INFRARED SPECTROSCOPY SUPPORT FOR THE CASSINI MISSION

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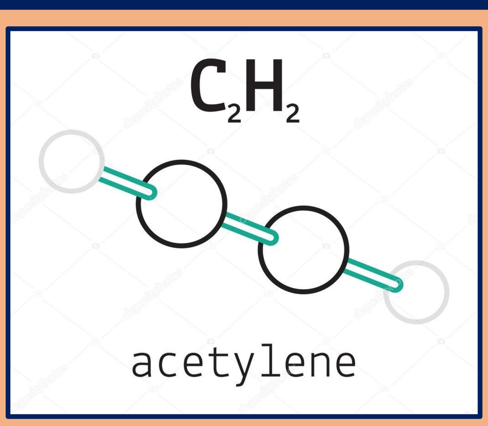
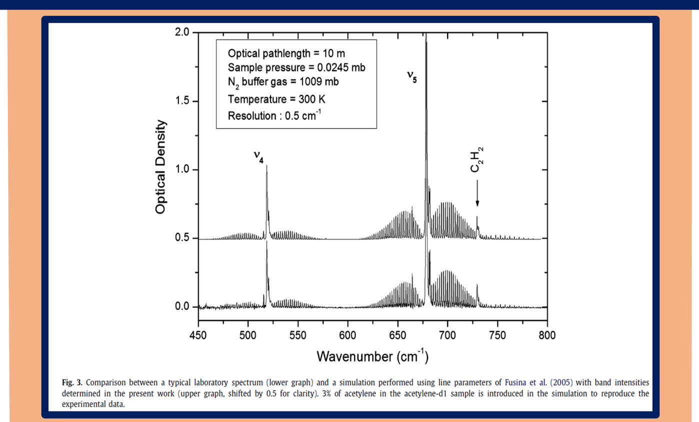
Introduction: The Composite Infrared Spectrometer (CIRS) on-board Cassini has recorded spectra in the far and mid-infrared from 2004 to 2017 with a spectral resolution of up to 0.5 cm^{-1}. One of the goals of the instrument was to detect minor species in Titan's atmosphere. Despite tremendous efforts from the spectroscopic community, a lack of spectroscopic knowledge still prevents us from a complete interpretation of the observations. During the mission we carried out many spectroscopic experiments, sometimes at low temperature to mimic Titan's environment, and sometimes at high resolution to reach the rotational structure. We have used different apparatus including a synchrotron source to reach the far infrared. Molecular samples have been synthesized and purified to obtain absolute intensity values that are necessary to determine precise abundances. Also, we have initiated a collaboration with André Fayt on the theoretical aspects which helped us to solve the complex problem of hot band contributions for linear molecules. Finally we used sophisticated spectroscopic models to calculate extensive line lists which have been made available to the CIRS team and most are now included in the HITRAN and GEISA databases.

Presentation: In the presentation, we show how spectroscopic studies could sometimes lead to detections of minor species or new interpretations of CIRS observations. In the case of C_2HD, precise intensity measurements and the first line lists where produced to ensure the quantification of a new deuterated molecule in Titan (Coustenis, 2008). For HC_3N and C_4H_2, high resolution spectra were reanalyzed with the help of a global model to obtain new extensive line lists including missing hot band contributions. With the help of the new spectroscopic parameters, CIRS observations could be precisely reproduced, with the exception of small features which turned out to be due to ^{13}C isotopologues of HC_3N *(Jennings 2008)* and C_4H_2 *(Jolly 2010)*. For C_4H_2, we also revised band intensities, in particular in the far infrared domain, measuring new values at the SOLEIL synchrotron facility *(Jolly 2014)*. In the meantime, new high resolution spectra were recorded at SOLEIL for C_2N_2 including the contribution of the ^{15}N isotopologues *(Fayt 2012)*. This time, the small separation between the specral features prevented us from detecting a new isotopic species. We also studied the longer carbon chains such as HC_5N, C_6H_2 and C_4N_2. Band intensity measurements were carried out for all three molecules and for C_4N_2 a careful analysis of high resolution data has led to the first line lists. No detection of this molecule was possible but a precise abundance upper limit of C_4N_2 in the gas phase in Titan's atmosphere was determined *(Jolly 2015)*. Photochemical models of Titan's atmosphere predict significant amounts of allene (CH_2CCH_2) and butane (C_4H_{10}) but they could not be detected by CIRS. Low temperature spectra of those molecules were recorded down to 150 K in the mid and far infrared. Line lists have been compiled for the first time for allene *(Jolly 2015- EPSC conf)* which led a precise abundance upper limit *(Lombardo 2018)*.

