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Search for evidence of Allene 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 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. Fundamental and hot band intensities, as well as 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 available 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 clues to understand the origin and the evolution of Titan's atmosphere [3]. The higher accuracy of spectroscopic data used to model CIRS spectra enables the search for longer carbon chains on Titan such as HC_5N, C_6H_2 and C_4N_2. Intensity measurements and a careful analysis of high resolution data has led to the first line lists for C_4N_2. No detection of this molecule has yet been possible, but a precise abundance upper limit of C_4N_2 in the gas phase in Titan's atmosphere could be determined [4].
One of the molecules that were often searched for in Titan's atmosphere is allene **(CH_2CCH_2)**.

2. Allene

Allene has not been observed so far in Titan's atmosphere although it has three active bending modes, ν_9 (999 cm^{-1}), ν_{10} (845 cm^{-1}) and ν_{11} (352cm^{-1}) in the CIRS observation range. Allene is also an isomer of propyne **(CH_3CCH)** which has been observed on Titan, thanks to two bending modes ν_9 (633 cm^{-1}) and ν_{10} (327 cm^{-1}) by the Voyager mission. These data have shown that the abundance of propyne in Titan's atmosphere has reached values as high as 10^{-6} at the north pole [5]. The clearly lower abundance of allene is not straightforward to understand since both isomers are very similar from a chemical point of view. The most obvious explanation is the existence of an isomerization process where allene transforms into propyne, but the efficiency of such a process is not easy to quantify. Another factor which could influence the abundances of allene and propyne would be differences in photolysis rates.

Anyway, the presence of allene on Titan cannot be ruled out yet. A tentative detection has in fact already been made from the ground with the TEXES instrument at high resolution. The identification concerns ν_{10} subbands close to 845 cm^{-1} among strong emission lines of ethane (C_2H_6). This tentative detection was presented at the EPSC-DPS joint meeting 2011 and, according to the authors, a definitive detection could not be made due to the lack of good line lists. No allene line list is present either in HITRAN or in GEISA, but Coustenis et al. [6] already investigated the detectability of allene in Titan's atmosphere using spectroscopic parameter by Chazelas et al. [7], for the ν_{10} band centered at 845 cm^{-1} and from Pliva and Kauppinen, for the ν_{11} band near 352 cm^{-1} [8]. Line intensities could be obtained from band intensity measurements by Koga et al.[9].

They concluded that the non-detection of allene implied an abundance below 5.10^{-9}.

In this work, we have used the same spectroscopic data but also added parameters obtained in high resolution studies by Nissen et al. [10] and Hegelund et al. [11], which also include spectroscopic parameters for the hot bands. The hot band contribution is particularly important at room temperature and needs to be included in order to compare the calculated line lists with room temperature spectra. Calculations have been tested against room and high temperature spectra taken at 0.08 cm-1 resolution in the ν_{10}/ν_9 wavenumber range. Concerning the far infrared region where the ν_{11} band of allene can be observed, we have recorded room temperature spectra with a resolution of 0.1 cm^{-1} at the SOLEIL-AILES synchrotron beamline with the same apparatus used for our previous studies [3, 4]. Figure 1 compares the laboratory spectra obtained in the far infrared with calculations using the new line list.

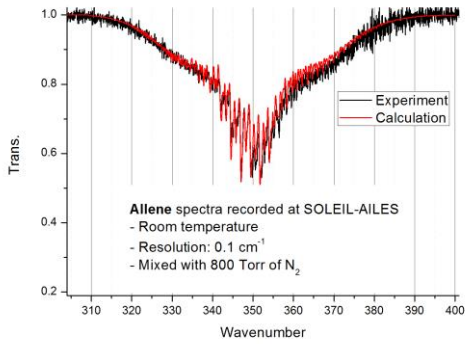

Figure 1: Allene ν_{11} laboratory spectra compared to calculated spectra.

As can be seen, our calculation reproduces the measured spectra quite satisfyingly. Very precise comparison between laboratory and calculated spectra in the ν_{10} /ν_9 region also give very good results.

This means that allene can be searched in CIRS spectra of Titan in both spectral regions with good confidence. The first attempts to detect allene in Titan's atmosphere with CIRS observations and the new line lists will be presented.

References

1. Jennings, D., et al., *Isotopic Ratios in Titan's Atmosphere from Cassini CIRS Limb Sounding: HC_3N in the North.* Astrophysical Journal, 2008. **681**: p. L109-L111.
2. Jolly, A., et al., *The n8 bending mode of diacetylene: from laboratory spectroscopy to the detection of C-13 isotopologues in Titan's atmosphere.* Astrophysical Journal, 2010. **714**(1): p. 852-859.
3. Fayt, A., et al., *Frequency and intensity analyses of the far infrared nu(5) band system of cyanogen (C2N2) and applications to Titan.* Journal of Quantitative Spectroscopy & Radiative Transfer, 2012. **113**(11): p. 1195-1219.
4. Jolly, A., et al., *Gas phase dicyanoacetylene (C4N2) on Titan: New experimental and theoretical spectroscopy results applied to Cassini CIRS data.* Icarus, 2015. **248**: p. 340-346.
5. Vinatier, S., et al., *Seasonal variations in Titan's middle atmosphere during the northern spring derived from Cassini/CIRS observations.* Icarus, 2015. **250**: p. 95-115.
6. Coustenis, A., et al., *Modelling Titan's thermal infrared spectrum for high-resolution space observations.* Icarus, 1993. **102**: p. 240.
7. Chazelas, J., et al., *Analysis of the V_9/V_{10} band system of allene.* Journal of Molecular Spectroscopy, 1985. **110**(2): p. 326-338.
8. Pliva, J. and J. Kauppinen, *High-resolution Fourier-transform study of the perpendicular band n_{11} of allene at 353 cm^{-1}.* Journal of Molecular Spectroscopy, 1985. **111**(1): p. 93-101.
9. Koga, Y., et al., *Infrared absorption intensities of allene.* J. Chem. Phys., 1979. **71**(6): p. 2404-2411.
10. Nissen, S., et al., *High-resolution infrared study of the nu(11) band of allene.* Journal of Molecular Spectroscopy, 2002. **216**(2): p. 197-202.
11. Hegelund, F., N. Andresen, and M. Koivusaari, *A high-resolution infrared study of the $N_9+N_{11}-N_{11}$, $N_{10}+N_{11}-N_{11}$ hot band sytem in allene.* Journal of Molecular Spectroscopy, 1993. **159**(1): p. 230-248.