Determination of accurate rest frequencies and hyperfine structure parameters of cyanobutadiyne, HC_5N

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Abstract

Very accurate transition frequencies of HC_5N were determined between 5.3 and 21.4 GHz with a Fourier transform microwave spectrometer. The molecules were generated by passing a mixture of HC_3N and C_2H_2 highly diluted in neon through a discharge valve followed by supersonic expansion into the Fabry-Perot cavity of the spectrometer. The accuracies of the data permitted us to improve the experimental ^{14}N nuclear quadrupole coupling parameter considerably and the first experimental determination of the ^{14}N nuclear spin-rotation parameter. The transition frequencies are also well suited to determine in astronomical observations the local speed of rest velocities in molecular clouds with high fidelity. The same setup was used to study HC_7N, albeit with modest improvement of the experimental ^{14}N nuclear quadrupole coupling parameter. Quantum chemical calculations were carried out to determine ^{14}N nuclear quadrupole and spin-rotation coupling parameters of HC_5N, HC_7N, and related molecules. These calculations included evaluation of vibrational and relativistic corrections to the non-relativistic equilibrium quadrupole coupling parameters; their considerations improved the agreement between calculated and experimental values substantially.

Keywords:
microwave spectroscopy, interstellar molecule, cyanopolyynes, hyperfine structure, quantum chemical calculation

1. Introduction

Cyanopolyynes $H(C{\equiv}C)_nCN$ occur abundantly in space, in particular the shorter members. Molecules up to cyanooctatetrayne, HC_9N ($n = 4$), were detected [1]. The next longer member, $HC_{11}N$, has not yet been found in space [2]. Isotopic species with D or with one ^{13}C were detected up to HC_7N [3], ^{15}N isotopologs up to HC_5N [4], even all three isotopomers of HC_3N with two ^{13}C were observed astronomically [5]. Measurements of the HC_3N species and the isotopomers with one ^{13}C were frequently used to determine $^{12}C/^{13}C$ ratios in various objects, such as the protoplanetary nebula CRL618 [6, 7] or in starless cores, where differences in the $^{12}C/^{13}C$ ratios were found [8].

Cyanobutadiyne, HC_5N, also known as cyanodiacetylene or pentadiynenitrile, was detected as early as 1976 toward the high-mass star-forming region Sagittarius B2 close to the Galactic center [9]. It was found soon thereafter in the dark and dense core Heile's Cloud 2 [10], nowadays better known as Taurus Molecular Cloud 1 or short as TMC-1 [11]. Cyanohexatriyne, HC_7N, also known as cyanotriacetylene or heptatriynenitrile, was discovered in that source [12]. Both molecules were also found early in the circumstellar envelope of the famous carbon rich asymptotic giant branch star CW Leonis, also referred to as IRC+10216 [13].

Molecules up to $HC_{17}N$ ($n = 8$) were investigated by rotational spectroscopy [14]. Alexander et al. were the first to investigate the rotational spectrum of HC_5N [15]. They assigned ground state rotational spectra of eight isotopic species in the microwave (MW) region from which they determined structural parameters. They also determined the ^{14}N nuclear quadrupole coupling parameter eQq(N) and the dipole moment of the main isotopic species. Winnewisser et al. improved eQq(N) [16] and expanded the assignments into the millimeter wave (mmW) region [17]. Bizzocchi et al. recorded the spectra of HC_5N and DC_5N in the mmW and sub-mmW regions [18]. Assignments for these two isotopologs were extended to 460 GHz. They also analyzed spectra of singly substituted isotopic variants of both isotopologs containing one ^{13}C or ^{15}N, and derived from the rotational parameters a semi-experimental equilibrium structure.

Kirby et al. analyzed the ground state rotational spectrum of HC_7N in the MW region [19]. McCarthy et al. subjected the main isotopic species as well as all singly substituted ones to a Fourier transform (FT) MW spectroscopic study and determined eQq(N) for all of them [20]. Similar studies were carried out for HC_9N and $HC_{11}N$, and ground state effective structural parameters for all three molecules. Soon thereafter, Bizzocchi et al. extended the assignments of the main isotopic species in its ground and several low-lying vibrational states into the

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mmW region [21].

