Journal of Molecular Spectroscopy 307 (2015) 1–5

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

The millimeter-wave spectrum of CCN ($\widetilde{X}^2\Pi_r$): A combined Fourier transform and direct absorption study

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ARTICLE INFO

Article history:
Received 2 September 2014
In revised form 21 October 2014
Available online 4 November 2014

Keywords:
FTmmW spectroscopy
Millimeter-wave direct absorption
CCN radical
Hyperfine structure
Lambda-doubling

ABSTRACT

New pure rotational measurements have been conducted for the CCN radical ($\widetilde{X}^2\Pi_r$) in the $\Omega = 1/2$ spin–orbit ladder using a combination of Fourier transform millimeter-wave (FTmmW) and millimeter direct absorption techniques. For the FTmmW work, the species was created in a supersonic jet in a pulsed DC discharge from a dilute mixture of CH_4 and $(CN)_2$ in argon, while an AC discharge of pure $(CN)_2$ in argon was used for the direct absorption study. Six hyperfine components arising from the nitrogen nuclear spin in the lambda-doublets of the $J = 5/2 \rightarrow 3/2$ transition of CCN near 59 GHz were recorded, partly as a test of the new FTmmW system. Four transitions were also measured in the 224–296 GHz range using direct absorption, as well; at the higher frequencies, lambda-doubling was resolved but the hyperfine structure was effectively collapsed. All measurements required significant signal-averaging. The spectra were analyzed in a combined fit with the previous $J = 3/2 \rightarrow 1/2$, FTMW data, using a case (a) Hamiltonian. Rotational and lambda-doubling constants for CCN were significantly improved over previous analyses. Based on the hyperfine and quadrupole constants, the most dominant resonance structure for this radical is the ·C—C≡N arrangement. Unlike CN and C_3N, however, there is still substantial electron density on the nitrogen nucleus such that the C═C═N· structure is also important, as found for CCP and CCAs.

1. Introduction

The CCN radical ($\widetilde{X}^2\Pi_r$) has attracted spectroscopists for many decades since its initial detection by Merer and Travis in 1965 [1]. These authors measured the $\widetilde{A}^2\Delta_i - \widetilde{X}^2\Pi_r$, $\widetilde{B}^2\Sigma^+ - \widetilde{X}^2\Pi_r$, and $\widetilde{C}^2\Sigma^+ - \widetilde{X}^2\Pi_r$ electronic transitions of this molecule, discovering evidence of significant Renner-Teller interactions in the $^2\Delta$ state. This work was followed by a series of other electronic studies, the first in 1982 by Kakimoto and Kasuya [2], who used Doppler-limited laser excitation to examine the $\widetilde{A}^2\Delta(0\,0\,0) - \widetilde{X}^2\Pi(0\,0\,0)$ vibronic transition and established rotational constants with accuracies of about 0.0027 cm^{-1} (81 MHz). Kawaguchi et al. [3] subsequently measured several of the hot bands of this electronic transition, while Hakuta and Uehara recorded LIF $\widetilde{A} - \widetilde{X}$ spectra [4]. A few years later, Bernath and co-workers re-examined the $\widetilde{A} - \widetilde{X}$ transition of CCN with resolution of 0.003 cm^{-1} using Fourier transform (FT) spectroscopy [5,6], determining vibrational and Renner-Teller parameters for the ground state. More recently, Kohguchi et al. [7] investigated the $\widetilde{C} - \widetilde{X}$ transition, greatly expanding on the Merer and Travis work [1], while the ν_1 band of the radical has been further explored employing both diode-laser and Laser Magnetic Resonance (LMR) techniques [8,9].

The first pure rotational study of CCN did not occur until 1995, when Ohshima and Endo [10] recorded the $J = 3/2 \rightarrow 1/2$ transition in the $\Omega = 1/2$ ladder of the ground state using Fourier transform microwave (FTMW) spectroscopy. Both the Λ-doublets and hyperfine components were resolved in this work, resulting in the most accurate spectroscopic constants to date. However, because only one rotational transition was measured, not all spectral parameters could be independently determined, such as that for centrifugal distortion. Also, because transitions originating in the $\Omega = 3/2$ ladder were not measured, only the hyperfine constants b, d, and $h = a - (b + c)/2$ were established, as well as the quadrupole parameters eQq_0 and eQq_2. Nonetheless, this work was a major achievement, as the CCN dipole moment is small at 0.425 D. The Ohshima and Endo work was complemented in 2000 by the LMR study of the ν_2 bending mode by Allen et al. [11]. These authors measured numerous transitions between the (010) $\mu^2\Sigma^-$ vibronic state and the ground state, including several originating in the $\Omega = 3/2$ ladder. A combined, weighted fit of these data, the previous

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http://dx.doi.org/10.1016/j.jms.2014.10.008
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Table 1
Observed transition frequencies of CCN ($X^2\Pi_r$: Ω = 1/2).

