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Isotopic Ratios In Titan's Methane

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Abstract

This paper describes the first simultaneous measurement of the abundances of all three known minor isotopologues of methane in Titan's atmosphere ($^{13}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$), by fitting of Cassini CIRS mid-infrared spectra at 7-9 µm. Two separate estimates of each isotopic ratio – D/H and $^{12}C/^{13}C$ – are therefore derived, and give a combined D/H = $(1.59\pm0.26)\times10^{-4}$ and $^{12}C/^{13}C$ = 86±8. These are in general agreement with terrestrial ratios, and also recent Titan estimates from the Huygens probe GCMS [5]. Cosmological implications of these values are discussed.

1. Introduction

Methane (CH_4) is the second most abundant species in Titan's atmosphere after nitrogen (N_2), with a stratospheric abundance of ~1.5% [5]. Three of its minor isotopologues have now been identified through infrared spectroscopy in addition to $^{12}CH_4$: these are $^{13}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$ [1,6]. Measurement of their abundances therefore provides estimates of the 'stable' isotopic ratios $^{12}C/^{13}C$ and D/H in the bulk atmospheric reservoir of carbon and hydrogen. While D/H has wide variations throughout the solar system, $^{12}C/^{13}C$ varies much less, yet both ratios can provide constraints on formation and evolution scenarios of planetary atmospheres, and are therefore of key importance. In this work we show results from the first simultaneous analysis of the infrared emissions from all four methane isotopes, enabling us to determine two independent estimates of both D/H and $^{12}C/^{13}C$. We then discuss the implications of these results.

2. Observations and Analysis

CIRS is the Composite Infrared Spectometer on the Cassini Saturn-orbiting spacecraft, consisting of a far-infrared spectrometer (10-600 cm^{-1}) and a mid-infrared spectrometer (600-1500 cm^{-1}) [2]. The mid-IR range covers the CH_4 isotopologue bands: the ν_4 bands of $^{12}CH_4$ (1304 cm^{-1}) and $^{13}CH_4$ (1295 cm^{-1}) and the ν_6 bands of $^{12}CH_3D$ (1156 cm^{-1}) and $^{13}CH_3D$ (1148 cm^{-1}). For this analysis we selected data from a 4-hour limb integration observation during the T55 flyby (May 21st 2009) at 25°S, and range 1.15-1.77×10^5 km (distance from Titan center). We averaged together 941 spectra viewing tangent altitudes 225-275 km (mean 247 km) with apodized (Hamming FWHM) spectral resolution of 0.48 cm^{-1}. Spectral sub-ranges of 1140-1160 cm^{-1} (for $^{12}CH_3D$ and $^{13}CH_3D$) and 1260-1350 cm^{-1} (for $^{12}CH_4$ and $^{13}CH_4$) were chosen to minimize difficulties in fitting the wavelength-dependent signature of Titan's haze, which contributes to a slowly-varying baseline (continuum). Our modeling closely follows earlier work [6], using the NEMESIS [4] spectral synthesis program and optimal estimation (retrieval) model to accomplish the parameter fitting and error estimation. All methane spectral parameters were obtained from HITRAN 2008; weak bands of C_2H_4 and C_2H_2 were also included from GEISA 2003. Our methane $^{12}CH_4$ vertical profile is from the Huygens GCMS [5], with scaled copies for the minor isotopologues set initially to terrestrial ratios. The initial temperature profile was from Huygens HASI [3], but the temperature at the tangent altitude was retrieved from fitting the $^{12}CH_4$ band. Simultaneously, linear scaling factors applied to the profiles of $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$, C_2H_4 and C_2H_2 were varied to obtain fits to those bands. In addition, we fitted the haze continuum using spectral coefficients from [7] and allowing two independent scale factors for the opacities in the ν_4 and ν_6 spectral regions.

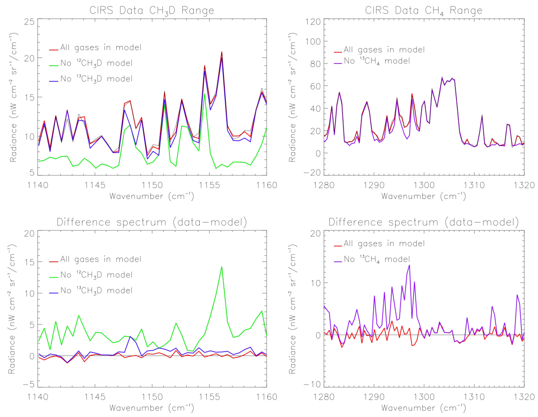

Figure 1: Upper panels: CIRS spectral data (black lines) and model fits. Lower panels: model-data residual, showing the locations of the isotopologue emissions.

3. Results

Fig. 1 shows the fit obtained to the spectrum with the best-fit model (red) and also several models with the minor isotopologues omitted to show their locations. We measure volume abundances of: $q(^{13}CH_4) = (1.71\pm0.13) \times10^{-4}$, $q(^{12}CH_3D) = (9.39\pm1.89) \times10^{-6}$ and $q(^{13}CH_3D) = (1.09\pm0.29)\times10^{-7}$. By ratioing these to each other and the $q(^{12}CH_4) = (1.48\pm0.09) \times10^{-2}$ from GCMS, and correcting for the number of hydrogen atoms, we derive four isotopic ratios: $^{12}C/^{13}C$ (CH_4) = 86±8; $^{12}C/^{13}C$ (CH_3D) = 86±29; D/H ($^{12}CH_4$) = $(1.59\pm0.33) \times10^{-4}$; D/H ($^{13}CH_4$) = $(1.59\pm0.44)\times10^{-4}$.

4. Discussion and Conclusions

These D/H estimates are in good agreement with the most recent determination from GCMS = $(1.35 \pm 0.30)\times10^{-4}$ [5] in H_2, and several prior measurements from CIRS (e.g. $(1.32\pm0.13)\times10^{-4}$ [1]), and also close to the terrestrial value (1.54×10^{-4}). Our $^{12}C/^{13}C$ estimates also agree well with the most recent analysis from GCMS (91.1±1.4) [5], and the terrestrial inorganic standard value (89.4), as well as previous CIRS determinations [1,6]. The good agreement of $^{12}C/^{13}C$ between the terrestrial and giant planets points towards little fractionation in the solar nebula materials. However, the dramatic enrichment in D/H from the giant planets, when compared to the Earth and Titan (~8x enriched) seems to indicate that D/H was heavily fractionated during the formation of icy planetesimal building blocks from nebular gas.

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