Rotational spectrum of 4-methylcyanoallene ($\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$), a chiral molecule of potential astrochemical interest[★]

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ABSTRACT

Context. A successful identification of an interstellar compound requires that its spectrum has first been assigned in the laboratory. New and sensitive radiotelescopes, such as ALMA, will make it possible to detect interstellar molecules in much smaller concentrations than before. Cyanoallene ($\text{CH}_2=\text{C}=\text{CH}-\text{CN}$) has recently been observed in the dense molecular cloud TMC-1 by means of its rotational spectrum. Its methyl congener, 4-methylcyanoallene ($\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$), may also be present in the interstellar medium (ISM). This chiral compound exists in two forms, which are mirror images. Chirality is an essential feature of life. So far, no chiral compounds have been detected in the ISM.

Aims. The synthesis and assignment of the rotational spectrum of $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$, will facilitate the potential detection of this compound in the ISM.

Methods. The spectrum of 4-methylcyanoallene has been recorded between 13 and 116 GHz using the microwave spectrometer at the University of Oslo. The spectroscopic study has been augmented with high-level quantum chemical calculations at the B3LYP/cc-pVTZ and CCSD/cc-pVTZ levels of theory.

Results. The rotational spectra of $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$ in the ground vibrational state and in the first vibrationally excited state are reported for the first time and accurate spectroscopic constants have been obtained from a large number of transitions.

Key words. methods: data analysis – surveys – molecular data – methods: analytical – techniques: spectroscopic

1. Introduction

Almost 30 nitrile molecules, which contain the cyano group ($\text{C}\equiv\text{N}$), have been detected in the interstellar medium (ISM) so far. The simplest of these nitriles, the cyano radical $\text{C}\equiv\text{N}$, was found in 1940 (McKellar 1940; Hakobian & Crutcher 2011). The most complex of all nitriles, HC_{11}N , having a total of 13 atoms, was detected in 1997 (Bell et al. 1997). The vast majority of these nitriles have been observed in the dense molecular clouds Sgr A and B, and TMC-1 by means of their rotational spectra. The formation mechanisms of many of these compounds are not well understood.

Two interesting nitrile series of some relevance to the present study have been detected in the ISM. The first of these has the general formula $\text{H}(\text{C}\equiv\text{C})_n-\text{CN}$, where $n = 0-5$ (Snyder & Buhl 1971; Turner 1971; Avery et al. 1976; Broten et al. 1976; Kroto et al. 1978; Little et al. 1978; Winnewisser & Walmsley 1978; Broten et al. 1978; Bell et al. 1997). The hydrogen atom is replaced by a methyl group in the second series $\text{CH}_3(\text{C}\equiv\text{C})_n-\text{CN}$, where $n = 0-2$ (Solomon et al. 1971; Broten et al. 1984; Snyder et al. 2006).

Recently, cyanoallene $\text{CH}_2=\text{C}=\text{CH}-\text{CN}$ was observed in the dense molecular cloud TMC-1 (Lovas et al. 2006). This compound seems to be more abundant than its methyl cyanoacetylene isomer, $\text{CH}_3\text{C}\equiv\text{C}-\text{CN}$. The present work deals with the corresponding methyl substituted cyanoallene, namely, 4-methylcyanoallene or 2, 3-pentadienylnitrile $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$. In this molecule, one hydrogen atom in cyanoallene has been replaced by a methyl group. We suggest that 4-methylcyanoallene is an interesting candidate for a future radioastronomical detection. There are several reasons for this suggestion. First, $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$ is chemically closely related to the interstellar molecule $\text{CH}_2=\text{C}=\text{CH}-\text{CN}$. Second, the existence in the ISM of the $\text{H}(\text{C}\equiv\text{C})_n-\text{CN}$ and $\text{CH}_3(\text{C}\equiv\text{C})_n-\text{CN}$ series referred to above indicates that replacement of a hydrogen atom attached to an unsaturated carbon atom with a methyl group may occur not only for the cyanoacetylene series, but perhaps for cyanoallenes as well.