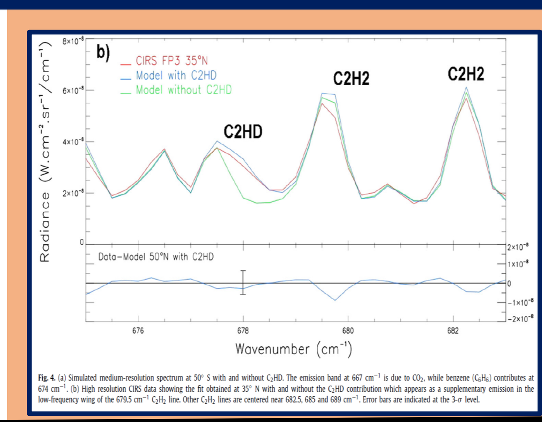
Conclusion: Many spectral features are still unidentified in CIRS spectra that could be due to new molecules or to imperfection in spectroscopic data. The need for better spectroscopic parameters is still high and will grow even more with future higher resolution observations.

Molecules | *Laboratory studies* | *Spectroscopic results* | *Titan Observations* | *Observation results*

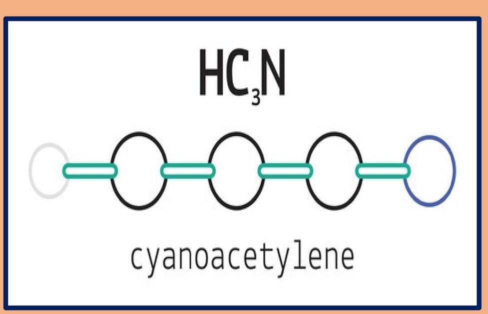


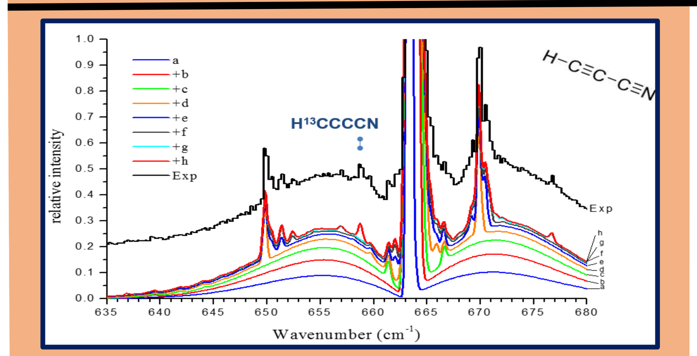


First linelist calculation for C_2HD based on new absolute band intensity measurements between 5 and 25 µm. Reanalysis of old high resolution spectra (Jolly et al. 2008). Available in GEISA 2009 and HITRAN 2012

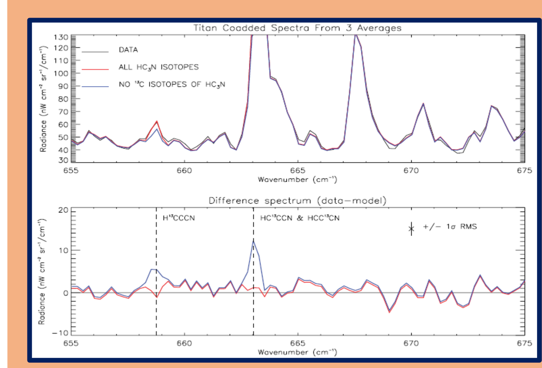


First detection of deuterated acetylene (C_2HD) on Titan through the ν_4 and ν_5 bending modes enabling a new D/H determination (Coustenis et al. 2008)

