Astronomy in Focus, Volume 1, Focus Meeting 9
XXIXth IAU General Assembly, August 2015
Piero Benvenuti, ed.

doi:10.1017/S1743921316003033

^{15}N fractionation in star-forming regions and Solar System objects

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Abstract. We briefly review what is currently known of ^{14}N/^{15}N ratios in interstellar molecules. We summarize the fractionation ratios measured in HCN, HNC, CN, N_2 and NH_3, and compare these to theoretical predictions and to the isotopic inventory of cometary volatiles.

Keywords. astrochemistry, molecular data, solar system: formation, ISM: abundances, ISM: molecules, radio lines: ISM, astrobiology

1. Introduction

Cometary ices are believed to be the least modified in the Solar System and as such may have the closest connection to the pristine interstellar material which comprised the presolar molecular cloud. Molecular isotopic ratios offer the prospect of understanding the provenance and processing of the volatile material found in comets, meteorites and interplanetary dust particles (Mumma & Charnley 2011; Marty 2012; Bockelée-Morvan *et al.* 2015). For example, the enhanced deuterium fractionation in primitive Solar System matter has long been considered a marker for low-temperature ($\sim$10 K) fractionation chemistry and recent theoretical work indicates that even the relatively modest D/H ratios measured in comets (a few times 10^{-4}) could not have been generated in the Sun's protoplanetary disk (Cleeves *et al.* 2014).

Anomalies (i.e. ^{15}N enrichments) in nitrogen isotope ratios are found in both the soluble and insoluble organic matter in meteorites and IDPs (Marty 2012). Isotopic measurements indicate that ^{15}N and D enrichments are present in the bulk material and can be even higher in small localized regions (Aléon 2010). Observations of HCN, CN and NH_3 in cometary comae also indicate enhanced ^{15}N fractionation (Jehin *et al.* 2009; Rousselot *et al.* 2014), with ^{14}N/^{15}N ratios lower than both the Solar value (440) and the nominal value of the local ISM (300, Adande & Ziurys 2012).

In this article we briefly summarize our theoretical and observational understanding of ^{14}N/^{15}N ratios in interstellar molecules and their possible connection to cometary molecules.

2. Interstellar Nitrogen Fractionation: Theory and Observations

As with deuterium fractionation, it was posited that the ^{15}N enrichments in Solar System matter could have their origin in low-temperature ion-molecule reactions (e.g. Bernatowicz 1997). Candidate ion-neutral isotope exchange reactions were identified and evaluated although only modest enhancements were found in related model calculations of molecular cloud chemistry (Terzieva & Herbst 2000). The most important of these are those that can lead to fractionation in N_2, and consequently in ammonia, and in the nitriles HCN, HNC and CN:

$$^{15}\mathrm{N} + {}^{14}\mathrm{N_2H^+} \leftrightharpoons {}^{14}\mathrm{N} + {}^{14}\mathrm{N}^{15}\mathrm{NH^+} \quad (2.1a)$$

$$\leftrightharpoons {}^{14}\mathrm{N} + {}^{15}\mathrm{N}^{14}\mathrm{NH^+} \quad (2.1b)$$

$$^{15}\mathrm{N} + \mathrm{HC}^{14}\mathrm{NH^+} \leftrightharpoons {}^{14}\mathrm{N} + \mathrm{HC}^{15}\mathrm{NH^+} \quad (2.1c)$$

These molecular ion-neutral atom processes and other ion-molecule reactions proposed by Terzieva & Herbst (2000) have formed the basis of most subsequent theoretical studies of fractionation in molecular clouds. These studies have shown that enhanced gas-phase and solid-phase $^{14}N/^{15}N$ ratios can be attained depending on the initial atomic/molecular N ratio and, when all the nitrogen is initially molecular, on the level of CO depletion (Charnley & Rodgers 2002; Rodgers & Charnley 2008). More recent calculations show that the spin state of molecular hydrogen can play an important role in the combined evolution of molecular D/H and $^{14}N/^{15}N$ ratios (Wirström *et al.* 2012).

These time-dependent models show that ^{15}N fractionation in the nitriles occurs on a much shorter timescale than that which occurs in N_2 and NH_3. Overall, they predict $^{14}N/^{15}N$ ratios in interstellar molecules consistent with the meteoritic values, and with the nitrile ratios measured in comets (see below).

Until recently, both the theoretical models and the proposed ISM-comet connection were largely unconstrained because of lack of $^{14}N/^{15}N$ ratio measurements in interstellar clouds (cf. Ikeda *et al.* 2002). However, motivated by the meteoritic and cometary measurements, in the last few years, molecular $^{14}N/^{15}N$ ratios have now been determined for HCN, HNC, CN, N_2 and NH_3 in a variety of interstellar and protostellar environments. Table 1 summarizes these observations and also lists the corresponding range of cometary $^{14}N/^{15}N$ ratios. For each molecule, we can compare the observed interstellar $^{14}N/^{15}N$ ratios with the theoretical predictions and each of these with the range of cometary values.

