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Frequency and intensity analyses of the far infrared ν_5 band system of cyanogen (C_2N_2) and applications to Titan

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ABSTRACT

The far infrared spectrum of cyanogen has been studied at high resolution to improve the rotational analysis of the ν_5 band system around 234 cm^{-1}. Present in the sample in natural abundances, both isotopologues $N^{13}CCN$ and $^{15}NCCN$ have also been studied. The weak ν_4–ν_5 difference band centered at 270 cm^{-1} has been studied for the first time. On the basis of a global rovibrational analysis limited to the ν_2, ν_4, and ν_5 modes, energy levels up to 2300 cm^{-1} have been considered to contribute to the overall spectrum intensity at room temperature leading to a new line list of 196,994 lines. The line intensity prediction has been used to correct previous line intensity measurements by taking into account line mixing. A new vibrational transition moment has been deduced and compared to new band intensity measurements obtained by low resolution studies which are also presented in this paper. The agreement between both approaches is very good and rules out the apparent disagreement between line intensity and band intensity measurements observed in the past. An intensity study of $^{15}NCCN$ is also proposed here thanks to the availability of a pure sample. Those results open the way to the search for isotopologues of cyanogen in Titan's atmosphere.

1. Introduction

Cyanogen was first identified in Titan's atmosphere in 1981 [1] by the infrared spectrometer IRIS on board the Voyager spacecraft. The detection has been later confirmed by the infrared instrument CIRS of the CASSINI mission [2]. The quality of the new observations has even allowed to detect cyanogen on Titan at equatorial and southern latitudes for the first time with abundances as low as 5×10^{-11} [3]. The abundance reaches a maximum of 3×10^{-9} in the north polar region, showing an important enrichment towards northern latitudes, in agreement with the behavior observed for other species. All the detections are done in the far infrared at 234 cm^{-1} through the only infrared active bending mode ν_5. It is also, by far, the strongest feature in the whole infrared domain and in most conditions the unique detection possibility. Together with the absence of any rotational spectra, this is probably the reason why cyanogen has so far not been detected in any other spatial environment.

At the time of the first detection of C_2N_2, the fundamental vibration frequencies were relatively well established, including the ν_5 infrared active mode which

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was observed by Jones [4]. A rotational analysis of ν_5 was provided by Jolma [5] at medium resolution (0.02 cm^{-1}) and later at high resolution (0.0018 cm^{-1}) by Grecu et al. [6]. In that work, the assignments were limited to the ν_5 manifold up to $\nu_5=4$, although many hot bands involving the ν_4 and ν_2 infrared inactive modes and higher ν_5 values are expected to contribute to the spectrum. The stimulated Raman spectrum of the ν_2 stretching mode has been observed and analyzed by Bermejo et al. [7]. In 2003, the collaboration of the Giessen group with Maki has considerably improved the knowledge about the infrared spectrum of cyanogen for the doubly substituted species $N^{13}C^{13}CN$ and $^{15}NCC^{15}N$ [8], but the corresponding analysis for the normal species was not published up to very recently [9]. The opportunity to record the ν_5 band at the synchrotron radiation facility SOLEIL and the development of a global rovibrational analysis for NCCN were the occasion to improve the knowledge of the cyanogen energy levels up to about 2000 cm^{-1} (the ν_1 and ν_3 modes appear at higher energies and are outside the scope of this work).

Concerning the intensities, band intensity measurements at low resolution have been carried out for the ν_5 mode by Miyazawa [10] and Kim and King [11] with a good agreement, confirmed by the theoretical predictions of Botschwina and Sebald [12]. Nevertheless, line intensities measured by Grecu et al. [13] show a large disagreement with Kim and King when comparing the vibrational transition moments derived in both studies. This difference, corresponding to almost a factor of 2 in intensity, was one of the motivations for this new study on the ν_5 band of cyanogen. Another motivation was to extend the line list of C_2N_2 used to analyze the observations in order to improve the radiative transfer modeling and get the chance to detect and quantify isotopic species of cyanogen in Titan's atmosphere. Improvements in the knowledge of spectroscopic parameters have recently been successful, leading to the detection of ^{13}C and ^{15}N bearing molecules in Titan's atmosphere including $H^{13}CCCN$ [14], $H^{13}CCCCH$ [15], $H^{13}CN$, and $HC^{15}N$ [16]. While the $^{12}C/^{13}C$ isotopic ratio was measured in Titan for many molecules and found to be close to the terrestrial value [17], the $^{14}N/^{15}N$ isotopic ratio was only measured in the infrared for HCN [16] and in-situ by the Huygens probe for N_2 [18], showing strong enrichment in ^{15}N by a factor 4.9 and 1.8, respectively. After failing to detect $HCCC^{15}N$ [14], cyanogen is the only nitrile left to look for ^{15}N in Titan's atmosphere. Better spectroscopic parameters are also necessary, in the frame of Titan studies, for molecules like propane for which recent studies have led to significant improvements in the analysis of Titan's infrared spectra [19,20,21].