The aim of the present work is twofold. The first target was the improvement of the hyperfine structure (HFS) parameters of HC_5N and potentially of HC_7N, and secondly, we wanted to investigate how accurately HFS parameters can be evaluated by high-level quantum-chemical calculations, and in particular trends among related molecules. An earlier study of isotopic species associated with DC_3N showed that very good agreement can be achieved for the nuclear quadrupole parameters in high-accuracy coupled-cluster calculations by employing large basis sets together with vibrational corrections [22].

2. Experimental details

Spectra between 5 and 22 GHz were recorded at the Leibniz-Universität in Hannover employing a supersonic-jet Fourier transform microwave (FTMW) spectrometer [23] in the coaxially oriented beam-resonator arrangement (COBRA) [24] which combines a very sensitive setup with an electric discharge nozzle [25]. Cyanobutadiyne was generated by passing a mixture of equal amounts of 1% HC_3N in neon and 1% C_2H_2 in neon at a pressure of ∼100 kPa through the discharge nozzle and expanding the products into the cavity of the spectrometer. Cyanohexatriyne was obtained initially by the same procedure and subsequently by modifying the ratio of diluted HC_3N and C_2H_2 from 1 : 1 to 1 : 2. Uncertainties of frequencies of 0.3 kHz and below can be achieved under favorable conditions [26, 27].

3. Observed spectra and determination of spectroscopic parameters

Prediction of the microwave spectra of HC_5N and HC_7N were very reliable based on earlier data [16, 18, 20, 21]. Pickett's SPCAT and SPFIT programs [28] were used for prediction and fitting of the spectra, respectively. Each rotational level of HC_5N and HC_7N with $J > 0$ is split by spin coupling effects caused by the ^{14}N nucleus ($I = 1$) into three HFS components. The rotational and spin angular momenta are coupled sequentially: $\mathbf{J} + \mathbf{I}(^{14}N) = \mathbf{F}$. At higher values of J, the strong HFS components are the ones conserving the spin orientation, i. e. those with $\Delta F = \Delta J$. The very narrow linewidths of a few kilohertz for an isolated line permits the corresponding HFS components to be resolved for all investigated transitions of HC_5N and HC_7N. However, the high sensitivity of the present HC_5N data allowed us to observe the weaker spin-reorienting HFS components with $\Delta F = 0$ for all transitions and the even weaker ones with $\Delta F = -\Delta J$ for the lowest two transitions ($J = 2 - 1$ and $3 - 2$). The transition frequencies obtained in the present investigation are summarized in Table 1 together with their quantum number assignments, uncertainties, and differences between experimental frequencies and those calculated from the global fit. The signal-to-noise ratios (S/N) of the spectral recordings of HC_5N were very high such that almost all lines were accurate to 0.2 kHz (1σ), see also Refs 26, 27.

The very high quality of the HC_5N data prompted us to try to improve the data situation also for HC_7N. We recorded first data

Table 1: Rotational transitions of HC_5N with quantum numbers J and F recorded in the present study, their frequencies (MHz), uncertainties Unc. (kHz), residuals O−C (kHz) between observed transition frequencies and those calculated from the global fit.

$J' - J''$	$F' - F''$	Frequency	Unc.	O−C
2 – 1	2 – 2	5324.04642	0.20	0.05
	1 – 0	5324.26054	0.20	−0.06
	2 – 1	5325.32957	0.20	−0.24
	3 – 2	5325.42182	0.20	0.03
	1 – 2	5326.18468	0.20	0.20
	1 – 1	5327.46808	0.20	0.16
3 – 2	3 – 3	7986.61752	0.20	0.03
	2 – 1	7987.77870	0.20	0.02
	3 – 2	7987.99286	0.20	−0.05
	4 – 3	7988.04414	0.20	0.00
	2 – 3	7988.54163	0.20	0.27
	2 – 2	7989.91689	0.20	0.11
4 – 3	4 – 4	10649.22745	0.20	0.27
	3 – 2	10650.56191	0.20	0.06
	4 – 3	10650.65418	0.20	0.34
	5 – 4	10650.68658	0.20	0.04
	3 – 3	10652.48571	0.20	−0.02
5 – 4	5 – 5	13311.85257	0.20	0.06
	4 – 3	13313.26074	0.20	0.10
	5 – 4	13313.31208	0.20	0.21
	6 – 5	13313.33461	0.20	0.00
	4 – 4	13315.09264	0.20	0.11
6 – 5	6 – 6	15974.48392	0.20	−0.29
	5 – 4	15975.93351	0.20	−0.08
	6 – 5	15975.96655	0.20	0.25
	7 – 6	15975.98302	0.20	−0.03
	5 – 5	15977.71410	0.20	−0.15
7 – 6	7 – 7	18637.11750	0.20	−0.05
	6 – 5	18638.59378	0.20	0.12
	7 – 6	18638.61629	0.20	−0.10
	8 – 7	18638.62933	0.20	0.06
	6 – 6	18640.34150	0.20	−0.11
8 – 7	8 – 8	21299.74993	0.50	0.23
	7 – 6	21301.24497	0.20	0.30
	8 – 7	21301.26134	0.20	−0.08
	9 – 8	21301.27125	0.20	−0.40
	7 – 7	21302.96959	0.20	−0.30