Moreover, a very interesting property of 4-methylcyanoallene is its chirality, the fact that this compound exists in two non-superimposable mirror-image forms (see Fig. 1). Most of the amino acids and sugars that are considered as the building blocks of life on the Earth are chiral and only one enantiomer is present in the known living systems. To date, the only detected extraterrestrial chiral compounds came from

[★] Full Tables 3 and 4 are only available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via <http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/564/A82>

Fig. 1. Models of the two mirror-image (enantiomers) forms of 4-methylcyanoallene where the blue atom is a nitrogen atom. The two forms have identical rotational spectra and spectroscopic constants.

meteorites after an aqueous acidic treatment to extract the organic compounds. Therefore, some amino acids with an enantiomeric excess have been found (Pizzarello & Groy 2011). In the ISM neither branched nor chiral compounds have been detected. Even if it is not possible to distinguish between different enantiomers in astronomical radio spectra, the detection of chiral compounds in the ISM will be helpful to understand the origin of the chiral species encountered in meteorites and to demonstrate that more complex compounds than those observed to date are present in the ISM. Many microwave spectra of chiral compounds have been assigned. Searches for two of them, propylene oxide (Cunningham et al. 2007) and aminopropionitrile (Møllendal et al. 2012) were unsuccessful.

The abundance of $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$, a compound consisting of 11 atoms, is not expected to be high in the ISM. Fortunately, its dipole moment is quite large (~ 4.5 D; see below) resulting in relatively intense rotational transitions, which should facilitate its detection using the spectroscopic material presented in this article. The increased sensitive and spectral resolution of radiotelescopes, for example ALMA or the Jansky VLA, may lead to the identification of this molecule in the ISM.

2. Experimental

We purchased from the Aldrich Company the 3-Bromo-1-butyne used in the synthesis without further purification. The synthesis of 4-methylcyanoallene was performed as described in the literature (Brandsma & Verkruijsse 1981) and obtained in 83% yield. The synthesis and nuclear magnetic resonance (NMR) data are given in the Appendix.

The Stark-modulated spectrometer of the University of Oslo that was used in this study has been described elsewhere (Møllendal et al. 2005, 2006). This spectrometer has a resolution of 0.5 MHz and measures the frequency of isolated transition with an accuracy of 0.1 MHz. The spectrometer employs a 50 kHz home-built Stark generator. The microwave radiation is generated using a 1730B Systron Donner frequency synthesizer operating in the 2–26.5 GHz frequency range. Several Millitech frequency multipliers are used to generate radiation in the 26.5–116 GHz spectral interval. The lock-in amplifier is a Perkin Elmer model 5209. Double resonance radio-frequency microwave experiments (RFMWDR), similar to those performed by Wodarczyk and Wilson (Wodarczyk & Wilson 1971), have been employed to unambiguously assign several transitions using the equipment described elsewhere (Leonov et al. 2000). The radio frequency source is a Rohde & Schwarz SML01 signal generator operating in the 9 kHz–1.1 GHz

Table 1. Spectroscopic constants¹ of $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$.

Parameter	Experimental values (ROTFIT program)		Theoretical values
	Ground	First ex. bending	CCSD
A (MHz)	12732.907(15)	12765.402(55)	12811.3
B (MHz)	1576.05831(83)	1581.9800(14)	1569.9
C (MHz)	1488.96638(81)	1492.0504(13)	1485.3
D_J (kHz)	0.586265(10)	0.596914(37)	0.502
D_{JK} (kHz)	−22.93721(33)	−22.7018(12)	−21.36
D_K (kHz)	327.05(85)	338.2(47)	340.6
d_1 (kHz)	−0.1050828(96)	−0.105874(59)	−0.0887
d_2 (kHz)	−0.0033843(32)	−0.003614(37)	−0.00256
H_J (Hz)	0.002362(40)	0.002362	0.00079
H_{JK} (Hz)	−0.037678(16)	−0.037678	−0.038
H_{KJ} (Hz)	−1.0664(26)	−0.6914(69)	−0.017
rms	1.36	1.43	
N	654	379	

