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Simulating the density of $HC^{15}N$ in the Titan atmosphere with a coupled ion-neutral photochemical model

V. Vuitton (1), R. V. Yelle (2), S. J. Klippenstein (3), P. Lavvas (4) and S. M. Hörst (5)
(1) Institut de Planétologie et d'Astrophysique de Grenoble, Univ. Grenoble Alpes, CNRS, Grenoble, F-38000, France, (2) Lunar and Planetary Laboratory, Univ. of Arizona, Tucson, AZ 85721, USA, (3) Chemical Sciences and Engineering Division, Argonne National Lab., Argonne, IL 60439, USA, (4) Groupe de Spectrométrie Moléculaire et Atmosphérique, Univ. Reims Champagne-Ardenne, CNRS, Reims, F-51687, France, (5) Department of Earth and Planetary Sciences, Johns Hopkins Univ., Baltimore, MD 21218, USA (veronique.vuitton@obs.ujf-grenoble.fr)

Abstract

The $^{14}N/^{15}N$ ratio for HCN in the atmosphere of Titan has been measured to be 2 to 3 times as less as the corresponding ratio for N_2. Using a coupled ion-neutral photochemical model incorporating state-of-the-art chemistry and cross-sections for N_2, we show that the difference in the ratio of $^{14}N/^{15}N$ between HCN and N_2 can be explained exclusively by the photo-induced isotopic fractionation of $^{14}N^{14}N$ and $^{14}N^{15}N$, *without any further putative nitrogen input*.

1 Introduction

The $^{14}N/^{15}N$ ratio has now been retrieved in N_2 as well as in HCN. A summary of the available observations is given in Table 1. The HCN-derived values are a factor of 2-3 larger than the N_2-derived values, showing enrichment of the heavier isotope of nitrogen in HCN.

Photo-induced isotopic fractionation has been proposed to explain this ^{15}N enrichment [8]. When incorporating in a photochemical model high-resolution photoabsorption cross sections for $^{14}N^{14}N$ and $^{14}N^{15}N$, isotope-selective shielding allows more dissociative photons for $^{14}N^{15}N$ to penetrate deeper into Titan's atmosphere, resulting in higher photolytic efficiency for $^{14}N^{15}N$ than for $^{14}N^{14}N$, therefore, leading to a higher $HC^{15}N$ production rate.

However, previous calculations give a $HC^{14}N/HC^{15}N$ ratio of 23, which is smaller than the observed value by a factor of $\sim$3. An additional source of atomic nitrogen in the upper atmosphere was then invoked to obtain the observed ratio. With a $^{14}N/^{15}N$ = 183 - 260, the N input is constrained to be in the range $(1 - 2) \times 10^9$ cm^{-2} s^{-1}. This value, in agreement with the understanding of N_2 dissociation by Saturnian magnetospheric ion/electron impact at that time, is now believed to be overestimated by about two orders of magnitude [5], which implies that the origin of the $^{14}N/^{15}N$ fractionation needs to be reevaluated.

2 Photochemical model

The 1-dimensional photochemical model of Titan used in this investigation is adapted from several elements described previously. The background atmosphere (including $^{14}N^{14}N$ and $^{14}N^{15}N$), eddy diffusion coefficient and aerosol distribution are based on Cassini observations [18, 6]. The chemical network includes hydrocarbons [16], nitrogen [19] and oxygen [4] bearing species and takes into account both neutral and ion chemistry [15]. Detailed calculations for the energy deposition of photons and photoelectrons are performed, which include high-resolution temperature-dependent cross-sections for the absorption and dissociation of $^{14}N^{14}N$ and $^{14}N^{15}N$ [5].

In order to make the reaction lists, we start from our ^{14}N chemistry and generate analogous reactions in which ^{14}N is replaced by ^{15}N. Because they do not impact N chemistry, we do not include reactions with oxygen species and negative ions. We also leave out reactions where ^{15}N bearing species would react with each other (i.e. $^{15}N + C_2N$ and $N + C_2^{15}N$ are taken into account but not $^{15}N + C_2^{15}N$). The total rate coefficient is taken to be that of the analogous ^{14}N reaction, i.e. we neglect mass-dependent kinetic isotope effects, since replacing a ^{14}N with ^{15}N represents only a 7% increase in mass. Reactions in which both reactants contain nitrogen, or in which a species contains more than one nitrogen atom, creates special problems and some general rules have to be applied, which is the main uncertainty behind this procedure.

Table 1: $^{14}N/^{15}N$ isotopic ratio in N_2 and HCN.

Formula				
N_2 (thermosphere)	193.5 ± 21.5 (a)			
N_2 (troposphere)	188 ± 16 (b)	147.5 ± 7.5 (c)	183 ± 5 (d)	167.7 ± 0.6 (e)
HCN (stratosphere)	65 ± 5 (f)	$72 \pm 9^{*}$; $94 \pm 13^{**}$ (g)	56 ± 8 (h)	76 ± 6 (i)

*Assuming the temperature profile from [7]; **Assuming the temperature profile from [2].
(a) INMS [17]; (b) INMS extrapolated to surface [17]; (c) INMS extrapolated to surface [9]; (d) GCMS [12]; (e) GCMS [13]; (f) IRAM [11]; (g) SMA [3]; (h) CIRS [14]; (i) Herschel [1].

3 Results and conclusions

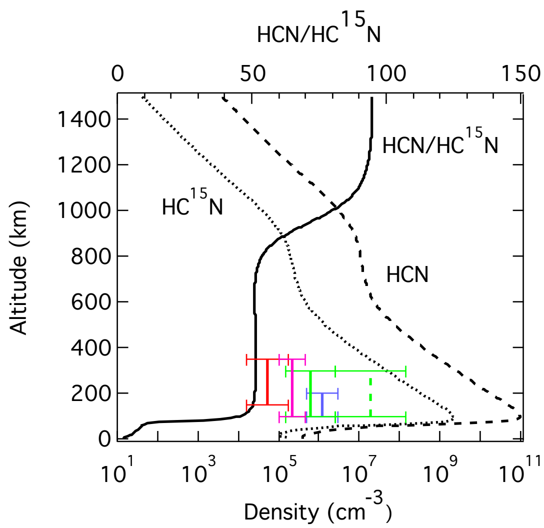

Figure 1: Modeled $HC^{14}N$ and $HC^{15}N$ vertical density profiles (bottom axis) and associated $HC^{14}N/HC^{15}N$ ratio (top axis). The boxes represent the observed $^{14}N/^{15}N$ isotopic ratio in HCN (see Table 1).

Figure 1 shows the simulated $^{14}N/^{15}N$ isotope ratio in HCN, which exhibits a constant value of 51 from 700 to 150 km. This profile is in good agreement with the CIRS value of 56 ± 8, which shows no evidence for vertical variations [14]. However, an average of the four consistent observations (the higher value of Gurwell [3] is at odds with the other values) gives a slightly higher value of $\sim$67. More observations are needed to constrain the vertical profile of $HC^{15}N$ at mid-latitudes as well as potential temporal or latitudinal variations. Observations of the $^{14}N/^{15}N$ in other species, in particular HC_3N, would be of great interest to further constrain the nitrogen chemistry on Titan.

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