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 \(\text{H}_2\) mole fraction and ortho-to-para (o-p) ratio in Titan’s troposphere. We confirm that the \(\text{N}_2\text{-CH}_4\) collision-induced absorption (CIA) coefficients used up to now need to be strongly increased at temperatures of 70-85 K. We find that the \(\text{N}_2\text{-N}_2\) CIA coefficients are also too low in the \(\text{N}_2\) band far wing, beyond 110 cm\(^{-1}\). We derived a tropospheric \(\text{H}_2\) mole fraction equal to \((0.88 \pm 0.13) \times 10^{-3}\), which agrees with a previous determination based only on the \(\text{H}_2\text{-N}_2\) dimer transition in the \(S_0(0)\) line. We find that the \(\text{H}_2\) 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 \(\text{H}_2\) 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 \(\text{H}_2\) 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 \(\text{H}_2\) with \(\text{CH}_4\), and to a lesser extent \(\text{N}_2\), 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 \(\text{H}_2\) in the mid-troposphere implied by CIRS measurements.

1. Introduction

Molecular hydrogen (\(\text{H}_2\)) is formed in the upper atmosphere of Titan from the photodissociation of methane (\(\text{CH}_4\)) 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 \(\text{H}_2\) mole fraction around \(1 \times 10^{-3}\) 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 \(\text{H}_2\) and standard eddy mixing profile [2]. The previous CIRS determination was based on \(\text{N}_2\text{-H}_2\) dimer transitions occurring in the region of the \(S_0(0)\) rotational transition of para \(\text{H}_2\) and had to assume ortho-para (o-p) thermodynamical equilibrium [1]. The goal of this study is i) to infer simultaneously the \(\text{H}_2\) mole fraction and o-p ratio using both the \(S_0(0)\) (para) and \(S_0(1)\) (ortho) \(\text{H}_2\) 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 \(\text{N}_2\text{-CH}_4\) collision-induced absorption (CIA) coefficients used up to now by about 52\%, in agreement with previous analyses of CIRS spectra, and also increase the \(\text{N}_2\text{-N}_2\) CIA coefficients beyond 110 cm\(^{-1}\), in agreement with recent quantum mechanical calculations. We derived a \(\text{H}_2\) mole fraction equal to \((0.88 \pm 0.13) \times 10^{-3}\), which pertains to the \(\sim 1\text{-}3\text{.}4\text{ km}\) altitude range probed by the \(S_0(0)\) and \(S_0(1)\) lines. We found that CIRS spectra can be fitted assuming either ortho-to-para \(\text{H}_2\) thermodynamical equilibrium at all levels or a constant para fraction in the range 0.49-0.53.
3. H₂ 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 CH₄, and to a lesser extent N₂, 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 2: Ortho-para H₂ conversion times due to H exchange in the gas phase (green lines), magnetic interaction with N₂ and CH₄ in the atmosphere (blue line), magnetic interaction on aerosol surface (cyan line), and all these processes together (black lines). The dashed and solid lines correspond to different H density profiles. Also shown is the dynamical mixing time calculated from the eddy mixing profile used in our model (red line).

We have developed a 1-D model for the H₂ 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 CH₄ or N₂ slightly larger than extrapolated from o-p conversion rate measured in natural H₂ are required.

4. Conclusions

Our study confirms that the H₂ 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 H₂ in the lower atmosphere, or a peculiar choice of the eddy mixing profile [3]. The H₂ o-p ratio is close to equilibrium in the 20-km region. Equilibration results from magnetic interaction of H₂ with CH₄ and N₂ in the gas phase.

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References

