H₂ abundance and ortho-to-para ratio in Titan’s troposphere

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Abstract

We have analyzed spectra recorded between 50 and 650 cm⁻¹ by the Composite Infrared Spectrometer (CIRS) aboard the Cassini spacecraft at low and high emission angles to determine simultaneously the H₂ mole fraction and ortho-to-para (o-p) ratio in Titan’s troposphere. We confirm that the N₂-CH₄ collision-induced absorption (CIA) coefficients used up to now need to be strongly increased at temperatures of 70-85 K. We find that the N₂-N₂ CIA coefficients are also too low in the N₂ band far wing, beyond 110 cm⁻¹. We derived a tropospheric H₂ mole fraction equal to (0.88 ± 0.13) × 10⁻³, which agrees with a previous determination based only on the H₂-N₂ dimer transition in the S₀(0) line. We find that the H₂ para fraction is close to equilibrium in the 20-km region. We have investigated different mechanisms that may operate in Titan’s atmosphere to equilibrate the H₂ o-p ratio and we have developed a one-dimensional model that solves the continuity equation in presence of such conversion mechanisms. We conclude that exchange with H atoms in the gas phase or magnetic interaction of H₂ in a physisorbed state on the surface of aerosols are too slow compared with atmospheric mixing to play a significant role. On the other hand, magnetic interaction of H₂ with CH₄, and to a lesser extent N₂, can operate on a timescale similar to the vertical mixing time in the troposphere. This process is thus likely responsible for the o-p equilibration of H₂ in the mid-troposphere implied by CIRS measurements.

1. Introduction

Molecular hydrogen (H₂) is formed in the upper atmosphere of Titan from the photodissociation of methane (CH₄) and other hydrocarbons. It exists in two forms: a singlet state with an anti-parallel configuration of the two proton spins (para-hydrogen) and a triplet state with the proton spins aligned parallel (ortho-hydrogen). A previous analysis of measurements with the Cassini/CIRS yielded a globally averaged H₂ mole fraction around 1 × 10⁻³ in Titan’s upper troposphere [1], in agreement with the Huygens/GCMS determination. This abundance is hard to reconcile with the 3-4 times larger value inferred from Cassini/INMS measurements around 1000 km, assuming no surface sink of H₂ and standard eddy mixing profile [2]. The previous CIRS determination was based on N₂-H₂ dimer transitions occurring in the region of the S₀(0) rotational transition of para H₂ and had to assume ortho-para (o-p) thermodynamical equilibrium [1]. The goal of this study is i) to infer simultaneously the H₂ mole fraction and o-p ratio using both the S₀(0) (para) and S₁(1) (ortho) H₂ lines, and ii) investigate the o-p equilibration in Titan’s atmosphere.

2. Analysis of Cassini/CIRS observations

We used low-latitude selections of CIRS spectra between 50 and 650 cm⁻¹ at 15-cm⁻¹ resolution recorded at low and high emission angles (Fig. 1). We analyzed the whole spectral range with a radiative transfer model that incorporates results from the Huygens probe measurements to better constrain the different opacity sources (gases and aerosols). We found that we need to increase the N₂-CH₄ collision-induced absorption (CIA) coefficients used up to now by about 52%, in agreement with previous analyses of CIRS spectra, and also increase the N₂-N₂ CIA coefficients beyond 110 cm⁻¹, in agreement with recent quantum mechanical calculations. We derived a H₂ mole fraction equal to (0.88 ± 0.13) × 10⁻³, which pertains to the ~1-34 km altitude range probed by the S₀(0) and S₁(1) lines. We found that CIRS spectra can be fitted assuming either ortho-to-para H₂ thermodynamical equilibrium at all levels or a constant para fraction in the range 0.49-0.53.
The line), and all these processes together (black lines). Exchange in the gas phase (green lines), magnetic interaction with CH$_4$, and N$_2$, is the only one that can operate in Titan’s troposphere on a timescale comparable with that of dynamical mixing. H exchange and conversion through adsorption and magnetic interaction on aerosol surface are not efficient enough in regard to atmospheric mixing (Fig. 2).

Figure 1: Low (13°) and high (59°) emission angle spectra are compared with synthetic spectra assuming o-p H$_2$ equilibrium and uniform H$_2$ mole fractions of 0.5, 0.88 and $1.5 \times 10^{-3}$. The high-emission spectra are shifted by 0.5 erg s$^{-1}$ cm$^{-2}$ sr$^{-1}$/cm$^1$ for clarity.

3. H$_2$ ortho-para conversion in Titan’s atmosphere

From a careful survey of the mechanisms that can result in ortho-para (o-p) equilibration, we conclude that magnetic interaction with CH$_4$, and to a lesser extent N$_2$, is the only one that can operate in Titan’s troposphere on a timescale comparable with that of dynamical mixing. H exchange and conversion through adsorption and magnetic interaction on aerosol surface are not efficient enough in regard to atmospheric mixing (Fig. 2).

We have developed a 1-D model for the H$_2$ para fraction that solves the continuity equation and incorporates the conversion mechanisms in terms of time constants. Our nominal model produces a para fraction profile that is about 10% smaller than required to fit the observations. To reproduce the inferred o-p ratio in the 20-km region, low atmospheric mixing in the troposphere down to 15-20 km and conversion rates with CH$_4$ or N$_2$ slightly larger than extrapolated from o-p conversion rate measured in natural H$_2$ are required.

4. Conclusions

Our study confirms that the H$_2$ mole fraction in the troposphere is 3 to 4 times smaller than inferred from in situ measurements by Cassini/INMS. If those are correct, this discrepancy points to some unidentified physical or chemical mechanism at work to deplete H$_2$ in the lower atmosphere, or a peculiar choice of the eddy mixing profile [3]. The H$_2$ o-p ratio is close to equilibrium in the 20-km region. Equilibration results from magnetic interaction of H$_2$ with CH$_4$ and N$_2$ in the gas phase.

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References

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