Notes. ⁽¹⁾ The spectroscopic constants are in the Watson S -reduction I representation form. The uncertainties represent one standard deviation. Additional sextic constants are initially set equal to zero in the least-squares fit. rms is the root-mean-square deviation defined by $\text{rms}^2 = \sum[(\nu_{\text{obs}} - \nu_{\text{calc}})/u]^2 / (N - P)$, where ν_{obs} and ν_{calc} are the observed and calculated frequencies, u the uncertainty of the observed frequency, N the number of transitions used in the least-squares fit, and P the number of spectroscopic constants used in the fit.

spectral region. An EIN Model 503L amplifier provides 3 W linear amplification of the radio signals between 2 and 510 MHz. Mixing of the radio signal with the Stark modulation signal is provided using a Hewlett-Packard 10 514 mixer. The pressure in the spectrometer cell was approximately 10 Pa during measurements. The temperature was maintained at -30°C by cooling the 2 m Hewlett-Packard absorption cell with small portions of dry ice when recording the spectrum in order to enhance spectral intensities.

3. Microwave spectrum and assignment

Quantum-chemical calculations were performed to obtain estimates of useful spectroscopic parameters employing the Gaussian09 program package (Frisch et al. 2009) running on the Abel Linux cluster at the University of Oslo. Becke’s three-parameter hybrid functional (Becke 1988) employing the Lee, Yang, and Parr correlation functional (B3LYP; Lee et al.) was used in the density functional theory calculations (DFT) to calculate rotational constants and Watson’s S -reduction quartic and sextic centrifugal distortion constants (Watson 1977) observing the precautions of McKean et al (McKean et al. 2008). Very high level ab initio coupled-cluster calculations with singlet and doublet excitations (CCSD; Purvis & Bartlett, Scuseria et al. 1988) were also undertaken to calculate the structure, rotational constants, and dipole moment components along the principal inertial axes. Peterson and Dunning’s correlation consistent cc-pVTZ basis set was used in the calculations (Peterson & Dunning 2002).

The CCSD rotational constants of $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CN}$ (Table 1) show that this compound is close to the prolate rotor limit, with Ray’s asymmetry parameter $\kappa \approx -0.986$ (Ray 1932). The major dipole moment component is found along the a -axis (~ 4.36 D), whereas $\mu_b \sim 1.57$ and $\mu_c \sim 0.39$ D.

The survey spectrum revealed the expected pattern of strong pile-ups of a -type R -branch transitions separated by almost

Fig. 2. A portion of the $J = 35 \leftarrow 34$ ground vibrational state aR -transitions of the rotational spectrum of CH₃CH=C=CH-CN taken at a Stark field of 50 V/cm. The intensity (y -axis) is in arbitrary units. The transitions have positive amplitudes, whereas the Stark lobes have negative amplitudes. The numbers above the assigned peaks refer to the K_{-1} pseudo quantum number. The unlabeled and most intense line to the extreme left consists of the unresolved $K_{-1} = 6$ and 8 transitions. The line corresponding to $K_{-1} = 17$ is overlapped by an excited state transition as well as by Stark lobes. The minor lines presumably belong to vibrationally excited states. Stark lobes interfere with the other lines to a very minor degree, but are not completely absent.

exactly the sum of the B and C rotational constants. These pile-ups generally have a complicated and crowded fine structure due to the presence of a number of vibrationally excited states, and to a more or less resolved K_{-1} fine structure. Overlapping transitions therefore occur frequently. A portion of the $J = 35 \leftarrow 34$ transitions illustrating this complexity is shown in Fig. 2. The most intense lines here belong to the ground vibrational state, while the smaller lines belong to vibrationally excited states. Most of the prominent vibrationally excited states are found at higher frequencies (not shown in this figure).