Table 2: Rotational transitions of HC_7N with quantum numbers J and F recorded in the present study, their frequencies (MHz), uncertainties Unc. (kHz), residuals O−C (kHz) between observed transition frequencies and those calculated from the global fit.

$J' - J''$	$F' - F''$	Frequency	Unc.	O−C
5 − 4	4 − 3	5639.9580	1.0	−0.12
	5 − 4	5640.0104	1.0	1.19
	6 − 5	5640.0325	1.0	0.72
6 − 5	5 − 4	6767.9778	1.0	0.38
	6 − 5	6768.0107	1.0	0.72
	7 − 6	6768.0261	1.0	−0.47
12 −11	11 − 10	13535.9917	1.0	−0.54
	12 − 11	13535.9978	1.0	−1.21
	13 − 12	13536.0055	1.0	1.61

for the $J = 12 - 11$ and $6 - 5$ transitions which had been studied earlier [20]. The S/N were considerably lower than in the case of HC_5N, as was expected. Therefore, only the $\Delta F = \Delta J$ HFS components were detected with reasonable S/N even after long integration. In addition to remeasure transition frequencies of these two transitions, we recorded the $J = 5 - 4$ transition at 5640 MHz, which was the lowest in frequency available at that time. The HC_7N transition frequencies obtained in the present study are given with additional information in Table 2. The accuracies were 1 kHz (1σ) in all instances.

Our present HC_5N and HC_7N data were fit together with previous data. Since the number of spectroscopic parameters is small with respect to the total number of lines of each molecule, the quality of the reproduction of the lines of each source is a good indication for the accuracies of the lines. These were 10 kHz for the hyperfine free MW center frequencies from Alexander et al. [15] and 7 kHz for the mmW data from Winnewisser et al. [17] and for the mmW and sub-mmW data from Bizzocchi et al. [18] in the case of HC_5N. The accuracies were 1 kHz for the MW transition frequencies with HFS splitting from McCarthy et al. [20] and 10 kHz for those without HFS splitting in the MW region from Kirby et al. [19] and those in the mmW region from Bizzocchi et al. [21] for the HC_7N molecule. The resulting spectroscopic parameters of HC_5N and HC_7N are given in Table 3 together with the most recent previous data.

The line lists and spectroscopic parameters are available as supplementary material to this article; the line, parameter, and fit files along with additional files are deposited in the data section of the Cologne Database for Molecular Spectroscopy[2] [29].

The large body of very accurate HC_5N transition frequencies from the present study not only led to an improvement in eQq(N) by more than two orders of magnitude but also resulted in a very well determined value for the nuclear magnetic spin-rotation coupling parameter C, the coefficient of $\mathbf{I}\cdot\mathbf{J}$. In addition, the uncertainties of B and D got reduced; the correlation of these parameters with H is likely responsible for the improvement in the accuracy of H. The differences in the uncertainties of eQq(N) for HC_7N between present and previous data are modest; and we should point out that part of the improvement is caused by assigning an uncertainty of 1 kHz to the earlier FTMW data [20] whereas 2 kHz were reported initially. The nuclear spin-rotation parameter C could not be determined for HC_7N, therefore, it was kept fixed to the value determined in a quantum chemical calculation. This treatment led to a change in eQq(N) from -4.299 ± 0.050 MHz to -4.275 ± 0.050 MHz. The smaller uncertainty in the earlier B value [21] is caused by the fact that in that work unsplit (i.e. HFS free) transition frequencies were derived for the FTMW data [20] to which much smaller effective uncertainties were assigned. A more detailed discussion of the HFS parameters is presented in section 6.

