EPSC Abstracts
Vol. 7 EPSC2012-468-1 2012
European Planetary Science Congress 2012

Far infrared band intensities for CIRS: C_4H_2 and C_4N_2

A. Jolly (1), Y. Benilan (1), M-C. Gazeau (1), J-C Guillemin (2), F. Kwabia-Tchana (1), L. Manceron (3)

(1) LISA, Université Paris 7 et 12, 61 Av. du Général de Gaulle, 94010 Créteil Cedex, France. (2) ENSC Rennes, Université de Bretagne, UMR 6226 CNRS, Avenue du Général Leclerc, 35708 Rennes Cedex 7, France. (3) Synchrotron SOLEIL, L'orme des Merisiers, Saint-Aubin-BP 48, 91192 Gif-sur-Yvette Cedex and LADIR, CNRS-U. Paris 6, 4, place Jussieu 75252, France.

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_4H_2 in the far and mid infrared domain have shown strong discrepancies with previous results [4]. Band intensities of C_4N_2 have also been studied in the far infrared. Errors in previous publications have been found and the intensity of the ν_9 has been determined for the first time.

2. C_4H_2 and C_3H_4

Diacetylene can be studied in the atmosphere of Titan through two bending modes at 628 cm^{-1} (ν_8) in the mid infrared and at 220 cm^{-1} (ν_9) in the far infrared. Abundances of diacetylene can be determined independently from either band. Abundances obtained in both domains using FP1 and FP3 have been compared and found to be consistent at equatorial latitudes but divergent north of 45° [5]. In the same study, a similar comparison has been done for propyne (C_3H_4) which also has two bands in the different domains (633 and 331 cm^{-1}). The result for propyne is a disagreement by a factor of 2 between the abundances retrieved in the mid and the far infrared. The discrepancy could be due to the inaccuracy of the relative band strengths and this subject is already under study. But in the mean time, we have studied the relative band strength of both bending modes of C_4H_2 in particular because the far infrared band at 220 cm^{-1} had only been studied once in the past and not in optimal conditions. Our first results show that the ν_9 band of diacetylene is more than two times stronger than previously measured. This means that the band strength ratio is considerably reduced compared to the value used until now and that the consistency in the retrieved abundances could be revised.

3. 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. [6] 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, Dellorusso and Khanna [7] 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) [8] 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) [9] 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) [10] 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. [11] 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 not been confirmed so far by the CIRS data, neither at 478 nor at 121 cm^{-1}.

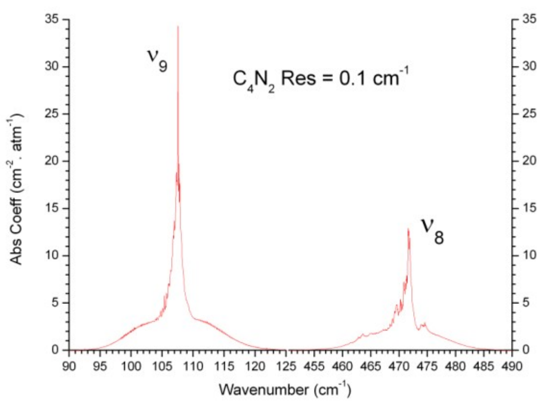

Figure 1: Measured band intensities for the ν_8 and ν_9 band of C_4N_2 at room temperature and at a resolution of 0.1 cm^{-1}.

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. [11]. 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 109 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} (see figure 1). These results open the way to new accurate determination of C_4N_2 abundance upper limits in Titan's atmosphere.

References

[1] Jennings DE, Nixon C., Jolly A, Bézard B, Coustenis A,Vinatier S,, et al., Isotopic Ratios in Titan's Atmosphere from Cassini CIRS Limb Sounding: HC3N in the North. Astrophysical Journal, **681**: p. L109-L111 (2008).

[2] Jolly A, Fayt A., Benilan Y, Jacquemart D, Nixon CA, Jennings DE., The ν_8 bending mode of diacetylene: from laboratory spectroscopy to the detection of ^{13}C isotopologues in Titan's atmosphere. Astrophysical Journal, **714**(1): p. 852-859 (2010).

[3] Fayt, A., Jolly A, et al., Frequency and intensity analyses of the far infrared ν_5 band system of cyanogen (C2N2) and applications to Titan. JQSRT. **113**(11): p. 1195-1219 (2012).

[4] Koops, T., T. Visser, and W.M.A. Smit, The harmonic force field and absolute infrared intensities of diacetylene. J. Molec. Struct., **125**: p. 179-196 (1984).

[5] Teanby, N.A., et al., Titan's stratospheric C_2N_2, C_3H_4, and C_4H_2 abundances from Cassini/CIRS far-infrared spectra. Icarus, **202**(2): p. 620-631 (2009).

[6] Khanna, R.K., M.A. Perera-Jarmer, and M.J. Ospina, Vibrational Infrared and Raman spectra of dicyanoacetylene. Spectrochim. Acta,. **43A**(3): p. 421-425 (1987).

[7] DelloRusso, N. and R.K. Khanna, Laboratory infrared spectroscopic studies of crystalline nitriles with relevance to outer planetary systems. Icarus, **123**(2): p. 366-395 (1996).

[8] Cousténis, A., et al., Plausible condensates in Titan's stratosphere from Voyager infrared spectra. Planetary and Space Science, **47**(10/11): p. 1305-1329 (1999).

[9] Samuelson, R.E., et al., C_4N_2 ice in Titan's North Polar Stratosphere. Planet. Space Sci. **45**(8): p. 941-948 (1997).

[10] de Kok, R., P.G.J. Irwin, and N.A. Teanby, Condensation in Titan's stratosphere during polar winter. Icarus, **197**(2): p. 572-578 (2008)

[11] Khlifi, M., et al., Gas infrared spectra, assignments, and absolute IR band intensities of C_4N_2 in the 250-3500 cm^{-1} region: implications for Titan's stratosphere. Spectrochimica Acta Part A,. **53**: p. 702-712 (1997).