J'	↔	J''	F'	↔	F''	Parity	ν_{obs} (MHz)	$\nu_{obs} - \nu_{calc}$ (MHz)
1.5	→	0.5	0.5	→	0.5	*e*	35442.944 [a]	0.007
1.5	→	0.5	1.5	→	0.5	*e*	35429.397 [a]	0.002
1.5	→	0.5	0.5	→	1.5	*e*	35453.776 [a]	0.002
1.5	→	0.5	1.5	→	1.5	*e*	35440.233 [a]	0.001
1.5	→	0.5	2.5	→	1.5	*e*	35422.684 [a]	−0.005
1.5	→	0.5	0.5	→	0.5	*f*	35486.587 [a]	0.002
1.5	→	0.5	1.5	→	0.5	*f*	35510.660 [a]	0.008
1.5	→	0.5	0.5	→	1.5	*f*	35403.858 [a]	0.001
1.5	→	0.5	1.5	→	1.5	*f*	35427.932 [a]	0.007
1.5	→	0.5	2.5	→	1.5	*f*	35472.589 [a]	−0.006
2.5	→	1.5	3.5	→	2.5	*e*	59062.835	0.017
2.5	→	1.5	2.5	→	1.5	*e*	59063.981	0.020
2.5	→	1.5	1.5	→	0.5	*e*	59067.007	−0.043
2.5	→	1.5	3.5	→	2.5	*f*	59107.303	−0.012
2.5	→	1.5	2.5	→	1.5	*f*	59114.769	−0.001
2.5	→	1.5	1.5	→	0.5	*f*	59115.163	0.002
9.5	←	8.5	10.5	←	9.5	*f*	224549.223	0.175
9.5	←	8.5	9.5	←	8.5	*f*	224549.223	−0.057
9.5	←	8.5	8.5	←	7.5	*f*	224549.223	0.077
10.5	←	9.5	11.5	←	10.5	*e*	248185.616	0.147
10.5	←	9.5	10.5	←	9.5	*e*	248185.616	−0.023
10.5	←	9.5	9.5	←	8.5	*e*	248185.616	0.115
10.5	←	9.5	11.5	←	10.5	*f*	248190.029	0.058
10.5	←	9.5	10.5	←	9.5	*f*	248190.029	0.267
10.5	←	9.5	9.5	←	8.5	*f*	248190.029	0.229
11.5	←	10.5	12.5	←	11.5	*e*	271822.734	0.057
11.5	←	10.5	11.5	←	10.5	*e*	271822.734	−0.068
11.5	←	10.5	10.5	←	9.5	*e*	271822.734	0.070
11.5	←	10.5	12.5	←	11.5	*f*	271836.598	−0.088
11.5	←	10.5	11.5	←	10.5	*f*	271836.598	0.131
11.5	←	10.5	10.5	←	9.5	*f*	271836.598	0.133
12.5	←	11.5	13.5	←	12.5	*e*	295460.689	−0.061
12.5	←	11.5	12.5	←	11.5	*e*	295460.689	−0.154
12.5	←	11.5	11.5	←	10.5	*e*	295460.689	−0.016
12.5	←	11.5	13.5	←	12.5	*f*	295484.662	−0.321
12.5	←	11.5	12.5	←	11.5	*f*	295484.662	−0.095
12.5	←	11.5	11.5	←	10.5	*f*	295484.662	−0.063

[a] From Ref. [10].

microwave frequencies, and other optical work providing spin–orbit splitting, yielded global spectroscopic constants for the ground state, including *a*, *b*, *c* and centrifugal distortion *D*.

CCN is also of astrophysical interest. The CN group is one of the most common moieties found in interstellar molecules, making its appearance in various long-chain cyanoacetylene species such as C_3N, HC_3N, and HC_5N. [12–14]. It is even found in metal-bearing species such as MgCN, KCN, and FeCN [15–17]. Understanding the relative abundances of such chains in a given series, for example, HCN, HCCN, HC_3N, etc., has been in fact used to establish reaction pathways [18]. Given the ubiquitous presence of CN and C_3N in circumstellar envelopes of evolved, carbon-rich stars [19], CCN is an obvious candidate for interstellar identification. Several searches for this radical have been conducted using radio telescopes towards the chemically-rich envelope of the star IRC+10216, beginning in 1991 by Guélin and Cernicharo [20], followed by Fuchs et al. in 2004 [21]. Neither search was successful, in part because the dipole moment is small, and line contamination in high sensitivity spectra requires knowledge of the rotational frequencies to better than 1 MHz.