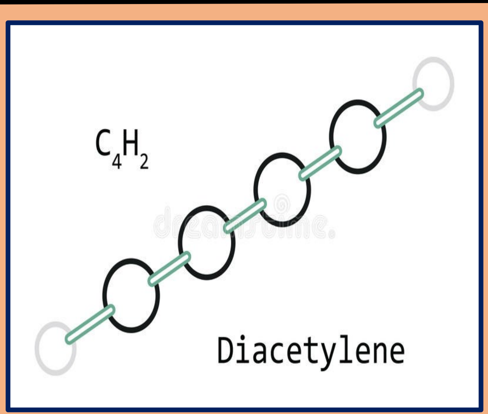


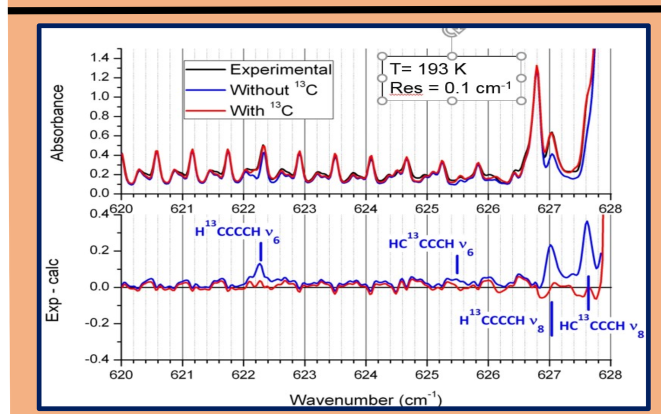


New extensive linelist for the bending modes of HC_3N based on new absolute band intensity measurements and global analysis of old high resolution spectra (Jolly et al. 2007) . Available in GEISA 2009 and HITRAN 2012. Linelists for isotopes available for the CIRS team

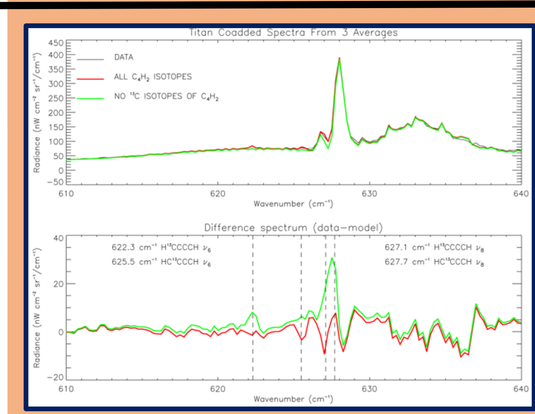


First detection of ^{13}C isotopologues of HC_3N ($H^{13}CCCN$ distinguishable from $HC^{13}CCN$ and $HCC^{13}CN$) leading to new $^{12}C/^{13}C$ isotopic ratio determination (Jennings et al. 2008)

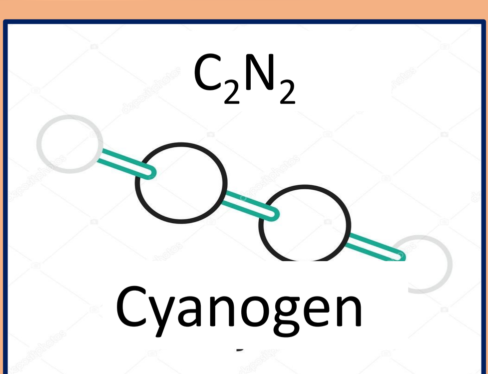


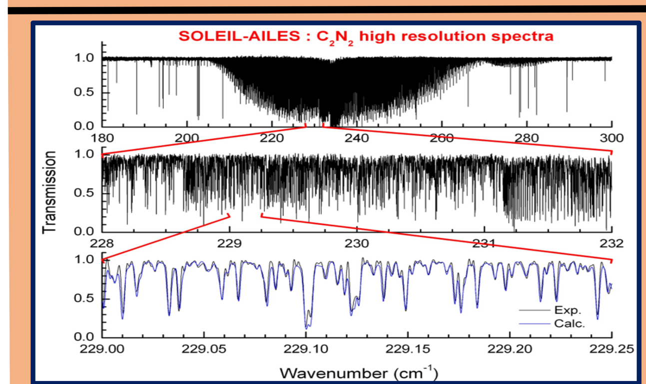


New extensive linelist for the bending modes of C_4H_2 based on global analysis of old high resolution spectra and first low temperature study (Jolly et al. 2010). Revision for the absolute band intensities for the bending modes (Jolly et al. 2014). Available in GEISA 2015. Linelists for isotopes available for the CIRS team.