[2]Webaddress: https://cdms.astro.uni-koeln.de/classic/predictions/daten/

4. Application in astronomical observations

Emission lines of HC_5N may be prominent in dense cold molecular clouds such as TMC-1 [30]. Therefore, the very accurate rest frequencies from this and previous studies may be used to determine the local speed of rest in such a cloud with great accuracy, even more so as transitions occur with a spacing of ∼2660 MHz and because the ^{14}N HFS splitting is usually resolved at low values of J. Table 4 lists some molecules which are often abundant in dense molecular clouds and have an at least moderately dense rotational spectrum and rest frequencies known very accurately at least in part. HC_3N in its ground vibrational and low-lying vibrational states [31] or its isotopomers with one ^{13}C [32] or with D [22] have larger rotational spacings, but may be used over a much wider frequency and rotational temperature ranges. The same applies to propyne [33] and methyl cyanide [34, 35, 36]. Carbonyl sulfide [37, 38] can be quite abundant in dense parts of molecular clouds. Sulfur dioxide is more suited for spectra of hot cores and hot corinos, the warm and dense parts of high- and low-mass star-forming regions, respectively. Its rotational spectrum [39, 40, 41, 42] was also employed to calibrate rotational spectra of, e.g., H_2CS [43, 44]. Methanol is very abundant in many different types of molecular clouds, but most reported transitions frequencies have accuracies in the range of 50 kHz to 200 kHz; only limited data are available with better accuracies [40, 45, 46].

5. Quantum chemical calculations

Calculations for the equilibrium structure as well as the ^{14}N nuclear quadrupole and spin-rotation coupling parameters were performed at the coupled-cluster (CC) level [47] using the coupled-cluster singles and doubles (CCSD) approach augmented by a perturbative treatment of triple excitations (CCSD(T)) [48, 49, 50, 51] together with correlation consistent core-polarized valence (cc-pCVXZ, X = T, Q, 5, 6) [52, 53, 54] basis sets. In the calculations of the spin-rotation tensors, perturbation-dependent basis functions, as described in Ref. [55, 56], were used to ensure fast basis-set convergence.

Molecular equilibrium structures were obtained at the CCSD(T)/cc-pCVQZ level of theory, which was shown to

Table 3: Ground state spectroscopic parameters[a] (MHz) of HC5N and HC_7N in comparison to the most recent previous data.

	HC_5N		HC_7N	
Parameter	present	previous[b]	present	previous[c]
B	1331.332691 (4)	1331.332687 (20)	564.0011226 (75)	564.0011225 (44)
$D \times 10^6$	30.1099 (8)	30.1090 (15)	4.04117 (55)	4.04108 (54)
$H \times 10^{12}$	1.642 (19)	1.635 (29)	0.163 (10)	0.163 (10)
eQq(N)	−4.27680 (14)	−4.242 (30)	−4.275 (50)	−4.29 (16)
$C \times 10^3$	0.2896 (123)		0.123	

[a] Numbers in parentheses are one standard deviation in units of the least significant figures. The parameter C of HC_7N was kept fixed to the value of a quantum chemical calculation.
[b] B, D, H from Ref. [18]; eQq(N) from Ref. [16].
[c] B, D, H from Ref. [21]; eQq(N) from Ref. [20].

Table 4: Molecular species with a rich rotational spectrum suitable to determine the local speed of rest with high precision, approximate upper frequency ν (GHz) for a certain accuracy, approximate accuracy Acc. (kHz) and references Ref. and comments.