The aR -transitions of the ground state were readily assigned. Several of these assignments were confirmed by RFMWDR experiments. The Stark-modulation properties of the transitions were also useful in this respect. The b -type lines are significantly weaker than the a -type transitions and they were assigned by a trial and error procedure. No c -type transitions were unambiguously identified, presumably because they are too weak, which is consistent with a small μ_c (see above). No resolved hyperfine structures caused by ^{14}N nuclear quadrupole interaction or tunneling of the methyl group were seen.

Sørensen's program ROTFIT (Sørensen 1967) was used for a weighted least-squares fit of the assigned lines employing Watson's S -reduction and I' -representation Hamiltonian (Watson 1977). Sharp and well-isolated aR -transitions with normal Lorentzian shapes and not significantly perturbed by Stark lobes of neighboring lines or overlapped by vibrationally excited-state transitions were assigned an uncertainty of ± 0.10 MHz. Weaker lines in the same category were included in the fit, but larger uncertainties were assigned to them. The b -type transitions were generally weaker than the a -type lines and weights of at least ± 0.15 MHz were used for them. Because overlapping of transitions occurs frequently, only well-isolated lines were included in the fit. Ultimately, a total of 654 aR , bQ , and bR -branch transitions with values of J between 5 and 52 and

Table 2. Predictions of spectral properties of the strongest transitions of CH₃CH=C=CH-CN above 40 GHz at 10 K.

Transition						Rest freq. (MHz)	Δ (MHz)	Intensity	Upper level (K)
12	1	11	13	1	12	40357.866	0.014	2.200	14.10
13	1	13	14	1	14	42243.284	0.014	2.214	15.75
13	0	13	14	0	14	42680.558	0.014	2.354	15.40
13	2	12	14	2	13	42869.735	0.014	1.871	17.58
13	3	11	14	3	12	42935.875	0.014	1.396	20.28
13	3	10	14	3	11	42943.878	0.014	1.396	20.28
13	2	11	14	2	12	43092.914	0.014	1.884	17.63
13	1	12	14	1	13	43452.260	0.014	2.249	16.18
14	1	14	15	1	15	45252.011	0.014	2.208	17.92
14	0	14	15	0	15	45695.250	0.014	2.339	17.59
14	2	13	15	2	14	45924.776	0.014	1.865	19.79
14	3	12	15	3	13	46004.945	0.014	1.396	22.49
14	3	11	15	3	12	46016.258	0.014	1.396	22.49
14	2	12	15	2	13	46196.725	0.014	1.878	19.84
14	1	13	15	1	14	46544.239	0.014	2.230	18.42
15	1	15	16	1	16	48259.163	0.014	2.142	20.24
15	0	15	16	0	16	48704.090	0.014	2.260	19.93
15	2	14	16	2	15	48978.368	0.014	1.806	22.14
15	3	13	16	3	14	49074.266	0.014	1.356	24.85
15	3	12	16	3	13	49089.889	0.014	1.356	24.85
15	2	13	16	2	14	49304.693	0.014	1.819	22.21
15	1	14	16	1	15	49633.565	0.014	2.149	20.80
16	1	16	17	1	17	51264.700	0.014	2.024	22.70
16	0	16	17	0	17	51707.173	0.014	2.128	22.41
16	2	15	17	2	16	52030.421	0.014	1.703	24.63
16	3	14	17	3	15	52143.792	0.014	1.281	27.35
16	3	13	17	3	14	52164.929	0.014	1.282	27.35
16	2	14	17	2	15	52416.607	0.014	1.715	24.73
16	1	15	17	1	16	52719.991	0.014	2.016	23.33
17	1	17	18	1	18	54268.595	0.014	1.866	25.30
17	0	17	18	0	18	54704.694	0.014	1.954	25.03
17	2	16	18	2	17	55080.849	0.014	1.566	27.28
17	3	15	18	3	16	55213.464	0.013	1.180	30.00
17	3	14	18	3	15	55241.547	0.013	1.181	30.00
17	2	15	18	2	16	55532.152	0.014	1.576	27.40
17	1	16	18	1	17	55803.256	0.014	1.845	26.01
18	1	18	19	1	19	57270.829	0.014	1.679	28.05
18	0	18	19	0	19	57696.950	0.014	1.752	27.80
18	2	17	19	2	18	58129.566	0.013	1.405	30.07
18	3	16	19	3	17	58283.215	0.013	1.061	32.80
18	3	15	19	3	16	58319.922	0.013	1.061	32.80
18	2	16	19	2	17	58650.912	0.014	1.413	30.21
18	1	17	19	1	18	58883.090	0.014	1.647	28.83
19	1	19	20	1	20	60271.393	0.014	1.477	30.94
19	0	19	20	0	20	60684.321	0.014	1.536	30.71
19	2	18	20	2	19	61176.488	0.013	1.232	33.00
19	2	17	20	2	18	61772.385	0.014	1.237	33.17
19	1	18	20	1	19	61959.209	0.014	1.438	31.81
20	1	20	21	1	21	63270.290	0.014	1.272	33.98
20	0	20	21	0	21	63667.259	0.014	1.318	33.77
20	2	18	21	2	19	64895.993	0.014	1.059	36.28
20	1	19	21	1	20	65031.322	0.014	1.227	34.93
21	1	21	22	1	22	66267.528	0.014	1.071	37.16
21	0	21	22	0	22	66646.263	0.014	1.107	36.97

