

# $^{13}\text{C}$ and $^{15}\text{N}$ fractionation of $\text{CH}_4/\text{N}_2$ mixtures during photochemical aerosol formation: Relevance to Titan



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## ABSTRACT

The ratios of the stable isotopes that comprise each chemical species in Titan's atmosphere provide critical information towards understanding the processes taking place within its modern and ancient atmosphere. Several stable isotope pairs, including  $^{12}\text{C}/^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$ , have been measured *in situ* or probed spectroscopically by Cassini-borne instruments, space telescopes, or through ground-based observations. Current attempts to model the observed isotope ratios incorporate fractionation resulting from atmospheric diffusion, hydrodynamic escape, and primary photochemical processes. However, the effect of a potentially critical pathway for isotopic fractionation – organic aerosol formation and subsequent deposition onto the surface of Titan – has not been considered due to insufficient data regarding fractionation during aerosol formation. To better understand the nature of this process, we have conducted a laboratory study to measure the isotopic fractionation associated with the formation of Titan aerosol analogs, commonly referred to as 'tholins', via far-UV irradiation of several methane ( $\text{CH}_4$ ) and dinitrogen ( $\text{N}_2$ ) mixtures. Analysis of the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic signatures of the photochemical aerosol products using an isotope ratio mass spectrometer (IRMS) show that fractionation direction and magnitude are dependent on the initial bulk composition of the gas mixture. In general, the aerosols showed enrichment in  $^{13}\text{C}$  and  $^{14}\text{N}$ , and the observed fractionation trends can provide insight into the chemical mechanisms controlling photochemical aerosol formation.

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## 1. Introduction

A comprehensive understanding of the chemical and physical processes taking place in Titan's atmosphere, both past and present, not only requires consideration of the compounds present in the atmosphere, but also the ratios of the stable isotopes that make up the individual species. Observations from several of the instruments onboard the Cassini spacecraft along with Earth-based observations have allowed for the measurement of several stable, non-radiogenic, isotope pairs including D/H,  $^{12}\text{C}/^{13}\text{C}$ ,  $^{14}\text{N}/^{15}\text{N}$  and  $^{16}\text{O}/^{18}\text{O}$  (Bézard et al., 2014). Of particular interest are the  $^{12}\text{C}/^{13}\text{C}$  ratio of Titan's atmospheric methane and the  $^{14}\text{N}/^{15}\text{N}$  in molecular nitrogen. The value of the carbon isotope ratio can be used in determining the age and history of the methane in the atmosphere (Mandt et al., 2012; Nixon et al., 2012), while the nitrogen isotope

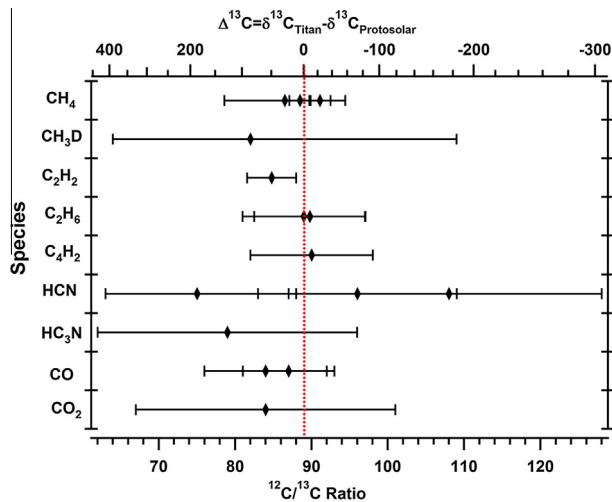
ratio is important for understanding the origin of nitrogen on Titan (Mandt et al., 2014).

Recent measurements from Titan indicate that the  $^{12}\text{C}/^{13}\text{C}$  ratio in  $\text{CH}_4$  is similar to that found in carbonaceous chondrites ( $^{12}\text{C}/^{13}\text{C} \sim 89$ ) (Alexander et al., 2007; Martins et al., 2007), indicating either that the methane is relatively young and has not evolved away from the protosolar ratio, or that it has been recently replenished, possibly through cryovolcanism (Mandt et al., 2009). Measurements of other carbon-bearing species do not show further isotopic fractionation within the sensitivity of current mission instruments, as summarized in Fig. 1. This apparent lack of carbon isotope fractionation during processing in the Titanian atmosphere is contrary to that expected for a chemically active atmosphere subjected to escape processes (Mandt et al., 2009, 2012).