HCN and HNC show a range of $^{14}N/^{15}N$ ratios in (pre-stellar) dark clouds that are consistent both with the cometary values and the predictions of published models; in protostars, these molecules appear to be less-enriched in ^{15}N. The CN ratios tend to be larger which is difficult to understand if all three nitriles are produced mainly from dissociative recombination of protonated HCN.

Across the sample, $^{14}NH_3/^{15}NH_3$ ratios do not exhibit enhancements comparable to that in the nitriles and in fact show evidence for depletion in ^{15}N, the most extreme cases being in L1544 and L1689N. These trends are consistent with calculations of ammonia fractionation (Wirström *et al.* 2012) but none of the interstellar $^{14}NH_3/^{15}NH_3$ ratios come within a factor of two of the highly-enriched cometary values.

The molecular nitrogen $^{14}N/^{15}N$ ratios, as measured via N_2H^+, $^{15}N^{14}NH^+$ and $^{14}N^{15}NH^+$, exhibit an extremely wide range of values across all types of sources. Theoretical models of dense cores actually predict that N_2 should be as enriched as the nitriles but never produce high $^{14}N/^{15}N$ ratios (i.e. ^{15}N depleted). Molecular nitrogen has only been measured in one comet (Rubin *et al.* 2015) and the prospects for detection of the associated $^{14}N/^{15}N$ ratio are slim.

However, the most serious issue for studies of nitrogen fractionation is that recent quantum-chemical calculations and chemical modeling by Roueff *et al.* (2015) indicate that ^{15}N atomic exchange reactions do not fractionationate N_2H^+ and $HCNH^+$ as efficiently as previously assumed (see Eq's 2.1). Have previous theoretical models been

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Table 1. Interstellar Nitrogen Isotope Ratios

Source	Type	NH_3	N_2H^+ §	HCN	HNC	CN	Ref.
L1544	dark core	>700	1000±200	69-154	>27	500±75	4,1,3,3,9
			1000±200	140-360			1,2
L1498	dark core	619±100	…	>75	>90	500±75	3,3,3,9
				>813			5
L1521E	dark core	…	…	151±16	…	…	5
L1521F	dark core	539±118	…	>51	24-31	…	3,3,3
L1262-core	dark core	356±107	>297	…	…	…	3,3
			175±79				3
L183	dark core	$530\pm^{570}_{180}$	…	140-250	…	…	4,2
NGC 1333-DCO$^+$	dark core	$360\pm^{260}_{110}$	…	…	…	…	4
NGC 1333-4A	Class 0 protostar	344±173	…	…	…	…	6
		>270					4
B1	Class 0 protostar	$300\pm^{55}_{40}$	>600	$165\pm^{30}_{25}$	$75\pm^{25}_{15}$	240	10,10,10,10,9
		334±50	$400\pm^{100}_{65}$				6,10
		$470\pm^{170}_{100}$					4
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	…	…	…	…	4
Cha-MMS1	Class 0 protostar	…	$729\pm^{212}_{135}$	…	135	…	16,7
IRAS 16293A	Class 0 protostar	…	…	163±20	242±32	…	13
R Cr A IRS7B	Class 0 protostar	…	…	287±36	259±34	…	13
OMC-3 MMS6	Class 0 protostar	…	…	366±86	460±65	…	13
L1262-YSO	Class I protostar	453±247	>410	…	…	…	3,3
			>410				3
Several	Massive starless cores	…	65-1100	…	…	330-400	15,15
			180-1445#				15
Several	Massive protostars	…	190-1000	…	…	190-450	15,15
			180-1300				15
Several	UC HII regions	…	320-900	…	…	230-430	15,15
			350-700				15
Comets	JFC & Oort Cloud	127‡	…	139±26	…	135-170†	11,12,8

References: (1) Bizzocchi *et al.* (2013); (2) Hily-Blant *et al.* (2013a); (3) Milam & Charnley (2012), Adande *et al.* (2015); (4) Gerin *et al.* (2009); (5) Ikeda *et al.* (2002); (6) Lis *et al.* (2010); (7) Tennekes *et al.* (2006); (8) Hutsemékers *et al.* (2008); (9) Hily-Blant *et al.* (2013b); (10) Daniel *et al.* (2013); (11) Rousselot *et al.* (2014); (12) Bockelée-Morvan *et al.* (2008); (13) Wampfler *et al.* (2014); (15) Fontani *et al.* (2015); (16) Cordiner *et al.*, private communication.