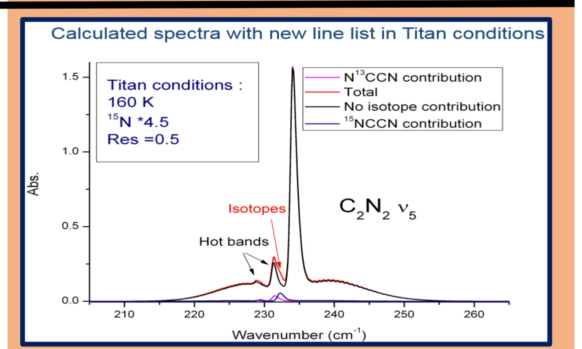


First detection of ^{13}C isotopologues of C_4H_2 on Titan ($H^{13}CCCCH$ distinguished from $HC^{13}CCCH$ through the symetric bending mode ν_6. New $^{12}C/^{13}C$ isotopic ratio determination (Jolly et al. 2010).

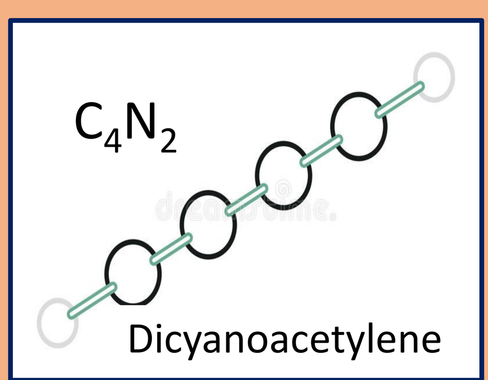


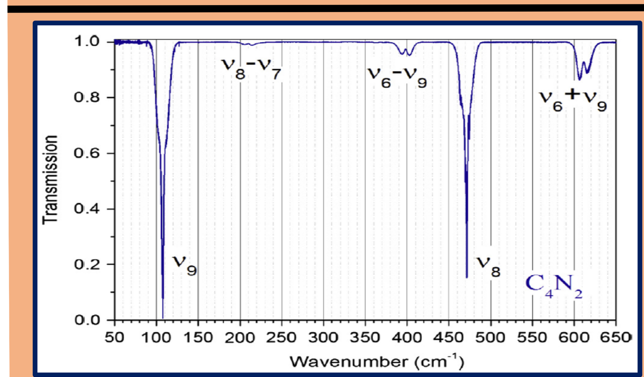


New high resolution experiment (SOLEIL synchrotron facility) and global analysis of the far infrared ν_5 bending mode of C_2N_2. including ^{13}C and ^{15}N isotopes (Fayt et al. 2012). New linelist available in GEISA 2015. Linelists for isotopes available for the CIRS team.

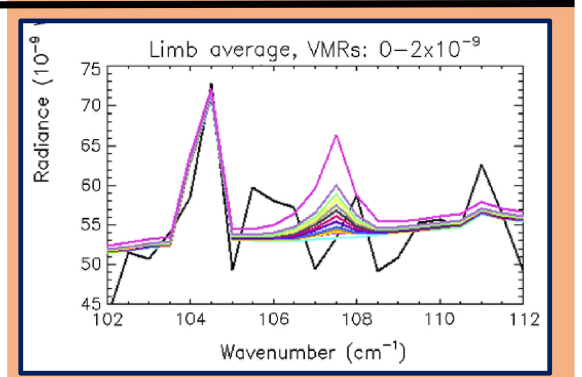


Due to low sensitivity in the far infrared and overlap of ^{13}C and ^{15}N contribution with a hot band, $^{15}NCCN$ is not detectable but the C_2N_2 is very well reproduced by the new line list (Teanby et al. 2009).