In contrast, the  $^{14}\text{N}/^{15}\text{N}$  ratio does show considerable fractionation between different species (Table 1). The  $^{14}\text{N}/^{15}\text{N}$  ratio has been measured for both molecular nitrogen ( $\text{N}_2$ ) for and hydrogen cyanide (HCN), with HCN showing a near 3-fold enrichment in  $^{15}\text{N}$  over the bulk  $\text{N}_2$  (Vinatier et al., 2007). Both are significantly

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**Fig. 1.** The  $^{12}\text{C}/^{13}\text{C}$  ratios for several carbon containing compounds in Titan's atmosphere shows no significant change compared to the protosolar value (vertical dashed line), within measurement scatter and uncertainties. Adapted from data in Bézard et al. (2014).

**Table 1**  
 $^{14}\text{N}/^{15}\text{N}$  ratios of nitrogen in the Solar System.

Object	Species	$^{14}\text{N}/^{15}\text{N}$
Titan	$\text{N}_2$	167–211 <sup>a</sup>
	HCN	58–76 <sup>a</sup>
Protosolar	$\text{N}_2$	~430 <sup>b,c</sup>
	$\text{NH}_3$	~130 <sup>b,c</sup>
Terrestrial	$\text{N}_2$	272 <sup>d</sup>

<sup>a</sup> Bézard et al. (2014).

<sup>b</sup> Shinnaka et al. (2014).

<sup>c</sup> Rousselot et al. (2014).

<sup>d</sup> Lodders and Fegley (1998).

enriched in  $^{15}\text{N}$  compared to the protosolar value for  $\text{N}_2$ , but the  $^{14}\text{N}/^{15}\text{N}$  in  $\text{N}_2$  is within the range measured for the protosolar value of  $\text{NH}_3$  based on comet measurements (Shinnaka et al., 2014; Rousselot et al., 2014). The similarity between comets and Titan, the depletion of primordial noble gases relative to nitrogen (Niemann et al., 2005, 2010), along with limits to the amount of fractionation possible over time (Mandt et al., 2014), suggests that Titan's nitrogen originated as  $\text{NH}_3$  from the protosolar nebula.

While several models have been developed to account for the observed isotope ratios, there are still gaps in our understanding of the entire system, for which laboratory data are needed. Current models assume fractionation occurs through three main processes: atmospheric diffusion, various escape processes, and primary chemical reactions (Mandt et al., 2009, 2012; Hunten, 1982; Liang et al., 2007; Nixon et al., 2012). Atmospheric diffusion causes isotope fractionation with altitude, where lighter isotopes diffuse more effectively into the upper atmosphere, while heavier isotopes remain closer to the surface (Hunten, 1982). Coupled with escape, the preferential loss of lighter isotopes from the atmosphere leads to an increase in the fraction of heavy isotopes in the bulk atmosphere (Hunten, 1982; Mandt et al., 2012).

Chemical processing is the least understood fractionation pathway. Photochemical models (e.g. Wilson and Atreya, 2009) identify five processes for methane depletion and creation. Assuming that the initial photochemical reactions undergo a kinetic isotope effect (KIE), the lighter isotopes react slightly faster, and therefore more often (~1.004:1 for  $^{12}\text{C}$  versus  $^{13}\text{C}$ ). This causes products to be enriched in lighter isotopes and residual reactant to be enriched

in heavier isotopes (Mandt et al., 2012; Nixon et al., 2012). For example, the conversion of  $\text{CH}_4$  to methyl radical ( $\text{CH}_3$ ) by ethynyl radical – the largest single source of methane loss in Titan's atmosphere (Wilson and Atreya, 2009) – proceeds such that the rate of loss of  $^{12}\text{CH}_4$  versus  $^{13}\text{CH}_4$  only differ by a few percent [ $k(^{12}\text{CH}_4)/k(^{13}\text{CH}_4) \approx 1.01\text{--}1.08$ ]. This should cause a slight enrichment in  $^{13}\text{CH}_4$  in the atmosphere over geologic time scales (>50 Myr), but uncertainties in the loss rates can increase or decrease the time scale by as much as a factor of four (Nixon et al., 2012).

