

**SPIN-STATE-DEPENDENT ION-MOLECULE CHEMISTRY AS THE ORIGIN OF  $^{15}\text{N}$  AND D ISOTOPIC ANOMALIES IN PRIMITIVE MATTER.** E. S. Wirström<sup>1</sup>, S. B. Charnley<sup>1</sup>, M. A. Cordiner<sup>1</sup>, S. N. Milam<sup>1</sup>, <sup>1</sup>*Astrochemistry Laboratory, Code 691.0, NASA Goddard Space Flight Center, 8800 Greenbelt Rd., Greenbelt, MD 20771, USA (email: eva.s.wirstrom@nasa.gov).*

**Introduction:** Many meteoritic and IDP samples contain bulk enhancements and hotspots rich in  $^{15}\text{N}$  (e.g. [1, 2, 3]). Similarly low  $\text{C}^{14}\text{N}/\text{C}^{15}\text{N}$  ratios have been observed in numerous comets [4]. An almost constant enrichment factor in comets from distinct formation zones in the nebular disk (i.e. both Jupiter Family and Oort Cloud comets), strongly suggests that this fractionation is primordial and was set in the protosolar cloud core [5]. Deuterium enrichment is observed in both meteorites and IDPs [6, 2, 7].

**Interstellar Chemistry:** Ion-molecule reactions at low ( $\sim 10$  K) temperatures can lead to an enhanced D and  $^{15}\text{N}$  fractionation in interstellar molecules [8, 9]. Atom-molecular ion reactions of the type  $^{15}\text{N} + ^{14}\text{N}_2\text{H}^+ \rightleftharpoons ^{14}\text{N} + ^{15}\text{N}^{14}\text{NH}^+$  are important in enriching molecules in heavy nitrogen and, as in the case of deuterium, significant CO depletion permits much larger isotopic effects [10]. Helium ion attack on  $^{14}\text{N}^{15}\text{N}$  releases the  $^{15}\text{N}$  nuclei, as well as  $^{15}\text{N}^+$  ions which may react with  $\text{H}_2$  to form  $^{15}\text{NH}^+$  and subsequently ammonia. Condensation of these gaseous products on dust grains leads to ices with bulk enhancements in ammonia of +800‰, and peak monolayer enhancements of a factor of seven (i.e.  $\delta^{15}\text{N} = +6000$ ‰, [11]). CO depletion and a negligible rate for the reaction  $\text{N} + \text{CN} \rightarrow \text{N}_2 + \text{C}$  prevents recycling of N atoms back into  $\text{N}_2$  and leads to two distinct  $^{15}\text{N}$  fractionation pathways in dense interstellar gas [12]: a slow one to ammonia ( $\sim 10^6$  years) and more rapid one to HCN and other nitriles ( $\sim 10^5$  years).

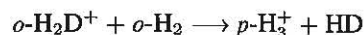
**Isotopic Carriers and Correlations:** The major goals for theories of isotopic fractionation in primitive materials based on interstellar chemistry are the explanations of isotopic correlations, or lack thereof, the highly variable enrichment in specific molecular functional groups, and the identification of candidate interstellar fractionation environments and precursor molecules [13, 14, 15, 16]. In principle, the nature of the functional groups which display isotopic enhancements should be related to the interstellar molecules from which they derive. For example, we may expect that isotopic anomalies measured in carbonyl, nitrile, amine, aliphatic and aromatic functional groups [17, 18, 13, 2, 7, 19] should be related to the isotope ratios in potential interstellar progenitors such as CO, HCN,  $\text{NH}_3$ ,  $\text{CH}_4$  &  $\text{C}_2\text{H}_6$ , and PAHs.

The most pressing problem, however, concerns the fact that, while  $^{15}\text{N}$  and D hotspots do seem to correlate in some samples (e.g. [18]), they clearly do not in others (e.g. [2, 7]), even down to the level of molecular subgroups in amino acids [16]. Yet, as has been noted

by several authors [20, 21], the interstellar environments most conducive to producing enormous  $^{15}\text{N}/^{14}\text{N}$  ratios, should also produce concomitantly large molecular D/H ratios (e.g. in ammonia or HCN). Thus, one would expect  $^{15}\text{N}$  and D hotspots to *always* be spatially correlated, contrary to what is seen. This presents a serious challenge for interstellar-type ion-molecule chemistry.

**Spin-State-Dependent Isotopic Chemistry:** The reaction rates associated with  $^{15}\text{N}$  and D fractionation vary strongly in the temperature range  $\sim 5$ –40 K [15]. Although a temperature regime may exist where modestly-deuterated molecules with minimal  $^{15}\text{N}$  enrichment could exist, the converse – large  $^{15}\text{N}$  enrichments and no deuteration –, as seen in primitive matter, cannot occur. However, careful consideration of interstellar chemistry suggests a possible resolution of this problem. Some interstellar molecules can exist in either of two distinct states depending upon the relative alignment of the spins of their H nuclei (parallel or antiparallel), giving rise to *ortho* and *para* forms. For molecular hydrogen, the *o*- $\text{H}_2$  ground state ( $J = 1$ ) is 170 K above the *p*- $\text{H}_2$  ground state ( $J = 0$ ); this internal energy difference can have a profound effect on ion-molecule chemistry at low temperatures, especially deuteration [22, 23].