Molecule	ν	Acc.	Ref. and comments
HC_5N	22	0.2	This work.
HC_5N	500	7	[18] and references therein.
HC_3N	120	1.0	[31].
HC_3N	900	10	[31] and references therein; including several excited states.
HC_3N	620	10−20	[32]; isotopic species with ^{13}C.
CH_3CCH	720	0.5	[33]; $K \leq 12$.
CH_3CN	800	1.0	[34]; $K \leq 12$.
CH_3CN	1500	20−30	[35]; $v_8 \leq 2$, $K + l \leq 12$.
CH_3CN	1200	20−50	[36]; isotopic species with ^{13}C, $K \leq 9$.
OCS	520	1.0	[37, 38]; better than 0.1 kHz for several lines.
SO_2	120	2.0	[39, 40, 41]; $v_2 \leq 1$, also $v = 0$ of $^{34}SO_2$, many lines.
SO_2	2000	10−30	[42]; $v_2 \leq 1$, several lines; many better than 50 kHz.
CH_3OH	120	1−10	[40, 45, 46] and references therein; selected lines, possibly up to 200 GHz.

yield molecular equilibrium structural parameters of very high quality for molecules carrying first-row atoms [57], which applies as well for the HCN [57] and HC_3N [22] systems studied here. Following the extensive basis set study presented in Ref. [22] for the equilibrium structure and the nuclear quadrupole as well as spin-rotation coupling parameters of HC_3N (and DC_3N) we apply a similar procedure here. The ^{14}N nuclear quadrupole coupling parameters of HCN, HC_3N, DC_3N, HC_5N, and HC_7N were determined at the CCSD(T)/cc-pCV5Z level augmented by relativistic corrections computed at the CCSD(T)/cc-pCVQZ level via second-order direct perturbation theory (DPT) [58] and vibrational corrections evaluated using a perturbational approach (VPT2) [59] as described in Ref. [60] for shieldings. Force fields at the MP2/cc-pVTZ level and nuclear quadrupole coupling parameters at the CCSD(T)/cc-pCVTZ level were employed for the vibrational corrections. The ^{14}N spin-rotation parameters were calculated without further corrections at the CCSD(T)/cc-pCVQZ level. All correlated computations were carried out correlating all electrons. A value of 20.44(3) mb was used for the ^{14}N nuclear quadrupole moment [61].

All quantum-chemical calculations were carried out using the CFOUR program package [62]; the parallel version of CFOUR was used for some of the calculations [63]. All results of calculations involving the coupled-cluster singles, doubles and triples (CCSDT) [64, 65] and coupled-cluster singles, doubles, triples and quadruples (CCSDTQ) [64, 66] approaches were obtained with the string-based many-body code MRCC [67] interfaced to CFOUR.

The resulting quantum chemically calculated ^{14}N nuclear quadrupole coupling parameters of HCN to HC_7N are summarized in Table 5 together with experimental values. The calculated and experimental ^{14}N nuclear spin-rotation parameters are given in Table 6.

6. Discussion of hyperfine parameters

The nuclear quadrupole coupling parameters are usually interpreted in terms of bonding of the respective atom [68, 69]. It is not surprising that the ^{14}N value of HCN is considerably different from that of HC_3N (and DC_3N), as shown in Table 5. Unsurprisingly, the difference is small between HC_3N and HC_5N, and very close to zero between HC_5N and HC_7N. The calculated non-relativistic equilibrium values differ slightly from the experimental ground state values. The calculated vibrational corrections are modest, of order of one percent. Relativistic corrections are even smaller, as may be expected for a molecule containing only light atoms, but are not negligible at the level with which most of the experimental values have been determined. The agreement between calculated and experimental ground state values is excellent for HC_3N and DC_3N and very good for all others. The agreement in the case of HC_7N needs to be taken with some caution as the uncertainty of the experimental value is one order of magnitude larger than the deviation. Nevertheless, the value of −4275 kHz, determined with keeping the nuclear spin-rotation parameter fixed the value calculated by quantum chemical means, fits the trend better than the value −4299 kHz without this parameter in the fit, even though both values are compatible within the experimental uncertainties.

The agreement between calculated equilibrium nuclear spin-rotation parameters and the experimental ground state values in Table 6 is very good. The very small deviations for HCN and HC_3N may well be caused by the neglect of vibrational contributions; their determination could not be carried out with the programs at our disposal.

While the differences between calculated and experimental nuclear quadrupole coupling parameters are relatively small, we note that this is most likely due to error compensation. The computed ^{14}N nuclear electric quadrupole parameters are found to depend sensitively on the equilibrium structure used. Moreover, they show very slow convergence with respect to basis set size and correlation treatment, which will be discussed in the following.