A limitation of these models is their inability to account for the isotope reaction preferences in all of the reactions on the pathway to aerosol formation. This is due to both the complex nature of aerosol formation chemistry, as well as the lack of laboratory measurements of isotope fractionation in the reactions leading up to aerosol formation. Yet the aerosol phase can be an important reservoir for carbon and hydrogen, and is a non-negligible reservoir for nitrogen atoms. Therefore, the lack of accounting of isotopic fractionation during aerosol formation pathways could lead to deficiencies in our understanding of isotopic cycling in the Titan atmosphere. At present, estimates of the haze column production rates from photochemical models vary widely from ~3 to  $12 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$  (Krasnopolsky, 2009; Wilson and Atreya, 2009; Vuitton et al., 2012), or from ~20% to 200% of the ethane production rates in the same models. Therefore, the haze layer is one of – and possibly the most – important carbon sinks of Titan's methane destruction, and understanding the fractionation mechanisms in haze production is critical to interpretation of the isotopic ratios (especially  $^{12}\text{C}/^{13}\text{C}$ ) measured in the gas phase (methane and ethane). If the chemistry leading to aerosol formation were sensitive to isotope effects, then aerosol particles, which can settle out to the surface, would also preferentially remove certain isotopes. However, this cannot be properly evaluated with the current scarcity of isotopic fractionation data from laboratory studies.

To date, there have been no studies of isotope fractionation in Titan aerosol analogs formed solely from UV irradiation, which is the primary energy source in Titan's atmosphere that leads to aerosol formation (Lavvas et al., 2011). There have been a few laboratory studies on isotope fractionation in aerosols produced from  $\text{CH}_4$ . Chang et al. (1983) used both a spark discharge and 124 nm photolysis on various mixtures (pure  $\text{CH}_4$ ,  $\text{CH}_4\text{--NH}_3\text{--H}_2\text{O}$  and  $\text{CH}_4\text{--N}_2\text{--H}_2\text{O}$ ) to produce aerosols. The resulting products, while not strictly relevant to Titan, all showed enrichment in  $^{12}\text{C}$ . In a later Titan-focused laboratory study by Nguyen et al. (2007, 2008), mixtures of 2%  $\text{CH}_4$  in  $\text{N}_2$  were initiated with cold plasmas yielding inconclusive results: products were enriched in either  $^{13}\text{C}$  or  $^{12}\text{C}$ , depending on the plasma source. The scope of this study was narrow with no follow-on work to clarify the carbon fractionation inconsistencies.

In a recent study by Kuga et al. (2014), mixtures with  $\text{CH}_4$  concentrations ranging from 1% to 10% in  $\text{N}_2$  were flowed through a plasma discharge that initiated the formation of aerosol products. The resultant aerosols show depletion in  $^{15}\text{N}$  of around ~20‰ relative to the initial  $\text{N}_2$  gas. While this is small compared to the ~4300‰ fractionation observed between HCN and  $\text{N}_2$  in Titan's atmosphere, it does suggest aerosols generated via electron impact with high rates of nitrogen dissociation are a sink for  $^{14}\text{N}$ . The plasma results were broadly consistent with isotopic fractionation driven by kinetic effects and aerosol formation resulting from polymerization of species such as HCN and/or  $\text{CH}_2\text{NH}$ . In this and other plasma-based studies there is UV light produced in the plasma. However the photon densities are not well quantified and are likely orders of magnitude lower than the energetic electrons, and therefore not a dominant source for the chemistry. Owing to the nature of the reactions within the plasma reactor and equal electron dissociation cross-sections for the  $\text{N}_2$  isotopologues,

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