemistry can indeed reproduce the requisite range of D and ^{15}N enrichments in nitrile and amine functional groups. Three fractionation patterns develop as the core evolves as following.

1. For times less than about $\sim 2 \times 10^5$ years, gaseous nitriles can develop large enrichments in ^{15}N ($\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N} \approx 50\text{--}260$) but will only be modestly enriched in D, as observed (e.g., $\text{DNC}/\text{HNC} \approx 0.01\text{--}0.05$; Hirota et al. 2001); this will be reflected in the accreted ices. Ammonia will be similarly enriched in D but less enriched in ^{15}N than

the nitriles. At this stage the nitrile gas-grain fractionation is complete.

2. Between $\sim 2 \times 10^5\text{--}10^6$ years, the remaining ammonia can become highly fractionated in D but is either not enriched, or even depleted, in ^{15}N .
3. Beyond 10^6 years, ammonia becomes very highly enriched in both D and ^{15}N .

Thus, the model naturally produces a range of D- ^{15}N fractionation in nitrile and amine functional groups that is qualitatively consistent with that found in primitive organic matter. In general, the highest ^{15}N enrichments and lowest D enrichments should be carried by nitriles. Amines could account for the fractionation of material that is highly enriched in D only, as well as the material that is simultaneously highly enriched in both D and ^{15}N . This functional-group dependency has already been noted in analyses of meteoritical samples. However, an important caveat is that conversion of nitriles to amines by H and D additions on grain surfaces (e.g., hydrogenation of HCN to CH_2NH and CH_3NH_2 ; Theule et al. 2011) has to be negligible. The 30% enrichment of the bulk ammonia ice cannot account for all the enhanced ammonia fractionation measured in carbonaceous chondrites ($^{14}\text{NH}_3/^{15}\text{NH}_3 \approx 185\text{--}256$; Pizzarello & Williams 2012). However, we predict $^{14}\text{NH}_3/^{15}\text{NH}_3 \approx 100$ as the highest gas-phase enrichment and this will lead to higher $^{14}\text{NH}_3/^{15}\text{NH}_3$ ratios in the uppermost monolayers of the stratified ices (Rodgers & Charnley 2008a).

Interstellar gas-phase $^{14}\text{N}/^{15}\text{N}$ ratios in nitriles have been measured in several Galactic sources selected for being unlikely to have experienced significant isotopic fractionation (Adande & Ziurys 2012). For cold dark cores, fewer measurements exist; our model predicts very low $^{14}\text{N}/^{15}\text{N}$ ratios for HCN and HNC. For ammonia, the observed $^{14}\text{NH}_3/^{15}\text{NH}_3$ ratios in dense protostellar cores (≈ 340 ; Lis et al. 2010) are consistent with the modest enrichments which can occur within 10^5 years. The measurement of $^{14}\text{NH}_3/^{15}\text{NH}_3 > 700$ in L1544 (Gerin et al. 2009) is consistent with the prediction that ^{15}N nuclei can be underabundant in ammonia. It also suggests a chemical age of

$\approx 3 \times 10^5$ years for the fractionated ammonia gas (Figure 3), and that it should exist in a region of the L1544 core spatially distinct from HCN and HNC (cf. Padovani et al. 2011).

4. CONCLUSIONS

By considering the ortho–para dependence in ion–molecule reactions involving H_2 , ammonia, and related molecules are expected to exhibit a wide range of fractionation in both ^{15}N and D , consistent with those found in primitive solar system organic matter. These include very large enrichments in both D and ^{15}N , as found in previous models, but also low ^{15}N enrichment or even depletion, coupled with modest to large D/H values. Nitrile functional groups on the other hand, while being the most likely source of ^{15}N hotspots, are not predicted to correlate with extreme D enrichment. These calculations support the premise that the ^{15}N isotopic anomalies found in meteorites were set in functional groups formed in a cold molecular cloud.

The predicted $^{14}\text{N}/^{15}\text{N}$ and D/H ratios can account for the limited measurements existing for interstellar cloud cores. To further test and constrain these theoretical models, surveys for key molecules and measurements of relevant $^{14}\text{N}/^{15}\text{N}$ ratios in molecular clouds are required. A more extensive analysis of how correlations between deuterium and ^{15}N enrichment in specific molecules are affected by spin-state-dependent chemistry is beyond the scope of this Letter and will be considered elsewhere (E. S. Wirström et al. 2012, in preparation). Predictions from these models can be tested by measurements of various multiply substituted isotopologues (e.g., DC^{15}N , $^{15}\text{NH}_2\text{D}$; Gerin et al. 2009), which will be facilitated with the Atacama Large Millimeter Array.

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