

Submillimetre-wave spectrum, ^{14}N -hyperfine structure, and dipole moment of cyclopropyl cyanide

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Dedicated to Herb Pickett and Ed Cohen.

Abstract

The room-temperature rotational spectrum of cyclopropyl cyanide ($c\text{-C}_3\text{H}_5\text{CN}$) has been investigated in selected frequency regions from 85 to 680 GHz using a source-modulation submillimetre-wave spectrometer. More than 450 transitions have been measured spanning the quantum numbers $12 \leq J \leq 103$ and $0 \leq K_a \leq 48$ for the most abundant isotopic species. All lines have been fit together with previously published data to yield refined rotational and centrifugal distortion constants that permit accurate frequency predictions. The rotational spectra of the ^{13}C - and ^{15}N -containing isotopologues, observed in natural abundance, have also been investigated at 85–410 GHz. Complementary measurements were performed also at 6.7–14.2 GHz on low- J lines of the normal isotopologue, which were observed in supersonic expansion and with fully resolved ^{14}N -nuclear quadrupole hyperfine structure. The electric dipole moment components of cyclopropyl cyanide were also redetermined from Doppler-free Stark effect measurements and are $\mu_a = 4.1221(31)$ D, $\mu_c = 0.9026(9)$ D, and $\mu_{\text{tot}} = 4.2197(30)$ D.

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1. Introduction

Cyclopropyl cyanide, the smallest ring molecule bearing the nitrile group ($\text{—C}\equiv\text{N}$), was the subject of early microwave spectroscopy investigations. The pure rotational spectra of the main isotopic species and of two deuterated variants were first studied in 1958 by Friend and Dailey [1]. Thereafter Pearson et al. [2] recorded the centimetre-wave (cm-wave) spectra of the two isotopic species containing ^{13}C in the ring, and this enabled the first evaluation of the geometry of the carbon ring. The study was extended by Harmony et al. [3] to the nitrile ^{13}C - and ^{15}N -containing

isotopologues, thus allowing for the complete heavy-atom substitution structure to be determined. The dipole moment of cyclopropyl cyanide was determined in 1967 by Carvalho [4] by Stark spectroscopy giving $\mu_a = 4.027(11)$ D and $\mu_c = 0.920(87)$ D. Additionally, the ^{14}N -hyperfine structure of the rotational transitions of cyclopropyl cyanide was studied by Brown et al. [5] using a Stark-modulation cm-wave spectrometer, and subsequently by Böttcher et al. [6], who employed a waveguide time domain spectrometer. None of the above mentioned investigations extended the study of the rotational spectrum of cyclopropyl cyanide above 40 GHz, and thus a satisfactory centrifugal distortion analysis is still lacking.

Cyclopropyl cyanide is a molecule of potential astrophysical interest; in particular it might be a constituent of the so called *hot cores*: dense star forming regions which show high abundances of complex organic molecules

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[7,8]. So far, definitive detections of cyclic molecules in the interstellar space have been rather scarce: only five species are known, all being three-membered ring compounds. They are the carbenes $c\text{-C}_3\text{H}_2$ [9] and $c\text{-C}_3\text{H}$ [10], cyclopropenone ($c\text{-C}_3\text{H}_2\text{O}$) [11], and the heterocyclic species $c\text{-SiC}_2$ [12] and oxirane ($c\text{-C}_2\text{H}_4\text{O}$) [13]. On the other hand, many searches for other cyclic molecules have been unsuccessful (see Ref. [14] and references therein). It has been pointed out [13,15] that the difficulty in identifying ring molecules in space may be due not only to their low chemical abundance, but also to the weakness of their spectral signals, since cyclic species typically have larger partition functions and lower dipole moments than their linear counterparts. As many species containing the $-\text{CN}$ group, cyclopropyl cyanide is a highly polar molecule; its rotational spectrum is characterised by very strong a -type features, making it a promising candidate for astronomical detection.