Although structures obtained at the CCSD(T)/cc-pCVQZ level are quite close to equilibrium structures derived from experiment [57], a shift in the ^{14}N value of HCN by −5.0 kHz is obtained at the CCSD(T)/cc-pCV5Z level upon going from the CCSD(T)/cc-pCVQZ equilibrium structure (r_e(CH) = 106.554 pm, and r_e(CN) = 115.384 pm) to the equilibrium structures derived from experiment (r_e(CH) = 106.501(8) pm, and r_e(CN) = 115.324(2) pm) [72]. It is assumed that similar deviations would be found if more accurate equilibrium structures would be available for HC_3N, HC_5N, and HC_7N. We would like to emphasize here that these corrections are rather small in relative terms, though not negligible in comparison with experimental accuracy, which is important to realize for the discussion that follows. Furthermore, the uncertainty of the value of the ^{14}N quadrupole moment (20.44 mb) is ±0.03 mb, which translates roughly to 0.15% or values between ±6.9 and ±6.3 kHz for the molecules under study.

In the cases of HCN and HC_3N, it was possible to evaluate the equilibrium ^{14}N values with an even larger basis. Separating the total ^{14}N value into contributions from Hartree−Fock (HF) and CCSD(T) reveals on the one hand that the HF contribution still changes by −12.7 kHz and −12.0 kHz when increasing the basis set quality from cc-pCV5Z to cc-pCV6Z for HCN and HC_3N, respectively. On the other hand, the correlation contribution at this level changes from cc-pCV5Z to cc-pCV6Z by less than 1 kHz in the same direction. An equal shift of −12.0 kHz was found for HC_5N at the HF level by increasing the basis set level from cc-pCV5Z to cc-pCV6Z.

Considering higher-level correlation effects beyond CCSD(T) by employing fc-CCSDT/cc-pVTZ and fc-CCSDTQ/cc-pVDZ computations shows corrections that differ in sign but also in magnitude. The difference between fc-CCSDT/cc-pVTZ and fc-CCSD(T)/cc-pVTZ is found to be −10.7 and −13.1 kHz for HCN and HC_3N, respectively. However, the corresponding differences between fc-CCSDTQ/cc-pVDZ and fc-CCSDT/cc-pVDZ are found to be about twice as large and positive with values of +20.5 kHz for HCN and +24.3 kHz for HC_3N.

Although the relativistic corrections obtained at the CCSD(T) level via second-order direct perturbation theory are

Table 5: Quantum chemically calculated non-relativistic equilibrium nuclear electric quadrupole parameters $eQq(N)_e$ (kHz) of HCN, HC_3N, DC_3N, HC5N and HC_7N, relativistic (Rel.) and vibrational (Vib.) corrections, and their sum (kHz) in comparison to experimental ground state parameters and difference O−C (kHz) between experimental and calculated values.

Molecule	$eQq(N)_e$[b]	Rel.[c]	Vib.[d]	Sum	Exptl.	O−C
HCN	−4668.9	1.8	−32.2	−4699.4	−4707.83 (6)[e]	−8.4
HC_3N	−4344.5	3.5	21.0	−4320.0	−4319.24 (1)[f]	0.8
DC_3N	−4344.5	3.5	22.6	−4318.3	−4318.03 (30)[g]	0.3
HC_5N	−4326.0	3.6	41.7	−4280.7	−4276.80 (14)[h]	3.9
HC_7N	−4326.2	3.6	52.3	−4270.3	−4275. (50)[h]	−4.7

[a] All quantum chemical results from this work; CCSD(T)/cc-pCVQZ structural parameters were used; see also section 5 for further details. Sources of experimental data are given separately. Numbers in parentheses of experimental data are one standard deviation in units of the least significant figures.
[b] Calculated at the CCSD(T)/cc-pCV5Z level.
[c] Calculated at the CCSD(T)/cc-pCVQZ level using second-order direct perturbation theory.
[d] Calculated employing MP2/cc-pVTZ for the required force field and CCSD(T)/cc-pCVTZ for the nuclear electric quadrupole parameters.
[e] Ref. [70].
[f] Ref. [71].
[g] Ref. [22].
[h] This work.

relatively small, they are overestimated for all molecules but HCN by about 40% if they are evaluated employing the smaller cc-pCVTZ basis set. In the case of HCN, they are overestimated by about 70% if the smaller basis is employed. However, for HCN the change when going from cc-pCVQZ to cc-pCV5Z is only −0.2 kHz (about 10%).