The key reaction for making molecular clouds molecular is the formation of  $\text{H}_2$  molecules on dust grains which are probably ejected into the gas upon formation with an *op* abundance ratio (OPR) of 3:1. At low temperatures, ion-molecule spin-exchange reactions involving  $\text{H}^+$  and  $\text{H}_3^+$  will tend to convert most *o*- $\text{H}_2$  to *p*- $\text{H}_2$ . The time-scale for this conversion depends on the ionization rate  $\zeta$ , but is generally shorter than, or comparable to, the estimated lifetime of molecular clouds [24]. If present, a high abundance of *o*- $\text{H}_2$  molecules acts as a ‘poison’ for deuterium fractionation because the reaction



can proceed rapidly, even at 10 K, and suppress interstellar deuteration [24].

Conversely, the internal energy of *o*- $\text{H}_2$  is necessary to overcome the small barrier in the initiating reaction for ammonia formation, and hence  $^{15}\text{NH}_3$  fractionation:



Early estimates concluded that an  $\text{H}_2$  OPR in excess of  $\sim 10^{-4}$  would be sufficient to account for the observed dense cloud ammonia abundances [25]. However, a recent re-assessment of the OPR dependence in the original experimental data indicates that the rate coefficient of this process has been overestimated by almost three orders of magnitude at low temperatures [26]. Thus, if

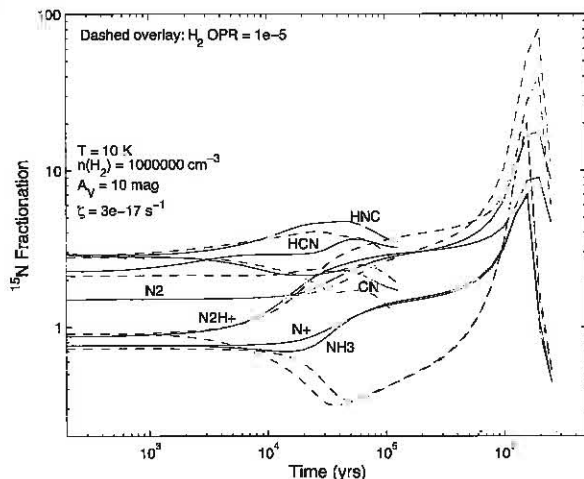


Figure 1: Time evolution of  $^{15}\text{N}$  enrichment in a cloud at physical parameters as given in the frame. The  $^{14}\text{N}/^{15}\text{N}$  abundance ratio is set to 400. Solid and broken curves are for  $\text{H}_2$  OPR values of 3 and  $1 \times 10^{-5}$  respectively. Values for gas-phase nitriles are not plotted after  $10^5$  yr because the molecular abundances are negligible (see [12]).

the  $\text{H}_2$  OPR is comparatively large, deuteration is inhibited but  $^{15}\text{N}$  fractionation can proceed. This leads to the expectation that, at low-temperatures, the  $\text{H}_2$  OPR could mediate a large range of D- $^{15}\text{N}$  fractionation ratios in interstellar molecules.

**Model:** To demonstrate the effect of the  $\text{H}_2$  OPR on interstellar  $^{15}\text{N}$  fractionation, we have incorporated the results of Dislaire et al. [26] into the chemical model of Rodgers & Charnley [12]. We consider OPR values of 3 and  $1 \times 10^{-5}$ , the latter consistent with observed limits [27]. Fig. 1 shows that a low OPR does suppress  $^{15}\text{N}$  fractionation in ammonia although the nitriles remain enriched. On this time-scale ( $t \sim 10^6$  yr) the gaseous molecules will become increasingly enriched in D as CO freezes out on dust. The fact that  $\text{N}^+ + \text{H}_2$  is less efficient when  $\text{OPR} = 1 \times 10^{-5}$  means that at later times ( $t \sim 10^6$  yr) the exchange reaction  $^{15}\text{N}^+ + ^{14}\text{N}_2 \rightleftharpoons ^{14}\text{N}^+ + ^{15}\text{N}^{14}\text{N}$  operates to enrich  $^{15}\text{N}$  in  $\text{N}_2$ ,  $\text{N}_2\text{H}^+$  and  $\text{NH}_3$ , although their abundances are quite low (cf. [11]).

**Summary:** A more sophisticated treatment of low-temperature ion-molecule chemistry, involving spin-state dependence in molecular reactants, has the potential to provide a natural explanation of the distribution of isotopic anomalies exhibited in primitive matter. Comprehensive theoretical models which account for these processes in D,  $^{15}\text{N}$  and  $^{13}\text{C}$  fractionation can be tested by comparison with future ALMA observations of multiply-fractionated molecules in analogues of the presolar cloud core, and allow us to quantify the interstellar contribution to (functional group) fractionation measured in

primitive materials.

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