§In each N_2H^+ entry the uppermost value is for the $^{15}N^{14}NH^+$ isotopologue. #Larger value is a lower limit. ‡'Average' based on optical observations of NH_3 daughter molecule NH_2 in an ensemble of comets. †This range can be taken as a surrogate for the HCN ratio, however in comets there may be additional sources of CN (see Mumma & Charnley 2011). Only 2 measurements have been made for HCN itself, in OC comets Hale-Bopp and 17P/Holmes.

able to predict and reproduce the meteoritic, cometary and interstellar $^{14}N/^{15}N$ ratios of nitriles and amines merely by chance?

3. Summary

The study of nitrogen isotopic fractionation in primitive matter, in comets and in astronomical environments has been the focus of much recent activity. For nitriles, $^{14}N/^{15}N$ ratios measured in interstellar and protostellar sources are comparable with cometary values, as are recent measurements of $HC^{14}N/HC^{15}N$ in disks (Öberg *et al.*, these proceedings). Interstellar ammonia does not appear to be as enriched as the nitriles and the interstellar $^{14}NH_3/^{15}NH_3$ ratios are significantly higher than those found in cometary ammonia. Molecular nitrogen exhibits the largest range of values with enrichments similar to the nitriles, but also very marked ^{15}N depletions. The theoretical perspective is

https://doi.org/10.1017/S1743921316003033 Published online by Cambridge University Press

rather puzzling and clearly something fundamental is missing from our understanding of interstellar nitrogen isotope fractionation. This is most likely not connected to isotope-selective photodissociation (Heays *et al.* 2014), but some proposed neutral-neutral processes remain viable (Rodgers & Charnley 2008; Roueff *et al.* 2015).

More measurements of the complete suite of important molecules - HCN, HNC, CN, N_2H^+ and NH_3 - in cold clouds, regions of low-mass and massive star formation, and in comets are necessary to confirm and explore these trends further.

ESW acknowledges generous support from the Swedish National Space Board. This work was supported by NASA's Origins of Solar Systems Program.

References

Adande, G. R. *et al.* 2015, in preparation

Adande, G.R. & Ziurys, L. M. *Astrophys. J.* 744, 194

Aléon, J. 2010, *Astrophys. J.* 722, 1342

Bernatowicz, T. J. 1997, in *From Stardust to Planetesimals*, eds. Y. Pendleton, A.G.G.M. Tielens, 122, 227. (Provo: Utah. Astron. Soc. Pac.)

Bizzocchi, L. *et al.* 2013, *Astron. Astrophys.* 555, A109

Bockelée-Morvan, D, *et al.* 2008. *Astrophys. J.* 679, L49

Bockelée-Morvan, D. *et al.* 2015, *Space Sci. Rev.*, Published online, DOI 10.1007/s11214-015-0156-9

Charnley, S. B. & Rodgers, S. D. 2002. *Astrophys. J.* 569, L133

Cleeves, L. I. *et al.* 2014, *Science* 345, 1590

Daniel, F. *et al.* 2013, *Astron. Astrophys.* 560, A3

Fontani, F. *et al.* 2015, *Astrophys. J.* 808, L46

Gerin, M. *et al.* 2009, *Astron. Astrophys.* 498, L9

Heays, A. N. *et al.* 2014. *Astron. Astrophys.* 562, 61

Hily-Blant, P. *et al.* 2013a, *Icarus*, 223, 582

Hily-Blant, P. *et al.* 2013b, *Astron. Astrophys.* 557, A65

Hutsemékers, D. *et al.* 2008. *Astron. Astrophys.* 490, L31

Ikeda, M., *et al.* 2002. *Astrophys. J.* 575, 250

Jehin, E. *et al.* 2009. *Earth, Moon, and Planets* 105, 167

Lis, D. C., *et al.* 2010, *Astrophys. J.* 710, L49

Marty, B. 2012, *EPSL*, 313-314, 56

Milam, S. N. & Charnley, S. B. 2012, *LPSC Meeting XLIII*, #2618

Mumma, M. J. & Charnley, S. B. 2011, *Annu. Rev. Astron. Astrophys.* 49, 471

Rodgers, S. D. & Charnley, S. B. 2008, *Astrophys. J.* 689, 1448

Roueff, E. *et al.* 2015, *Astron. Astrophys.* 576, A99

Rousselot, P. *et al.* 2014. *Astron. Astrophys.* 780, L17

Rubin, M. *et al.* 2015, *Science* 348, 232

Tennekes, P. P. *et al.* 2006, *Astron. Astrophys.* 456, 1037

Terzieva, R. & Herbst, E. 2000. *Mon. Not. R. Astron. Soc.* 317, 563

Wampfler, S. *et al.* 2014, *Astron. Astrophys.* 572, A24

Wirström, E. S. *et al.* 2012, *Astrophys. J.* 757, L11

Öberg, K. I. *et al.* 2015, these proceedings