In this work, the pure rotational spectrum of cyclopropyl cyanide has been thoroughly reinvestigated. We have measured 487 new rotational lines in the millimetre-wave (mm-wave) and submillimetre-wave (submm-wave) regions reaching a frequency as high as 680 GHz and a rotational quantum number J of 103, allowing for a very comprehensive centrifugal distortion analysis. The rotational spectra of the three ^{13}C - and of the ^{15}N -containing isotopic species have also been investigated: over 500 lines have been recorded in the 85–410 GHz frequency range, spanning J values from 12 to 62. In addition to high-frequency measurements, the cm-wave spectrum of the main isotopologue of cyclopropyl cyanide has been investigated using a cavity pulsed-jet Fourier Transform microwave (FTMW) spectrometer. Forty-eight hyperfine structure components belonging to low- J rotational transitions have been recorded, and their analysis yielded much improved values of the ^{14}N electric quadrupole coupling constants. Moreover, Stark effect measurements performed at sub-Doppler resolution using FTMW spectroscopy yielded more reliable values of the μ_a and μ_c dipole moment components of cyclopropyl cyanide.

2. Experimental

The rotational spectrum of cyclopropyl cyanide was investigated using a source-modulation submm-wave spectrometer located in Bologna (Dipartimento di Chimica “G. Ciamician”) and a cavity pulsed-jet FTMW spectrometer in Warsaw (Institute of Physics, Polish Academy of Sciences). In both cases, commercial samples of cyclopropyl cyanide (Sigma Aldrich) were used for the measurements without further purification.

The mm- and submm-wave lines were recorded in selected frequency regions between 87 and 690 GHz using the source-modulation spectrometer described earlier [16]. Briefly: Gunn oscillators (Farran, Carlstrom and RPG) were used as main radiation sources to cover the fundamental frequency range 52–115 GHz and higher frequen-

cies were generated using harmonic multiplication. The oscillators were phase-locked to a cm-wave solid state source which was in turn locked to a computer-controlled frequency synthesiser, which was finally referenced to an external rubidium frequency standard. The mm-wave oscillators were frequency modulated at 16.67 kHz and phase sensitive detection at $2f$ was employed, so that the second derivative of the actual spectrum profile was recorded by the computer-controlled acquisition system. A Schottky-barrier diode and a liquid-helium cooled InSb detector were used to record the spectra below and above 200 GHz, respectively, using a 3.5 m long free-space absorption cell kept at room temperature and filled with cyclopropyl cyanide vapour at pressures of 2–5 mTorr (0.3–0.7 Pa).

The spectrometer used for FTMW supersonic expansion measurements has been described in detail in Ref. [17]. It operates in the original Balle–Flygare configuration [18], in which the cavity axis is perpendicular to the expansion axis. In this configuration it is easier to apply an external electric field to the sample, and this was carried out with a special set of Stark electrodes developed in the Warsaw laboratory [19,20]. The electrodes were designed to provide increased uniformity of electric field at the large electrode separation enforced by the necessity of not perturbing the resonance mode of the Fabry-Perot cavity of the spectrometer.

3. Observed spectra and analysis

3.1. Millimetre- and submillimetre-wave spectra

Cyclopropyl cyanide is a near-prolate asymmetric-top molecule ($\kappa \approx -0.97$) with C_s symmetry, with two non-zero dipole moment components: along the a and c principal axes (see Fig. 1). The most prominent features of its rotational spectrum are a series of intense aR branches ($\Delta J = 1, \Delta K_a = 0$), whose maximum peak intensity is

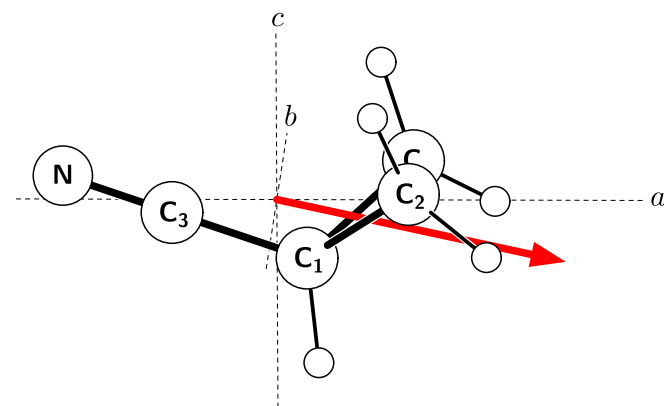


Fig. 1. Molecular structure and principal inertial axes of cyclopropyl cyanide. The b axis is perpendicular to the symmetry plane containing the N, C_3 and C_1 atoms. The arrow indicates the direction of the electric dipole moment in the molecule and is directed from the notional negative to the notional positive charge.

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