In order to better characterize the CCN radical, and provide more accurate rest frequencies for astronomical searches, we have conducted new pure rotational measurements of this molecule using a combination of Fourier transform millimeter-wave (FTmmW) and millimeter direct absorption spectroscopy. We have measured the hyperfine components of the $J = 5/2 \rightarrow 3/2$ transition in the $\Omega = 1/2$ ladder, as well as additional lines in the 200–300 GHz range, where the lambda-doubling was resolved. We have combined our data with the previous FTMW measurements to further refine the rotational constants. Here we present our measurements, their analysis, and a discussion of the bonding in CCN and related species in terms of the revised spectroscopic constants.

2. Experimental

Measurements for CCN were first obtained using the Fourier transform microwave (FTMW) spectrometer in the Ziurys group, which has just been upgraded to operate from 40–90 GHz, increasing the complete range to 4–90 GHz. This instrument consists of a large vacuum chamber evacuated with a cryopump, containing a Fabry–Perot cavity consisting of two spherical mirrors in a near confocal arrangement. In the 40–90 GHz region, the mirrors are 8.7 in. in diameter, with embedded waveguide to couple the radiation into and out of the cell. To generate radiation in the 40–60 GHz range, a doubler (Norden Millimeter) is used in conjunction with the base frequency source, a 4–40 GHz synthesizer (Agilent). A pulsed-valve nozzle, which lies at a 40° angle relative to the optical axis, is used to create a supersonic jet expansion. The nozzle, operated at a 10 Hz rate, contains a pulsed DC discharge source consisting of two copper ring electrodes. A low noise 40–60 GHz amplifier (Norden Millimeter) is used to detect molecular emission from the cavity, which is recorded by a computer in the time domain as the free induction decay (FID). The Fourier transform of the FID results in a spectrum. Because of the jet orientation to the cavity axis, every measured transition has a Doppler doublet line profile with a FWHM of about 6 kHz; the transition frequencies are simply taken as the average of the two Doppler components. More details can be found in Ref. [22]. At 59 GHz, the measurement accuracy is estimated to be ±3 kHz.

Following the FTmmW work, the millimeter/submillimeter spectrum of CCN was then measured in the range 224–295 GHz, using one of the direct absorption spectrometers of the Ziurys group. This system instrument consists of a radiation source, a single-pass free-space gas cell, and a detector. The frequency source is one of several Gunn oscillator/Schottky diode multiplier combinations that cover the range 65–850 GHz. The reaction cell is a 4 in. diameter glass cylinder chilled to −50 °C with liquid methanol. The detector is an InSb hot electron bolometer that is cooled to 4 K with liquid helium. The radiation from the source, modulated at 25 kHz, is directed through the cell quasi-optically by a series of Teflon lenses and into the detector. Demodulation of the signal from the detector is accomplished at 2*f* using a lock-in amplifier, producing second-derivative spectra. For further details, see Ref. [23].

For the FTMmmW experiments, CCN was produced in a supersonic jet in a pulsed DC discharge from a dilute mixture of 0.25% CH_4 and 0.25% $(CN)_2$ in argon. The duration of the discharge, operated at 1000 V, was about 1400 μs, initiated with the opening of the jet nozzle valve. The mixture was pulsed into the chamber with a backing pressure of ~35 psi with a mass flow of 45 sccm. Typically 12000–20000 nozzle pulses were needed to achieve an adequate signal-to-noise ratio for the CCN signals.

Several reaction mixtures were attempted to produce CCN in the mm-wave instrument, all in an AC discharge. First, based on the FTmmW results, a mixture of about 4 mtorr of CH_4, 2 mtorr of $(CN)_2$ and 15–20 mtorr of argon was used, subjected to 200–300 W AC discharge. In order to eliminate lines originating from hydrogen-containing products, 2 mtorr of CD_4 was substituted for the methane. Both methods yielded line-rich spectra that were impossible to unravel. Therefore, a combination of pure $(CN)_2$ in argon was tried in an effort to reduce line confusion. This synthesis