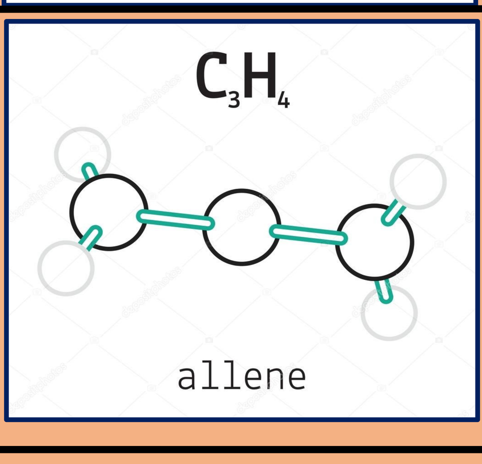


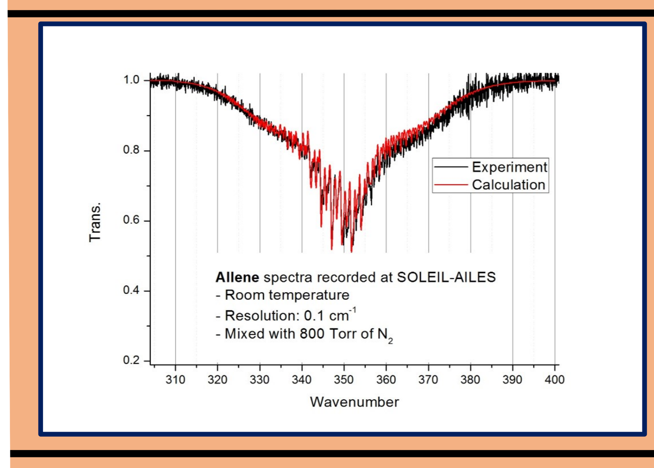


First band intensity determination of the ν_9 far infrared band of C_4N_2 using a new experimental study between 50 and 650 cm^{-1}. Global analysis of high resolution spectra and first line list for ν_9 and ν_8 (Jolly et al. 2015).

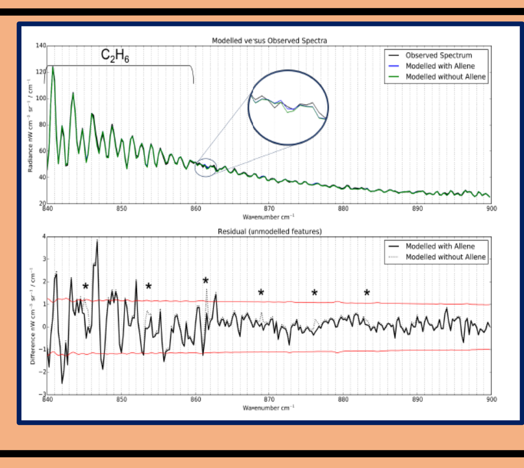


C_4N_2 abundance upper limit determination using the far infrared ν_9 band at 107.6 cm^{-1}. The low abundance value of 5-7 10^{-10} does confirm the inconsistency with the gas-to-solid ratio (Jolly et al. 2015).

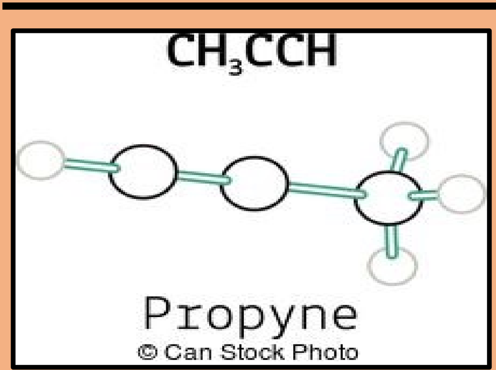


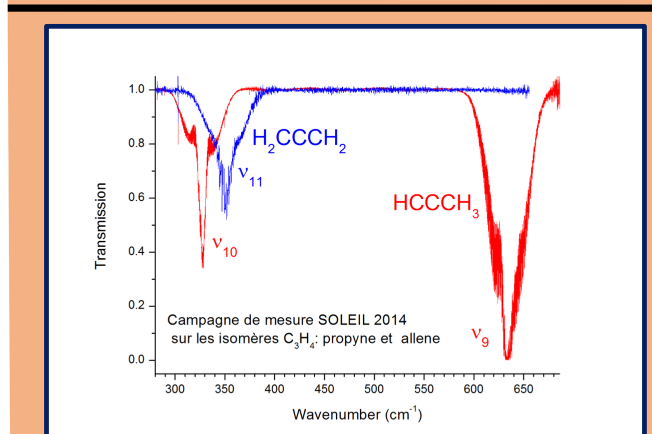


New band intensity and high resolution measurements of the infrared bands of allene have been performed (SOLEIL synchrotron facility) . New line list for ν_{11}, ν_{10} and ν_9 (Jolly et al. 2015) have been made available to the CIRS team in the absence of any GEISA or HITRAN line list. (Jolly et al. 2015 – EPSC conf.).