Notes. The J , K_{-1} and K_{+1} quantum numbers of the lower energy levels are given in the first three columns. The corresponding quantum number of the upper energy levels are given in the next three columns. The calculated rest frequencies are given in Col. 7 and their predicted uncertainties (one standard deviation) are given in Col. 8. The integrated intensities in units of 10^{-16} cm² MHz per molecule are given in Col. 9 and the energies of the upper energy levels are given in Col. 10.

Table 3. Rotational spectrum of CH₃CH=C=CH-CN in the ground vibrational state.

Watson <i>S</i> -reduction												
Total number of transitions: 654												
Transition						Obs. frequency	Obs. - calc.	Weight	<i>t</i>	Distortion corrections		Upper energy
										total	higher	
5	0	5	6	0	6	18 371.950	0.057	0.15	0.2	-0.497	1.1E-04	6.432897E+04
5	1	5	6	1	6	18 124.680	-0.042	0.15	-0.2	-0.139	6.6E-05	7.464370E+04
6	1	5	6	2	4	32 724.730	0.450	0.20	1.4	-1.852	-8.7E-04	1.091964E+05
6	0	6	7	1	7	31 458.240	0.049	0.15	0.2	0.474	6.2E-05	9.578716E+04
6	0	6	7	0	7	21 426.330	0.326	0.20	1.0	-0.783	2.4E-04	8.575497E+04
6	1	5	7	1	6	21 752.800	0.212	0.10	1.3	-0.623	1.7E-04	9.822469E+04
7	0	7	8	0	8	24 476.900	0.379	0.20	1.2	-1.158	4.6E-04	1.102315E+05
7	1	7	8	1	8	24 161.250	-0.043	0.10	-0.3	-0.610	3.7E-04	1.199485E+05
7	1	6	8	1	7	24 857.380	0.247	0.15	1.0	-1.040	3.7E-04	1.230818E+05
7	2	5	8	2	6	24 556.600	-0.129	0.10	-0.8	0.221	-1.1E-04	1.552332E+05
8	1	7	8	2	6	32 151.420	0.069	0.15	0.3	0.487	-1.7E-03	1.552332E+05
8	0	8	9	0	9	27 523.020	0.046	0.10	0.3	-1.630	8.3E-04	1.377545E+05
8	1	8	9	1	9	27 178.010	-0.082	0.10	-0.5	-0.974	7.1E-04	1.471265E+05
8	1	7	9	1	8	27 960.810	0.356	0.15	1.5	-1.585	7.1E-04	1.510423E+05
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Notes. The full version of Table 3 is online at CDS.