In this paper, we present both high and low resolution laboratory spectra of cyanogen. Experimental details are presented, followed by the assignment of the high resolution spectrum. The principle of the global rovibrational analysis is explained, followed by the model used for the main interactions. Resulting molecular and effective parameters are presented for the ν_5 band system, the ν_4–ν_5 band and for both $^{15}NCCN$ and $N^{13}CCN$ which are observed in natural abundance. We present a new determination of the vibrational transition moment of the ν_5 mode deduced from Grecu's line intensity measurement and the first determination of the intensity of the ν_4–ν_5 band. Results from low resolution experimental spectra are also presented and, in particular, a new determination of the integrated band intensity of ν_5 for the main isotopologue, as well as for $^{15}NCCN$. The comparison between band intensities and line intensity measurements is discussed and relevant formulas are given. Finally, new line lists are used to test the possible detection of $^{15}NCCN$ in Titan's atmosphere.

The conventional normal mode numbering for cyanogen is used throughout this paper. Modes 1 to 5 correspond to the symmetric CN σ_g^+ (ν_1) and CC σ_g^+ (ν_2) stretches, the antisymmetric CN stretch σ_u^+ (ν_3), and the *trans*−π_g (ν_4) and *cis*−π_u (ν_5) doubly degenerate bends. Labels n and t refer to stretching and bending vibrational modes, respectively, and s or i refer to any vibrational mode. The bends are further characterized by the usual vibrational angular momentum quantum numbers, ℓ_4 and ℓ_5, with $k=\ell_4+\ell_5$. In this paper, *state* refers to a vibrational state characterized by the $(\nu_1\nu_2\nu_3\nu_4\nu_5)$ set of vibrational quantum numbers. *Substate* indicates a ℓ_i-component of a state identified using $(\nu_1\nu_2\nu_3\nu_4\nu_5,\ell_4\ell_5)$. In some cases, the classical notations $v_i^{\ell_i}$ and $v_i^{\ell_i}$ can be used for the degenerate modes, for the quantum numbers and the states, respectively. *Level* refers to a specific J-value of a state or substate. The symmetry labels include *e*/*f* [22] and *u*/*g* properties. The same labels apply to $N^{13}CCN$ and $^{15}NCCN$ which are also considered in this investigation, except the missing *u*/*g* character. For the intensity calculations, m is classically defined as $J+1$, J, or $-J$ for $R(J)$, $Q(J)$, or $P(J)$ lines, respectively.

2. Experimental details

2.1. Synthesis and purification procedure

The sample of normal cyanogen was prepared in a flask containing AgCN (1.0 g, 7.5 mmol) that was adapted to a U-tube equipped with stopcocks in a vacuum line (0.1 mbar). The *U*-tube was immersed in a liquid nitrogen bath and the flask was heated with a Bunsen burner for about 2 min to form, via the cyanogen radical, the cyanogen molecule NCCN which was trapped in the *U*-tube. The stopcocks of the *U*-tube were then closed and the cyanogen (120 mg, 2.3 mmol) was finally obtained with a 62% yield.

The mono-labeled cyanogen ^{15}N has been synthesized in a two-step sequence using the approach of Wilmes and Winnewisser [23]. After dehydration of the oxamide with phosphorus pentaoxide and sea sand, the labeled cyanogen was trapped with huge amounts of carbon dioxide as shown in the following scheme: