



Rotational Spectra of Interstellar Cyanopolyynes HC_{2n+1}N ($n = 0-8$) Neutrals and Cations

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Abstract

We obtain the rotational spectra for cyanopolyynes HC_{2n+1}N ($n = 0-8$) and their cations through quantum chemical calculations. Rotational constants, quartic centrifugal distortion constants, and hyperfine constants are calculated. The rotational constants are determined at the theoretical level of B3PW91/cc-pVTZ, incorporating with the calibration for the moment of inertia. This significantly improves the accuracy with respect to the uncalibrated ones. Quartic centrifugal distortion constants are estimated using the empirical relation, achieving an accuracy of $\sim 0.02\%$ with respect to the experiment. Hyperfine constants are computed at the B3PW91/6-311+G (df, pd) and B3PW91/aug-cc-pVTZ levels. The overall frequency characteristics of all the target molecules are discussed and their detectability in the interstellar medium is also quantitatively evaluated. The rotational spectra of selected species (HC_{13}N , HC_{15}N , HC_{17}N , and HC_5N^+) are reproduced, showing satisfied consistency with experiments or observations. Our results provide useful reference for observations and experiments, even that more advanced calculation levels and basis sets are required to achieve better accuracy.

Key words: ISM: molecules – ISM: lines and bands – molecular data

1. Introduction

Carbon chain molecules (CCMs) are one of the main molecular components detected in the Universe (Taniguchi et al. 2024). They are very sensitive probes of the evolutionary stages and can trace dynamical process of molecular clouds (Dickens et al. 2001; Inostroza et al. 2011; Wu et al. 2019; Friesen et al. 2013). More importantly, such molecules may be carriers of the diffuse interstellar bands (DIBs; Maier et al. 2004). Since the first detection of CCMs in the interstellar medium (ISM) in the 1970s, their formation pathways have been studied extensively through experiments (Zack & Maier 2014) and chemical simulations (Loison et al. 2014). In the last few years, very complex CCMs, branching chain molecules (Fuentetaja et al. 2022) and molecules containing benzene rings (McGuire et al. 2018) have also been detected in the ISM. These new discoveries challenge for deeper understanding of the carbon chain chemistry in the ISM. CCMs not only reveal the complexity of chemical reactions in the ISM, but also help understand the chemical evolution during star formation.

Cyanopolyynes are one of the most important CCMs in the ISM (McGuire 2022). After the first detection of HC_3N in space (Turner 1971), five cyanopolyne species from HC_3N to HC_{11}N have been identified in the TMC-1 cloud. These species were also detected in IRC+10216, except HC_{11}N (Morris et al. 1976; Winnewisser & Walmsley 1978; Matthews et al. 1985; McGuire 2022). Especially, HC_3N and HC_5N are

detected in a variety of star-forming environments, e.g., in high-mass and low-mass star-forming regions, as well as around high-mass protostars (Taniguchi et al. 2018). The ALMA Band 3 data reveal the spatial distribution of HC_5N around high-mass star-forming regions, showing emission consistent with the CH_3OH line. This suggests that HC_5N forms in similarly high-temperature regions as complex organic molecules do (Taniguchi et al. 2023). The chemical diversity around massive protostars suggests that carbon chain chemistry differs from the warm carbon chain chemistry mechanism around low-mass stars. CCMs may exist in higher temperature regions than that of the warm carbon-chain chemistry.

Large molecules are often formed in the gas phase or on the interstellar dust grain surfaces. Cyanopolyynes are more likely formed in the gas phase from chemical and astronomical points of view (Giani et al. 2025). On one hand, cyanopolyynes are highly unsaturated with a cyano group at the end of a polyne chain. They would be readily react with hydrogen atoms on the dust grain or icy surfaces, forming the more saturated counterparts. On the other hand, most of the cyanopolyynes are observed at cold environments, like TMC-1, while there is no clear mechanism for releasing them from dust surfaces into the gas phase surroundings. The recent discovery of cyanopolyne cations, HC_3N^+ (Cabezas et al. 2024), HC_5N^+ and HC_7N^+ (Cernicharo et al. 2024), by the

QUIJOTE spectroscopic survey may bring up new formation pathways of cyanopolyynes in the gas phase reactions.

The identification of molecules essentially relies on the experimental measurements of the rotational spectra. The presence of higher-order cyanopolyynes was confirmed using the laboratory spectroscopy, including HC_7N , HC_9N and HC_{11}N (Iida et al. 1991; Travers et al. 1996a, 1996b). Nevertheless, for a long time cyanopolyynes cations were not identified due to the lack of laboratory spectra (Cernicharo et al. 2024). Cations are usually considered “short-lived” or transitional molecules in the terrestrial physical environment, and experimental spectroscopic measurements are often performed under complex in situ characterizations. Therefore, the quantum chemical calculations are now the main tools to get the theoretical rotational spectra for these cations. Now that the calculations are often challenged by the calibration, how to accurately calibrate the rotational spectra for cyanopolyynes cations is crucial for future radio observations and identification.

In this paper, we try to approach a satisfying calibration of the rotational spectra of cyanopolyynes, both neutral and cations. The paper is organized as follows. In Section 2, we describe our calculated sample and theoretical method. The main results for the calculation of rotational constants, quartic centrifugal distortion constants and hyperfine constants are given in Section 3. Since the existence of ^{14}N ($I = 1$) nuclei in our target molecules will bring pronounced hyperfine splitting, we also simulate the nuclear quadrupole and magnetic hyperfine structures. Then we discuss the astrophysical implication in Section 4, and a summary is given in Section 5.

2. Target Molecules and Theoretical Method

Our target molecules are cyanopolyynes families HC_{2n+1}N ($n = 0-8$). We terminate our targets at $n = 8$ for the following reasons. The rotational constants of the longer chains can be extrapolated from the short ones (Oka 1978). Also, the quartic centrifugal distortion and other lines splitting effects can be neglected for the longer chains (Travers et al. 1996a). In addition, the longer chains are less abundant and thus more challenging to detect in observation.

We use density functional theory (DFT) implemented in GAUSSIAN 16 (Frisch et al. 2016) to obtain spectroscopy constants for all the target molecules. Different basis sets with proper correction methods are adopted to obtain the spectroscopy constants. We calculate the rotational constants and test them with three different basis sets: CCSD/cc-pVTZ, CCSD/cc-pVDZ, and B3PW91/cc-pVTZ. For the hyperfine constants, including the nuclear quadrupole coupling constants and the magnetic fine-structure constants, calculations at both B3PW91/6-311G+(df, pd) and B3PW91/aug-cc-pVTZ levels are performed. The centrifugal distortion constants are calculated with our own physical model, in combination with

the calculated rotational constants. The details are discussed in Section 3. For the structure optimization, we use CCSD method in conjunction with the cc-pVTZ basis set, which gives the best estimation for the bond lengths. With our calculated constants, we simulate the rotational spectra with PGOPHER program (Western 2017).

3. Results and Discussion

3.1. Rotational Constants

For cyanopolyynes, the rotational transition frequency could be expressed as $\nu = 2B(J + 1) - 4D(J + 1)^3$ beyond the rigid-rotor approximation, where J is the rotational angular momentum of the lower level, B the rotational constant, and D the centrifugal distortion constant.¹

We first try to approach the best compromise between calculation accuracy and computer time. Using neutral cyanopolyynes series HC_{2n+1}N ($n = 0, 1, 2, 3$) as test molecules, we calculate their rotational and centrifugal distortion constants and compare with experiments. We use three distinct basis sets: CCSD/cc-pVTZ, CCSD/cc-pVDZ, and B3PW91/cc-pVTZ, and the calculated results are given in Table 1. For all the test molecules, the maximum percentage errors for the ground-state rotational constants B are 0.65%, 3.23% and 1.35% at levels CCSD/cc-pVTZ, CCSD/cc-pVDZ, and B3PW91/cc-pVTZ respectively. The mean errors are 0.51%, 2.89%, and 1.03%. All these calculations give unacceptable accuracy when compared with observation, since the identification of a molecule in the radio band requires the difference between the calculation and the observation $\leq 0.6\%$, and therefore the errors for the rotational constants B should be $\leq 0.3\%$ (McGuire 2022).

We then try to accurately calculate the rotational constant B by calibrating the moment of inertia (I , $B = h^2/8\pi^2I$). I could be determined using the lengths of the molecule (l). Thus, its difference between the calculation and the experiment ΔI , defined as $I_{\text{cal}} - I_{\text{exp}}$, could be fitted into a polynomial as a function of l (Etim & Arunan 2017). We fit the polynomial using the neutral HC_{2n+1}N , since the experiment rotational constants are available. Then this polynomial is applied to the cations. Employing the level of B3PW91/cc-pVTZ, we optimized the geometry for all the target molecules, and calculate their l values (see Table 2). Then I could be calibrated with ΔI , and therefore the corrected rotational constants B_{cor} are obtained and given in Table 2. We note here that the uncalibrated I are calculated from the B_{cal} , given at the B3PW91/cc-pVTZ level. The accuracy is greatly enhanced after the calibration, and the absolute error between B_{cor} and B_{exp} ranges from 0.03 to 0.04 MHz for all the cyanopolyynes neutrals. Therefore, we predict that the corrected rotational constants of

¹ The next term H in the centrifugal expansion only causes negligible error (e.g. at 300 GHz where $J \sim 900$, the error for the calculated rest frequencies is $\leq 1 \text{ km s}^{-1}$).

Table 1
Rotational Constants (B) and Quartic Centrifugal Distortion Constants (D) of Neutral Cyanopolyynes Series, HC_{2n+1}N ($n = 0, 1, 2, 3$), Obtained from Different Methods

Constant	Molecule	CCSD/cc-pVTZ	CCSD/cc-pVDZ	B3PW91/cc-pVTZ	Exp.
B (MHz)	HCN	44548.29990	43321.05200	44915.37000	44315.9757(4) ^a
	HC ₃ N	4534.78200	4415.89200	4593.50300	4549.0580(5) ^b
	HC ₅ N	1324.16770	1289.55900	1343.48100	1331.3313(10) ^c
	HC ₇ N	560.32100	545.77600	569.04400	564.00074(16) ^d
D (Hz)	HCN	82085.0529	76699.1452	82060.0049	87240.0(6) ^a
	HC ₃ N	503.6771	467.4835	497.3638	546.9(5) ^b
	HC ₅ N	25.5617	25.0565	26.5902	25.7(20) ^c
	HC ₇ N	3.7951	3.2709	3.4593	3.820(87) ^d

Notes.^a Delucia & Gordy (1969).^b de Zafra (1971).^c Alexander et al. (1976).^d Kroto et al. (1978).

Table 2
Calculated Molecular Total Lengths (l), Calculated (B_{cal}) and Corrected Rotational Constants (B_{cor}) for Target Molecules

Molecule	Neutral				Cation		
	l (Å)	B_{cal} (MHz)	B_{cor} (MHz)	B_{exp} (MHz)	l (Å)	B_{cal} (MHz)	B_{cor} (MHz)
HCN	2.213862	44915.370000	44315.814590	44315.9757(4) ^a	2.302192	40796.247000	40251.043979
HC ₃ N	4.788904	4593.503000	4549.050514	4549.0580(5) ^b	4.826613	4563.187000	4518.407349
HC ₅ N	7.353462	1343.481000	1331.329437	1331.3313(10) ^c	7.365605	1346.499000	1334.237618
HC ₇ N	9.914885	569.044000	564.000369	564.00074(16) ^d	9.910610	571.570000	566.487861
HC ₉ N	12.474175	293.131000	290.550399	290.518322(57) ^c	12.458292	294.627000	292.029566
HC ₁₁ N	15.032407	170.605000	169.105985	169.06294(3) ^f	15.007563	171.501000	169.993460
HC ₁₃ N	17.590061	107.960000	107.011473	106.97258(4) ^f	17.557848	108.526000	107.572617
HC ₁₅ N	20.146939	72.625000	71.986472	71.950133(6) ^g	20.108802	72.996000	72.354503
HC ₁₇ N	22.703941	51.183000	50.732532	50.70323(6) ^g	22.660265	51.441000	50.988547

Notes.^a Delucia & Gordy (1969).^b de Zafra (1971).^c Alexander et al. (1976).^d Kroto et al. (1978).^e Iida et al. (1991).^f McCarthy et al. (1997).^g McCarthy et al. (2000a).

the cations will be closer to future experimental results compared to the results from pure quantum chemical calculations.

3.2. Quartic Centrifugal Distortion Constants

Quantum chemical calculations are much less effective to predict the quartic centrifugal distortion constants D for the carbon chain molecules. As shown in Table 3, the calculated centrifugal distortion constant, D_{cal} , is about 10% smaller than that in experiment, D_{exp} . Here, we propose to infer D from their rotational constants B using the approach given by Travers et al. (1996b).

Travers et al. (1996b) assumed that the Young's modulus of cyanopolyynes is independent of length, like that of a solid elastic rod. The centrifugal distortion effect is contributed entirely by the in-line vibration at the lowest frequency. Therefore, we have $D/B \propto (N_{\text{C}} + 1)^{-4}$. Using the available B_{exp} and D_{exp} for cyanopolyynes, Travers et al. (1996b) gave $\log(D/B) = -4.53 - 4 \log(N_{\text{C}} + 1)$, where N_{C} is the number of carbon atoms. With this formula, they accurately predicted D for HC₁₃N. The prediction differs from the experimental value by less than 0.8%. Therefore, we adopt their formula to estimate D for the neutrals.

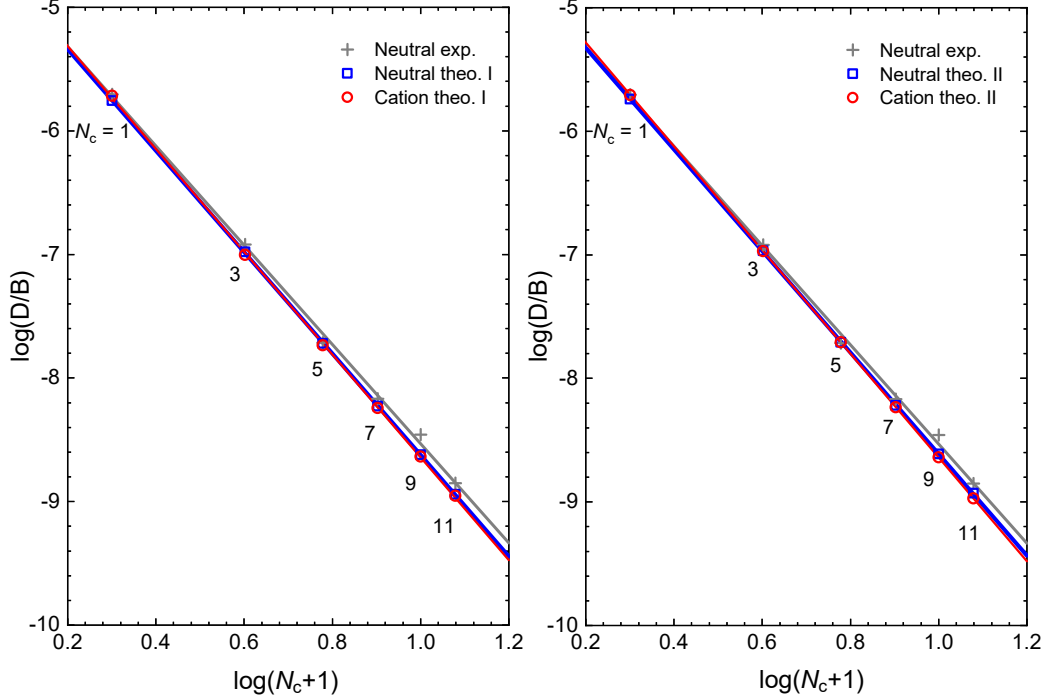


Figure 1. Log-log plot for the D/B vs. chain length $N_C + 1$ of cyanopolyynes neutrals (red) and cations (blue). Experimental data of neutral cyanopolyyne (gray) are also shown for comparison. The theoretical calculation methods, theo. I and II, are B3LYP/6-31G(d) and B3PW91/6-311+G(df, pd).

Table 3

Quartic Centrifugal Distortion Constants (D) for the Target Molecules

Molecule	Neutral			Cation
	D_{cal} (Hz)	D_{cor} (Hz)	D_{exp} (Hz)	D_{cor} (Hz)
HCN	82060.0049	87239.6828	87240(60) ^a	79237.8148
HC ₃ N	497.3638	546.9491	546.9(5) ^b	543.2648
HC ₅ N	26.5902	25.7000	25.7(20) ^c	25.7561
HC ₇ N	3.4593	3.8200	3.820(87) ^d	3.8368
HC ₉ N	0.7211	0.8741	0.874(78) ^e	1.0153
HC ₁₁ N	0.2013	0.2381	0.238(11) ^f	0.2393
HC ₁₃ N	0.0686	0.0920	0.0920(10) ^f	0.0925
HC ₁₅ N	0.0271	0.0369	0.0369(9) ^g	0.0371
HC ₁₇ N	0.0119	0.0250	0.025(7) ^g	0.0251

Note. ^{a-g} Same as Table 2.

The next question is whether this formula can be used for cations. We use quantum chemical calculations to test whether neutrals and cations have a similar length-dependent relation. We calculate B and D for six neutral cyanopolyyne and their cations using two different theoretical levels, B3LYP/6-31G(d) and B3PW91/6-311+G(df, pd). Figure 1 depicts the calculation results of $\log(D/B)$ versus carbon chain length and their fit to the linear model, $\log(D/B) = a_1 \log(N_C + 1) + a_0$. The fitted slopes a_1 and intercepts a_0 are given in Table 4.

Table 4

Fitting Parameters a_1 and a_0 for Different Methods

Method	a_1	a_0
Neutral exp.	-4.014(236)	-4.517(194)
Neutral theo. I ^a	-4.103(31)	-4.519(25)
Neutral theo. II ^b	-4.109(29)	-4.503(24)
Cation theo. I	-4.159(77)	-4.482(63)
Cation theo. II	-4.199(38)	-4.442(36)

Notes.

^a theo. I: B3LYP/6-31G(d).

^b theo. II: B3PW91/6-311G+(df, pd).

From Table 4, we see that there is tiny difference for a_1 and a_0 between the neutrals and cations. For neutrals, B3LYP/6-31G(d) level gives best consistency with experiments. Therefore, for cations we will adopt a_1 and a_0 given at the same level, and recommend the following formula to estimate centrifugal distortion constants.

$$\log(D/B) = -4.482 - 4.159 \log(N_C + 1) \quad (1)$$

The estimated centrifugal distortion constants (D_{cor}) for the neutrals and cations are given in Table 3. The average difference between D_{cal} and D_{exp} is $\sim 30\%$ for the neutrals, while only $\sim 0.02\%$ for D_{cor} . Therefore, our approach is accurate enough and recommended to estimate centrifugal distortion constants.

Table 5
 ^{14}N Nuclear Electric Quadrupole Coupling Constants (χ_{ij}) of the Target Molecules

Formula	ij	Exp. (MHz)	B3PW91/cc-pVTZ (uncorrected; MHz)	B3PW91/6-311+G(df, pd) (corrected; MHz)	B3PW91/aug-cc-pVTZ (corrected; MHz)
HCN	cc	$-4.70783(6)^a$	-5.113793	-4.736149	-4.804867
HC ₃ N	cc	$-4.319(1)^b$	-4.741734	-4.412313	-4.466312
HC ₅ N	cc	$-4.242(30)^c$	-4.694457	-4.373211	-4.431821
HC ₇ N	cc	$-4.29(16)^d$	-4.680332	-4.359576	-4.416901
HC ₉ N	cc	$-4.84(21)^d$	-4.675755	-4.355780	-4.412258
HC ₁₁ N	cc	...	-4.672700	-4.353819	-4.409312
HC ₁₃ N	cc	...	-4.671870	-4.352879	-4.408295
HC ₁₅ N	cc	...	-4.671601	-4.352459	-4.407905
HC ₁₇ N	cc	...	-4.671615	-4.353112	-4.408045
HCN ⁺	aa	...	-1.037014	-1.052735	-0.991449
	bb	...	7.697390	7.296184	7.282249
	cc	...	-6.660376	-6.243448	-6.290795
HC ₃ N ⁺	aa	...	0.654754	0.337470	0.371404
	bb	...	5.683444	5.356417	5.354699
	cc	...	-6.338198	-5.693887	-5.726107
HC ₅ N ⁺	aa	...	1.344654	1.096341	1.131486
	bb	...	4.580004	4.358604	4.366046
	cc	—	-5.924653	-5.454945	-5.497532
HC ₇ N ⁺	aa	...	1.705753	1.490326	1.524528
	bb	...	3.972210	3.781444	3.792321
	cc	...	-5.677964	-5.271770	-5.316848
HC ₉ N ⁺	aa	...	1.917172	1.720368	1.753529
	bb	...	3.594902	3.416517	3.429314
	cc	...	-5.512074	-5.136885	-5.182844
HC ₁₁ N ⁺	aa	...	2.005287	1.865535	1.897561
	bb	...	3.369570	3.167403	3.182402
	cc	...	-5.374857	-5.032937	-5.079963
HC ₁₃ N ⁺	aa	...	2.108271	1.961983	1.994378
	bb	...	3.182957	2.989966	3.005494
	cc	...	-5.291228	-4.951949	-4.999872
HC ₁₅ N ⁺	aa	...	2.180302	2.031580	2.061895
	bb	...	3.043742	2.856240	2.873677
	cc	...	-5.224043	-4.887816	-4.935577
HC ₁₇ N ⁺	aa	...	2.231205	2.036306	2.188933
	bb	...	2.936541	2.688388	2.480332
	cc	...	-5.167746	-4.724694	-4.669265

Notes.^a Ebenstein & Muentert (1984).^b Lafferty & Lovas (1978).^c Winnewisser et al. (1978).^d McCarthy et al. (2000b).

3.3. Hyperfine Constants

In molecules with quadrupole moment nuclei, the nuclear quadrupole coupling effect is the main cause of the splitting in the rotational lines. This splitting is particularly pronounced for nuclei with nuclear spin (e.g., ^{14}N , ^{35}Cl etc). The nuclear quadrupole coupling constant (χ_{ij}) represents energy associated with the interaction between the electric quadrupole moment of the nucleus with the gradient of the molecular electric field. By observing the fine structure induced by χ_{ij} , the physical and chemical conditions of interstellar molecular clouds can be studied. These data help understand the

formation, evolution and distribution of the interstellar molecules, and thus shed light on the complex processes of interstellar chemistry.

Although more than 50 yr have passed since the first discovery of the cyanopolyyne family, experimental reports of specific χ_{ij} measurements are scarce and limited to the short-chain HC_{2n+1}N ($n = 0, 1, 2, 3, 4$) (see Table 5).² Fortunately, the nuclear quadrupole coupling constants for the five molecules do not differ much between -4.3 and -4.8 MHz.

² In general, the nuclear quadrupole coupling effect is negligible for long carbon chains.

Table 6Fermi Contact Constant (b_F) and Dipole-dipole Interaction Tensor (T) for Hydrogen and Nitrogen Nuclei in Cyanopolyne Cations

Formula	$b_F(\text{H})$ (MHz)	$T_{aa}(\text{H})$ (MHz)	$T_{bb}(\text{H})$ (MHz)	$b_F(\text{N})$ (MHz)	$T_{aa}(\text{N})$ (MHz)	$T_{bb}(\text{N})$ (MHz)
HCN ⁺	-37.417	25.514	-6.149	-6.008	-27.275	55.562
HC ₃ N ⁺	-39.410	22.542	-3.921	-3.941	-17.369	38.023
HC ₅ N ⁺	-33.938	18.995	-2.920	-2.461	-11.322	26.232
HC ₇ N ⁺	-28.781	15.916	-2.313	-1.585	-7.870	19.311
HC ₉ N ⁺	-24.685	13.534	-1.939	-1.139	-5.725	14.926
HC ₁₁ N ⁺	-21.488	11.703	-1.696	-0.864	-4.291	11.944
HC ₁₃ N ⁺	-18.963	10.271	-1.529	-0.679	-3.279	9.800
HC ₁₅ N ⁺	-16.932	9.129	-1.409	-0.554	-2.535	8.196
HC ₁₇ N ⁺	-15.255	8.193	-1.317	-0.463	-1.974	6.968

Radio astronomers often adopt the typical value of ~ -4.3 MHz for larger HC_{2n+1}N neutrals ($n = 5, 6, 7, 8$) (McCarthy et al. 2000a). Our subsequent estimation will focus on the cations.

Unlike the neutrals that the nuclear quadrupole coupling effect can be expressed by one certain value, the electric field gradient of the cations exhibits significant anisotropy due to their more complex electronic structure. They should be in terms of the electric field gradient tensor q_{ij} ($i, j = a, b, c$, i.e., the principal axes of the rotational moment of inertia).³ Moreover, the electric field gradients between different cyanopolyne cations all differ from each other by more than 5% (Bailey 2000). Therefore, it is necessary to calculate the nuclear quadrupole coupling constant for the cation one by one.

We adopt the approach proposed by Bailey (2000) in the following calculations. They calculated the electric field gradients using B3PW91/6-311+G(df, pd) and B3PW91/aug-cc-pVTZ for more than 110 groups of molecules with experiment χ_{ij} available. Regression analysis of the experiment χ_{ij} with the calculational results yields correction factors eQ/h of 4.5617 and 4.5694 MHz au⁻¹ for the two levels, respectively. We note here that the corrections are the same for neutrals and cations at the same theoretical level.

We then calculate the q_{ij} at levels B3PW91/6-311+G(df, pd) and B3PW91/aug-cc-pVTZ, and corrected them with the correction factors given by Bailey (2000). The corrected results are given in Table 5. It shows that the corrected χ_{ij} given at B3PW91/6-311+G(df, pd) level is more consistent with the experiments than the B3PW91/aug-cc-pVTZ combination, which is consistent with the conclusions obtained by Bailey (2000).

We note here that Bailey (2000) used experimental molecular geometries in their calculation. However, for our

target molecules the experimental geometries are not available. Instead, we have to use the structure parameters from quantum chemical calculations. Therefore, we could not achieve the same accuracy as Bailey (2000) does. Even that, our calculations can still meet the accuracy requirements for the observations. Taking the observation for the smallest molecule with fine structures HC₃N as an example, for its $J = 0-1$ proton fine structure F_{1-2} , our calculated ¹⁴N nuclear quadrupole splitting error ~ 0.09 MHz is comparable to that of the observation at 9098.287(55) MHz. Therefore, we will adopt the nuclear quadrupole coupling constants obtained from the corrected B3PW91/6-311+G(df, pd) to simulate the rotational fine structure.

Hydrogen and nitrogen atoms in cyanopolyne cations are non-zero nuclear spin nuclei, and the magnetic hyperfine constants, Fermi contact constants (b_F) and dipole-dipole interaction tensors (T_{aa} and T_{bb}) have also been calculated at the B3PW91/6-311G+(df, pd) level. The results are tabulated in Table 6.

4. Astrophysical Implications

Rotational spectroscopy in radio astronomy has enabled the detection of the vast majority ($\sim 90\%$) of newly discovered molecules. Using the spectroscopic constants tabulated above, we can simulate the theoretical rotational spectra for all target cyanopolyne neutrals and cations, allowing quantitative assessment of their detectability in the ISM.

We model the population distribution among energy states by assuming a Boltzmann distribution at excitation temperature T_{ex} . Specifically, the fraction (F_n) of molecules in a given energy state E_n follows $F_n \propto e^{-E_n/kT_{\text{ex}}}$. Consequently, the ratio of populations between two states E_n and E_m is given by $F_n/F_m = e^{(E_m-E_n)/kT_{\text{ex}}}$. For example, a molecule in the n th energy level with $E_n = 5kT$ will have a population fraction $F_n = e^{-5} \sim 1\%$ relative to the ground state. As a first-order approximation, we consider states with energies below $5kT$ to represent the ensemble of nontrivial population states at a given temperature.

Figure 2 presents the rotational energy levels for cyanopolyne neutrals and cations ($n = 0-8$), whose rotational constants span three orders of magnitude. In general, longer cyanopolynes exhibit smaller rotational constants (B) compared to their shorter counterparts. Consequently, for a given rotational quantum number J , the corresponding energy level is lower in longer molecules. While the open-shell electronic structure of the cations restricts J to half-integer values, both neutrals and cations follow a similar trend in their energy level progression with increasing J , as illustrated in Figure 2. Due to the smaller rotational constants, longer cyanopolynes possess more energy levels below $5kT$, leading to a broader distribution of the total population across these states. For example, consider HCN⁺ and HC₇N⁺ at an excitation

³ q_{ij} relates with χ_{ij} as $\chi_{ij} = (-eQ/h)q_{ij}$, where $-e$ represents the charge of the proton, h Planck's constant, and Q the electric quadrupole moment of the ¹⁴N nucleus.

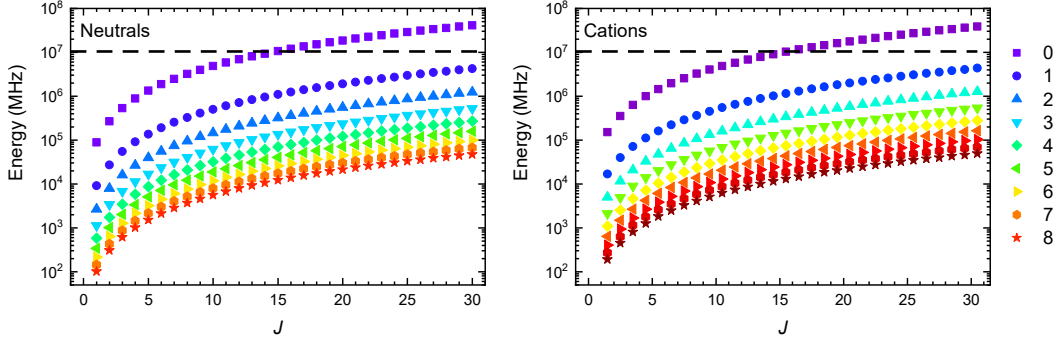


Figure 2. Rotational energy levels for cyanopolyynes ($n = 0-8$) neutrals (left) and cations (right). The dashed lines are drawn at 10.41×10^6 MHz, the value of $5 kT$ at $T = 10$ K; energy levels below this value are nontrivially populated.

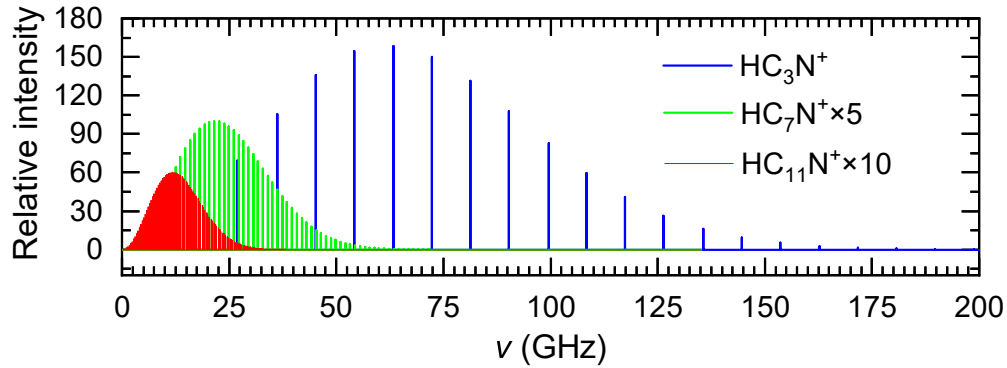


Figure 3. Rotational spectra of HC_3N^+ (blue), HC_5N^+ (green), and HC_7N^+ (red) at $T = 10$ K for the same number of molecules of each. The intensities of HC_5N^+ , and HC_7N^+ are multiplied by the factors of 5 and 10.

temperature $T_{\text{ex}} = 10$ K: the number of nontrivially populated states is 16 for HCN^+ but 135 for HC_7N^+ . As a result, the population per state is diluted in HC_7N^+ , reducing the number of molecules, undergoing any single rotational transition and thus yielding weaker spectral signals.

Figure 3 compares the rotational spectra of HC_3N^+ , HC_7N^+ , and HC_{11}N^+ at $T_{\text{ex}} = 10$ K, assuming equal molecular abundances for each species. As the molecular length increases, the spectra become increasingly dense, with intensities so low that they require scaling factors of 5 and 10 for HC_7N^+ and HC_{11}N^+ , respectively, to be clearly visible in the plot. The strongest rotational transitions at this temperature occur at transitions: $J = 15/2 \rightarrow 13/2$ for HC_3N^+ , $J = 37/2 \rightarrow 35/2$ for HC_7N^+ , and $J = 69/2 \rightarrow 67/2$ for HC_{11}N^+ . Notably, the peak intensity of HC_3N^+ is approximately 25 times stronger than that of HC_{11}N^+ . This intensity reduction, combined with the spectral line crowding, makes detection of longer cyanopolyynes increasingly challenging. The frequency shift to lower values with increasing molecular size reflects the growing moment of inertia and corresponding decrease in rotational constant B . This trend is clearly demonstrated in Figure 3, where the strongest

transitions progressively move from ~ 63 GHz (HC_3N^+) to ~ 22 GHz (HC_7N^+) and finally to ~ 12 GHz (HC_{11}N^+).

To verify the accuracy of our calculated rotational constants B_{cor} , we reproduce the experimental rotational frequencies of the long-chain cyanopolyynes molecules HC_{13}N , HC_{15}N and HC_{17}N , as tabulated in Table 7. Since their transition frequencies are closely harmonic with respect to the short chains, and thus the centrifugal distortion term D can be neglected. For the HC_{13}N , the next long cyanopolyne to be identified in the ISM, 20 rotational transition lines with $J \rightarrow J - 1$ from $J = 18$ to 43 have been detected in the gas phase experiment (McCarthy et al. 1997), corresponding to the frequency range of 6–15 GHz. For the longer cyanopolyynes, HC_{15}N and HC_{17}N , 18 and 9 transition lines have been measured in the frequency ranges 5–11 GHz and 5–7 GHz with uncertainty ~ 2 kHz (McCarthy et al. 2000b), which are covered with $J \rightarrow J - 1$ from $J = 38$ to 71 and $J = 55$ to 66. Our calculated frequencies are predicted within the average relative errors: 0.049% for HC_{13}N , 0.051% for HC_{15}N , and 0.058% for HC_{17}N with respect to that measured in experiments. We have to admit that although our results seem to be closer to the experimental values relative to the standard quantum chemical method, i.e., CCSD/pVTZ, the absolute

Table 7
Experimental and Calculated Transition Frequencies of HC₁₃N, HC₁₅N and HC₁₇N

$J' \rightarrow J$	HC ₁₃ N			HC ₁₅ N			HC ₁₇ N		
	Exp. ^a (MHz)	Cal. (MHz)	C-E ^b (MHz)	Exp. ^b (MHz)	Cal. (MHz)	C-E ^c (MHz)	Exp. ^b (MHz)	Cal. (MHz)	C-E ^c (MHz)
23→22	4920.733	4922.523	1.790	...	...	...	...	...	...
24→23	5134.682	5136.546	1.864	...	...	...	...	...	...
25→24	5348.622	5350.568	1.946	...	...	...	...	...	...
26→25	5562.566	5564.590	2.024	...	...	...	...	...	...
27→26	5776.514	5778.612	2.098	...	...	...	...	...	...
28→27	5990.458	5992.634	2.176	...	...	...	...	...	...
30→29	6418.340	6420.678	2.338	...	...	...	...	...	...
31→30	6632.290	6634.700	2.410	...	...	...	...	...	...
32→31	6846.235	6848.722	2.487	...	...	...	...	...	...
33→32	7060.178	7062.744	2.566	...	...	...	...	...	...
34→33	7274.120	7276.766	2.646	...	...	...	...	...	...
35→34	7488.066	7490.787	2.721	...	...	...	...	...	...
36→35	7702.009	7704.809	2.800	...	...	...	...	...	...
37→36	7915.955	7918.830	2.875	...	...	...	...	...	...
38→37	8129.894	8132.852	2.958	5468.202	5470.964	2.762	...	...	...
39→38	8343.839	8346.873	3.034	5612.102	5614.936	2.834	...	...	...
40→39	...	...	...	5756.001	5758.908	2.907	...	...	...
41→40	8771.727	8774.915	3.188	5899.901	5902.881	2.980	...	...	...
42→41	...	...	...	6043.800	6046.853	3.053	...	...	...
43→42	...	...	...	6187.700	6190.825	3.125	...	...	...
44→43	9413.556	9416.978	3.422	6331.599	6334.797	3.198	...	...	...
45→44	...	...	...	6475.499	6478.769	3.270	...	...	...
46→45	...	...	...	6619.398	6622.741	3.343	...	...	...
47→46	...	...	...	6763.297	6766.713	3.416	...	...	...
48→47	10269.327	10273.061	3.734	6907.196	6910.685	3.489	...	...	...
49→48	...	...	...	7051.096	7054.657	3.561	...	...	...
50→49	...	...	...	7194.995	7198.629	3.634	...	...	...
51→50	...	...	...	7338.894	7342.601	3.707	...	...	...
53→52	11339.040	11343.161	4.121	...	...	...	...	...	...
54→53	11552.980	11557.181	4.201	...	...	...	...	...	...
55→54	...	...	...	...	...	...	5577.339	5580.562	3.223
59→58	...	...	...	...	...	...	5982.961	5986.418	3.457
60→59	...	...	...	...	...	...	6084.366	6087.882	3.516
61→60	...	...	...	...	...	...	6185.771	6189.346	3.575
62→61	...	...	...	...	...	...	6287.177	6290.810	3.633
63→62	...	...	...	...	...	...	6388.582	6392.274	3.692
64→63	...	...	...	9209.578	9214.230	4.652	6489.987	6493.738	3.751
65→64	...	...	...	9353.477	9358.201	4.724	6591.392	6595.202	3.810
66→65	...	...	...	9497.375	9502.172	4.797	6692.798	6696.665	3.867
70→69	...	...	...	10072.968	10078.055	5.087	...	...	...
71→70	...	...	...	10216.866	10222.026	5.160	...	...	...

Notes.^a McCarthy et al. (1997).^b McCarthy et al. (2000b).^c C-E defined as (Cal.−Exp.).

error in frequency is still ~ 2 MHz, which is far from the $\sim$ kHz error required by radio astronomy observations.

In fact, even a tiny difference in rotational constants can result in large errors in rotational frequencies especially for high energy levels. This is more evident when we directly compare the rotational spectrum of HC₅N⁺ with that observed by the QUIJOTE line survey. Figure 4 (black lines) shows a

series of seven lines in harmonic relation with half-integer quantum numbers from $J = 25/2$ to $37/2$. Cernicharo et al. have fitted the observed frequencies to the standard expression $\nu = 2B_{\text{eff}}J - 4D_{\text{eff}}J^3$, with effective rotational constant $B_{\text{eff}} = 1336.662 \pm 0.001$ MHz and effective centrifugal distortion constant $D_{\text{eff}} = 27.4 \pm 2.6$ Hz. Figure 4 (red lines) depicts the simulated rotational spectrum of HC₅N⁺ by using

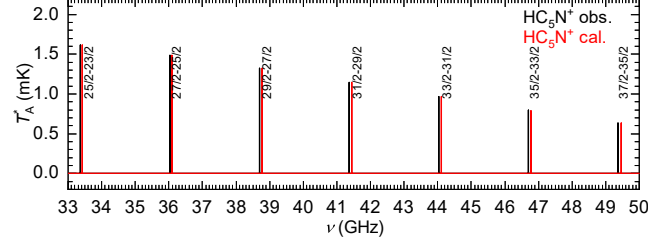


Figure 4. Observed (black) and calculated (red) rotational spectra of HC_5N^+ in TMC-1.

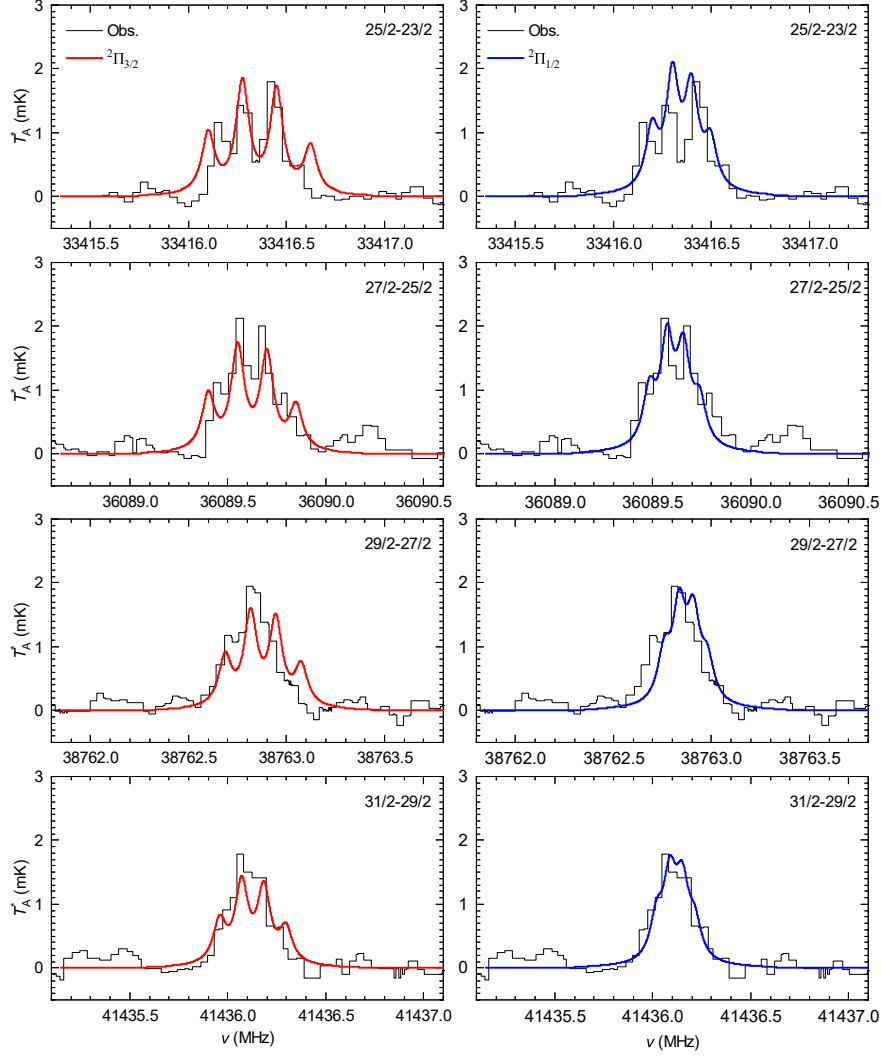


Figure 5. Observed (black) and calculated hyperfine structures of HC_5N^+ in the electronic states of $^2\Pi_{3/2}$ (red) and $^2\Pi_{1/2}$ (blue) in TMC-1.

our calculated spectroscopic constants $B = 1334.238$ MHz and $D = 25.756$ Hz. The average mismatch between observed and calculated frequencies is ~ 2.46 MHz at the central frequency ~ 40 GHz, and the relative error is only around 0.006%. Although the identification of HC_5N^+ is not robust enough for

that the absolute error required by radio astronomy is limited to several kHz, theoretical rotational spectrum from quantum chemical calculation is still an initial choice in detecting the interstellar molecules in the lack of experimental spectra. Therefore, it is urgent to develop a more accurate quantum

chemical method for the calculations of rotational constants and transition frequencies.

Although the robustness in rotational frequency is not enough to identify a new molecule in the ISM, the fine structure of rotational line provide a new horizon to support the identification. The first four transitions with fine or hyperfine structure components provide a possible indicator to the ladder of the rotational transitions. Figure 5 depicts the simulated rotational spectra using the hyperfine constants of HC_5N^+ derived from our calculations in the $\Omega = 3/2$ and $\Omega = 1/2$ ladders. To stand out the fine structure of each transition line, the effective rotational constant B_{eff} , effective centrifugal distortion constant D_{eff} fitted from astronomical observation are adopted to match the observed rotational frequencies. In addition, the line intensity and width of are also directly taken from observation. Although the agreement between the synthetic spectra and the observations is not perfect, a satisfying consistency can be observed in the rotational spectra with $\Omega = 3/2$. In fact, the $\Omega = 3/2$ ladder in HC_5N^+ is the lowest in energy, while the $\Omega = 1/2$ is more than 50 K above it. The kinetic temperature is ~ 9 K in TMC-1, therefore the rotational transitions will be dominated by $^2\Pi_{3/2}$, and the $^2\Pi_{1/2}$ ladder is relative weak.

Our analyses above suggest that our calculations provide a database of the rotational spectra for cyanopolyynes HC_{2n+1}N ($n = 0-8$, neutrals and cations), which can be applied to the future observations.

5. Summary

To reproduce the rotational spectra of cyanopolyynes HC_{2n+1}N ($n = 0-8$) and their cations, we calculated their rotational constants, quartic centrifugal distortion constants and hyperfine constants. The rotational constants are estimated from the calculation at the B3PW91/cc-pVTZ level, by employing calibration of the moment of inertia, which gives a much better accuracy than the uncalibrated results. The quartic centrifugal distortion constants are estimated using the relation $\log(D/B) = a_1 \log(N_C + 1) + a_0$. For the neutrals, $a_0 = -4.53$ and $a_1 = -4$ are adopted from the literature, while for the cations, we get them from our own calculation and recommend $a_0 = -4.482$ and $a_1 = -4.159$. Such estimation gives very high accuracy with a difference of $\sim 0.02\%$ with respect to the experiments. Finally, the hyperfine constants are calculated at levels B3PW91/6-311+G(df, pd) and B3PW91/aug-cc-pVTZ. We find that the corrected B3PW91/6-311+G(df, pd) gives a better consistency with experiments. With all the calculational results, we reproduce the rotational spectra for a selected sample (HC_{15}N , HC_{17}N and HC_5N^+), and find them very consistent with the experiments or the observations.

We conclude that our calculation can very well reproduce the rotational spectra for cyanopolyynes HC_{2n+1}N ($n = 0-8$) and their cations, and could be applied to the future observations.

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