Table 4. Rotational spectrum of CH₃CH=C=CH-CN in the lowest vibrationally excited state.

Watson <i>S</i> -reduction												
Total number of transitions: 379												
Transition						Obs. frequency	Obs. - calc.	Weight	<i>t</i>	Distortion corrections		Upper energy
										total	higher	
5	0	5	6	0	6	18 424.96	0.169	0.20	0.5	-0.506	1.100E-04	1.10E-04
5	1	5	6	1	6	18 170.15	0.172	0.15	0.7	-0.151	7.000E-05	7.90E-05
6	1	6	6	2	5	34 631.09	0.099	0.20	0.4	-2.396	-6.300E-04	-2.00E-04
6	1	6	7	1	7	21 196.25	0.106	0.15	0.4	-0.352	1.800E-04	1.90E-04
7	1	6	7	2	5	32 500.13	-0.160	0.20	-0.5	-0.980	-9.300E-04	-3.50E-04
7	2	6	7	3	5	56 145.40	0.340	0.20	1.2	-15.649	-3.100E-03	-5.90E-04
7	0	7	8	0	8	24 546.21	0.357	0.15	1.4	-1.178	4.600E-04	4.70E-04
7	1	7	8	1	8	24 221.28	-0.060	0.15	-0.2	-0.634	3.800E-04	3.90E-04
7	2	5	8	2	6	24 630.65	-0.384	0.20	-1.1	0.182	-1.700E-05	1.60E-04
8	1	8	8	2	7	35 313.92	0.062	0.22	0.2	-0.711	-1.300E-03	-5.90E-04
8	1	7	8	2	6	32 191.46	-0.030	0.20	-0.1	0.269	-1.300E-03	-5.80E-04
8	0	8	9	0	9	27 600.00	-0.164	0.20	-0.5	-1.658	8.400E-04	8.40E-04
8	1	8	9	1	9	27 245.57	0.121	0.15	0.5	-1.007	7.200E-04	7.30E-04
8	1	7	9	1	8	28 053.68	0.416	0.15	1.6	-1.622	7.200E-04	7.30E-04
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Notes. The full version of Table 4 is online at CDS.

K_{-1} between 0 and 29 of the ground vibrational state were used in the fit. These transitions together with the frequencies of the upper states are listed in Table 3.

The inverse squares of the uncertainties were used as weights in the least-squares fit. It was possible to obtain significant values for the five quartic and three of the seven sextic Watson constants, H_J , H_{JK} , and H_{KJ} , as shown in Table 1. The values of the remaining sextic constants, H_K , h_1 , h_2 , and h_3 , were preset at zero in the least-squares fit.

It can be seen from Table 1 that the experimental and CCSD rotational constants agree to better than 0.7%, which is very satisfactory given the different definitions of the two sets of constants. The experimental constants are effective constants, while the CCSD constants have been calculated from an approximate equilibrium structure. The B3LYP quartic centrifugal distortion constants deviate by as much as 24% (d_K), while no

comparison is warranted for the sextic constants because of their inaccuracy.

The spectrum of the first excited state of the lowest bending vibration was assigned in the same manner as described for the ground vibrational state (see Table 4). The spectroscopic constants obtained from 342 transitions are included in Table 1. The H_{JK} , and H_{KJ} centrifugal distortion constants were kept at their ground-state values in the least squares fit in this case. Relative intensity measurements yielded 107(25) cm⁻¹ for this vibration, compared to 97 cm⁻¹ (not given in Table 1) obtained for the anharmonic frequency in the B3LYP calculations. The rotational energies of the upper states are not given in this table, because they are very small compared to the vibrational energy (107(25) cm⁻¹ above the ground-state energy). The intensities of rotational transitions of this excited vibrational state are therefore very dependent on this vibrational frequency.

