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Search for evidence of C_4N_2 on Titan with new spectroscopic data

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1. Introduction

The Composite Infrared Spectrometer (CIRS) on-board Cassini has recorded spectra in the far and mid-infrared since 2004 with a spectral resolution of up to 0.5 cm^{-1}. Mismatch between observed spectra and model spectra obtained from the available line lists has led us to study the spectroscopic parameters of HC_3N, C_4H_2 and C_2N_2, the longest gas phase carbon chains observed so far on Titan. Band intensities, hot band intensities, and line lists were systematically verified by comparison with new laboratory spectra. Erroneous band intensities as well as an absence or shortage of hot band transitions in the line lists leading to model-data mismatches and inaccurate quantifications have been found.

Improvement in the spectroscopic parameters has led to the detection of ^{13}C isotopologues of HC_3N [1] and C_4H_2 [2]. The study on C_2N_2 opens the way to the detection of ^{15}N isotopologues whose abundances could give some clues to understand the origin and the evolution of Titan's atmosphere [3]. Also, the higher accuracy of spectroscopic data used to model CIRS spectra will facilitate the search for longer carbon chains on Titan such as HC_5N, C_6H_2 and C_4N_2. Our recent measurements obtained at the SOLEIL synchrotron far infrared beam line of band intensities of C_4N_2 in the far and mid infrared domain have shown strong discrepancies with previous results [4]. Following the intensity measurements, a careful analysis of high resolution data has led to the first line lists for C_4N_2, which gives us the chance to determine precise abundance upper limits of this molecule in Titan's atmosphere.

2. C_4N_2

C_4N_2 has not been observed so far in the gas phase in Titan's atmosphere. The strongest observable bands are situated in the far infrared at 472 and 107 cm^{-1}. In 1987, Khanna et al. [5] have measured the experimental infrared spectra of solid C_4N_2 and found a strong absorption band at 478 cm^{-1} matching an unassigned absorption feature in the thermal emission spectrum of Titan observed by the Voyager mission. Later, Dello Russo and Khanna [6] have extended the wavelength domain of their measurements towards the far infrared and observed another strong absorption feature in the spectra of solid C_4N_2 at 121 cm^{-1}. As suggested by the authors, the observation of the same feature in Titan would be a strong verification of the presence of solid C_4N_2 in Saturn's biggest satellite. But this feature has not been detected yet. Using radiative transfer modeling, Coustenis et al. (1999) [7] have confirmed the agreement between the observed spectral feature at 478 cm^{-1} and the laboratory spectrum of solid C_4N_2. An upper limit for the vapor mole fraction has been determined. As estimated by Samuelson et al. (1997) [8] it is two orders of magnitude lower than the inferred concentration of C_4N_2 ice. This is of course not expected under thermal equilibrium conditions. The authors thus proposed to explain the disequilibrium between the two C_4N_2 phases as due to the rapidly changing conditions in Titan's atmosphere after equinox. The proposed scenario is that a strong enhancement of C_4N_2 in both phases takes place during the dark polar winter. After equinox, the gas is rapidly destroyed by sunlight but because of delayed response to the changing seasons, Titan's polar atmosphere appears to be still cooling down enhancing the icy component. This scenario has been tested by de Kok et al. (2008) [9] using Cassini CIRS data from 2007 at the end of the winter season when significantly more C_4N_2 gas is expected. An upper limit of gaseous C_4N_2 is deduced from the intensity measured by Khlifi et al. [4] of a band at 614 cm^{-1} and a comparison with an observed band of HC_3N at 663 cm^{-1}. The obtained value of 9.10^{-9} does not appear to be in agreement with the scenario of a large build up of C_4N_2 during the polar winter. A plausible explanation to the disequilibrium observed by Voyager is still to be found. Note also that C_4N_2 ice has yet to be confirmed by CIRS observations, which are unfortunately of low sensitivity in this wavelength domain.

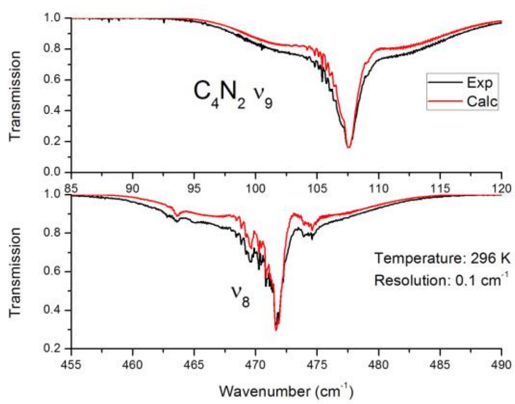

Figure 1: Comparison between ν_8 and ν_9 band transmission of C_4N_2 and line by line spectra calculation showing a perfect match of all spectral features and a small deficit in the intensity.

Band intensities are necessary to determine upper limits and C_4N_2 has been studied quantitatively only once in the past by Khlifi et al. [4]. Our recent measurements show that Khlifi's results are systematically two strong by a factor 2.3 due to confusion between common logarithm and natural logarithm. Another interesting result concerns the first measurement of the intensity of the band at 107 cm^{-1}(ν_9). Surprisingly, it turned out to be the strongest band in the whole infrared domain, 60% stronger than the ν_8 band at 472 cm^{-1}. Using the global analysis tools developed by A. Fayt, we were able to make a new analysis of old high resolution data and calculate the first line lists for C_4N_2. Due to very large values of the partition functions, the band intensities spread among a huge number of lines. As can be seen in figure 1, 700000 lines are not quite enough to match room temperature transmission spectra but all the spectral features are well reproduced. Since partition functions values decrease rapidly at lower temperature, we are confident that the line lists will be good enough in the temperature range of Titan's atmosphere sounded by the CIRS instrument. C_4N_2 gas phase abundance upper limits in Titan's atmosphere using the ν_9 band at 107 cm^{-1} and the ν_8 band at 472 cm^{-1} will be presented and compared to solid phase abundances. Compatibility between the solid and the gas phase abundances will be discussed.

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