The vibrational correction obtained using VPT2 at the MP2/cc-pVTZ level for the required force field and at the CCSD(T)/cc-pCVTZ level for the nuclear quadrupole coupling parameters could be improved for HCN to CCSD(T)/cc-pCVQZ for the force field and CCSD(T)/cc-pCV5Z for the nuclear quadrupole coupling, which resulted in a modest change of −0.6 kHz. For HC_3N/DC_3N, improved VPT2 computations at the CCSD(T)/cc-pCVTZ level yielded vibrational corrections that are 5.3/5.1 kHz smaller than those reported in Table 5.

Summarizing all the previously mentioned improvements for HCN, a total correction of −9.6 kHz is obtained, which would reduce the difference between observed and calculated from −8.4 kHz to +1.2 kHz. For HC_3N/DC_3N total corrections of −6.9/−6.7 kHz would be obtained, while the correction due to the uncertainty in the equilibrium structure remains unknown.

Since the discussed corrections can currently not be applied consistently to all molecules under study, it has to be assumed that similar compensation effects hold for the ^{14}N nuclear quadrupole coupling parameters of HC_5N and HC_7N, which is supported by the *too good* agreement with experiment observed.

With respect to the ^{14}N spin-rotation parameters, only little variations of the CCSD(T) results are found when increasing the basis set size. When going from cc-pCVQZ to cc-pCV5Z, changes of −0.028 and 0.004 kHz are found for HCN and HC_3N, respectively. Employing again fc-CCSDT/cc-pVTZ and fc-CCSDTQ/cc-pVDZ computations to estimate the higher-level correlation effects in HCN, which has the largest spin-rotation parameter value, changes of +0.022 and −0.029 kHz are found for CCSDT and CCSDTQ, respectively, which almost cancel each other. However, comparing the resulting corrected values of 10.001 kHz (HCN) and 0.990 kHz (HC_3N) with experiment, only an improvement for the value of HCN is observed, cf. Table 6.

Table 6: Experimental ground state nuclear magnetic spin-rotation parameters C^a (kHz) of HC_5N and HC_7N in comparison to experimental data for HCN, and HC_3N and in comparison to equilibrium data from quantum chemical calculations (QCC).

Molecule	Exptl.	QCC
HCN[b]	10.13 (2)	9.938
HC_3N[c]	0.976 (3)	0.986
HC_5N[d]	0.2896 (123)	0.290
HC_7N[e]		0.123

[a] Numbers in parentheses of experimental data are one standard deviation in units of the least significant figures. All quantum chemical results are from this work; calculations at the CCSD(T)/cc-pCVQZ level for both structures and values of C; see also section 5. Sources of experimental data are given separately.
[b] Ref. [70].
[c] Ref. [71].
[d] This work.
[e] The value was kept fixed in this work to the value of a quantum chemical calculation; see also Table 3.

7. Conclusions

Accurate transition frequencies of HC_5N and HC_7N were determined employing Fourier transform microwave spectroscopy. These data led to improvements of the spectroscopic parameters. In particular, we improved the accuracy of the ^{14}N nuclear quadrupole coupling parameter of HC_5N considerably and that of HC_7N slightly. In addition, we determined for the first time an experimental value of the nuclear ^{14}N nuclear spin-rotation parameter of HC_5N. Our quantum chemical calculations were able to reproduce the ^{14}N hyperfine parameter of HCN to HC_7N very well. Vibrational corrections to nuclear quadrupole coupling parameters were crucial and relativistic corrections were important to reach nearly the accuracies with which these parameters were determined experimentally. Inclusion of a calculated, very small nuclear spin-rotation value of HC_7N had a remarkable effect on the value of the nuclear quadrupole coupling parameter. Finally, we pointed out that the HC_5N rest frequencies may be useful for determining the local speed of rest in dense molecular clouds if these lines are sufficiently strong. Other examples of molecular species with comparatively rich rotational spectra have been mentioned in addition.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at ...

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