The spectroscopic parameters obtained in the present work should be able to predict very accurately the rest frequencies with associated intensities that can be used for a potential identification of CH₃CH=C=CHCN, as the following example will demonstrate. The cold TMC-1 cloud with a temperature of roughly 10 K should be a potential source for this compound. The ALMA observatory will ultimately operate in the 40–959 GHz spectral region (ALMA Sciences 2013; Di Francesco et al. 2013) and we have therefore calculated the rest frequencies of the 54 transitions that have the largest integrated intensities (Townes & Schawlow 1955) in this spectral interval at 10 K. All these transitions, which are listed in Table 2, are *a*-type *R*-branch transitions with the quantum number *J* between 12 and 22, and with *K*_{−1} equal to or less than 3. They are predicted to have uncertainties (one standard deviation) no larger than ±0.014 MHz. It can be seen from this table that all the strongest transitions occur below 67 GHz, which is due to the low temperature which produces unfavorable Boltzmann factors for energy levels with even higher *J* and *K*_{−1}.

4. Conclusion

The rotational spectra of the ground and of the first excited vibrational state of the lowest bending vibration of the chiral compound CH₃CH=C=CH-CN have been investigated in the 13–166 GHz spectral region. We have assigned 654 transitions of the ground state and 379 transitions of the first excited state of the lowest bending vibration. The dipole moment has been calculated at the high CCSD/pVTZ level of theory. The spectroscopic constants obtained from the least-squares fit of these transitions should be able to predict very accurately the rest frequency of transitions not appearing in the investigated spectral range. The accurate rest frequencies of the 54 strongest transitions at 10 K and which are within the range of the ALMA Band 1 project and/or with the Jansky VLA (Di Francesco et al. 2013), are listed in Table 2. It is hoped that the present spectral analysis of CH₃CH=C=CH-CN will facilitate its detection in the ISM, provided it is present in a suitable concentration.

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Appendix A: Details of the synthesis and NMR spectrum of 4-methylcyanoallene (CH₃CH=C=CH-CN)

Ethanol (5 mL), water (0.3 mL), finely powdered cuprous cyanide (0.30 g, 3.35 mmol) and 3-bromo-1-butyne (1.33 g, 10 mmol) were placed in a two-necked flask, equipped with a nitrogen inlet and a stirring bar. The mixture was warmed to 55 °C and a solution of potassium cyanide (0.65 g, 10 mmol) in water (2 mL) was added drop-wise. The temperature of the mixture was maintained close to 60 °C throughout the period of addition and then the mixture was heated to 70 °C under vigorous stirring for 30 min. After cooling to 20 °C, 10 mL of ice-water was added and the organic product

was extracted seven times with diethyl ether (7 × 10 mL). The organic phase was washed twice with saturated ammonium chloride solution, dried over magnesium sulfate and most of the diethyl ether was removed by distillation at atmospheric pressure. The 4-methylcyanoallene was purified on a vacuum line (0.1 mbar) by selective condensation in a trap immersed in a bath cooled at −50 °C. Yield: 0.66 g (8.34 mmol), 83%. ¹H NMR (CDCl₃, 400 MHz) δ 1.68 (dd, 3H, ³*J*_{HH} = 7.5 Hz, ⁵*J*_{HH} = 3.3 Hz, CH₃); 5.11 (dq, ⁴*J*_{HH} = 6.6 Hz, ⁵*J*_{HH} = 3.3 Hz, CHCN); 5.61 (qd, ³*J*_{HH} = 7.5 Hz, ⁴*J*_{HH} = 6.6 Hz, CHMe). ¹³C NMR (CDCl₃, 100 MHz) δ 12.3 (¹*J*_{CH} = 131.0 Hz (q), CH₃); 66.4 (¹*J*_{CH} = 185.8 Hz (d), HC-CN); 91.7 (¹*J*_{CH} = 165.1 Hz (d), C-Me); 113.5 (s, CN); 215.7 (s, C=C=C). The compound 4-methylcyanoallene is a colorless liquid with a vapor pressure about 100 Pa at room temperature.

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