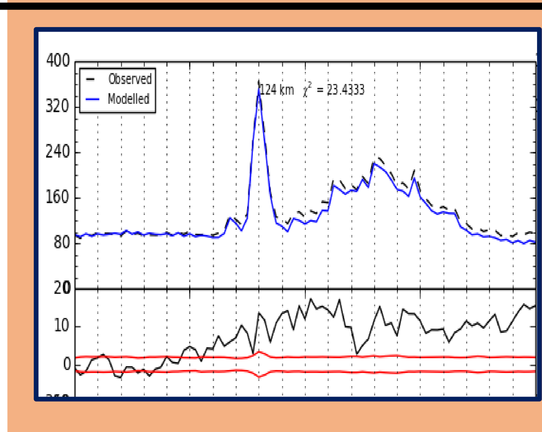


Allene could not be detected in Titan by CIRS neither by the far infrared ν_{11} band nor by the ν_{10} band. An abundance upper limit could be determined using the ν_{10} band estimated to be close to 1.10^{-9} (Lombardo et al. 2018).

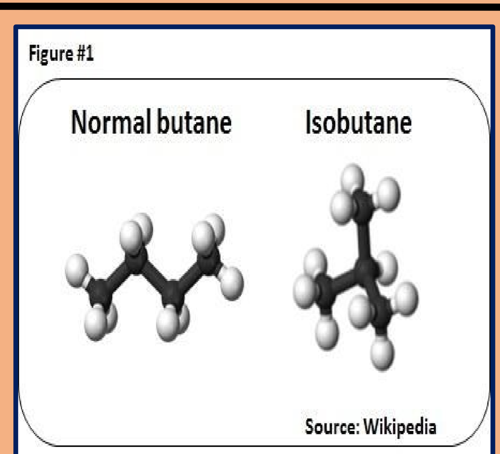


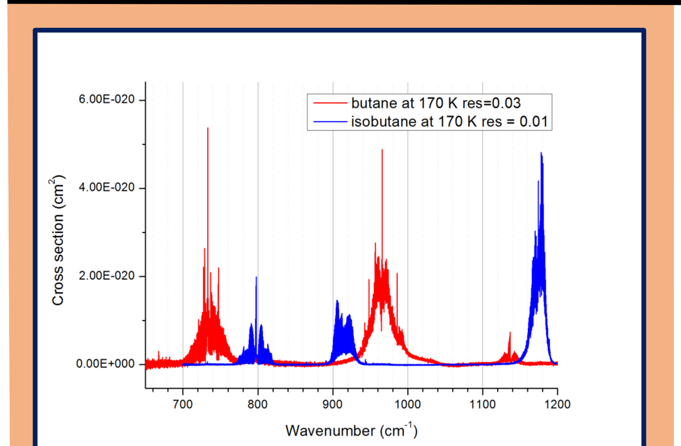


New band intensity measurements of the infrared bands of propyne have been performed in the range 50-650 cm^{-1} (SOLEIL synchrotron facility). Results confirm the previous the ν_{10} to ν_9 band intensity ratio. A new linelist is under construction for the ν_9 band to take into account the hot band contribution.

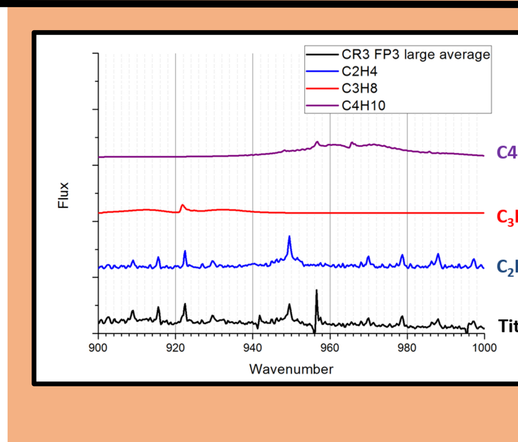


Propyne (or methylacetylene) is a well observed molecule on Titan but probable inconsistencies in the line lists are leading to modeling difficulties (Lombardo et al. 2018). Possible band intensity ratio errors have been claimed (Teanby et al. 2009).





First low temperature absorption cross section measurements of butane and isobutane have been performed (SOLEIL synchrotron facility). Temperature dependence of butane trans and gauche conformer have been observed.
(Jolly et al. 2017 – EPSC conf.).



Butane and isobutane are predicted to be almost as abundant as propane which is easily observed by CIRS on Titan. Measurements should help to test the presents of C_4H_{10} on Titan but an abundance upper limit could not yet be determined