Rotational spectroscopy of singly ^{13}C substituted isotopomers of propyne and determination of a semi-empirical equilibrium structure

Holger S.P. Müller[a,*], Sven Thorwirth[a], Frank Lewen[a]

[a] *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*

Abstract

Submillimeter spectra of three isotopomers of propyne containing one ^{13}C atom were recorded in natural isotopic composition in the region of 426 GHz to 785 GHz. Additional measurements were carried out near 110 GHz. Combining these with earlier data resulted in greatly improved spectroscopic parameters which permit reliable extrapolations up to about 1.5 THz. Coupled cluster quantum-chemical calculations were carried out in order to assess the differences between equilibrium and ground state rotational parameters of these and many other isotopic species to evaluate semi-empirical equilibrium structural parameters. In addition, we estimated the main spectroscopic parameters of the isotopomers of propyne with two ^{13}C atoms, which have not yet been studied in the laboratory, but which may be detectable in astronomical sources with a large amount of ^{13}C compared to the dominant ^{12}C.

Keywords:
rotational spectroscopy, interstellar molecule, propyne, symmetric top molecule, quantum-chemical calculation, structural parameters

1. Introduction

The detection of propyne, CH_3CCH, which is also known as methylacetylene, in the interstellar medium (ISM) was reported in 1973 [1], making it one of the molecules discovered early by radio astronomical means. The observations were made toward Sagittarius (Sgr) B2, one of the most massive star-forming regions in our Galaxy and located close to its center [2]. Even early observations of propyne, e.g. [3], were employed to infer temperature and density in this source. Symmetric top rotor molecules, such as propyne, are particularly suited to derive temperature conditions in the ISM because transitions with the same J and different K quantum numbers occur in a narrow frequency range, but sample a large range of energies. Methyl cyanide, CH_3CN, is another example of a molecule frequently used for this purpose [4, 5]. Temperatures of other star-forming regions were determined via early propyne observations, such as Orion and DR 21 [6], and of many other sources, including the cold and dense star-less core TMC-1 [7, 8]. The molecule was also detected in near-by galaxies, such as M82 and NGC253 [9], in more distant galaxies, such as the foreground galaxy at $z \approx 0.89$ in the direction of the quasar PKS 1810−211 [10], in translucent molecular clouds [11], and in the envelopes of late-type stars, such as the protoplanetary nebular CRL618 [12], the asymptotic giant branch star CW Leonis [13] and the planetary nebula K4−47 [14]. Infrared observations with Voyager led to the detection of CH_3CCH in the atmosphere of Titan [15]; the ISO satellite was employed later to discover propyne in the atmospheres of Saturn [16], Jupiter [17], and Uranus [18]. More recently, propyne was also observed in the atmosphere of Titan with the Atacama Large Millimeter/submillimeter Array (ALMA) [19].

Propyne is so abundant in some astronomical sources that minor isotopic species were discovered as well. Even though $CH_3C^{13}CH$ was found serendipitously [20], all isotopomers containing one ^{13}C were observed later [14, 21, 22]. The deuterated isotopologs CH_2DCCH [23] and CH_3CCD [24] were also detected. There is even evidence that $^{13}CH_2DCCH$ was seen [22].

Observations of molecules containing ^{13}C are important diagnostic tools because the ^{12}C/^{13}C ratio in space differs considerably from the terrestrial value of 89 [25]. It is as low as about 20 to 25 in the Galactic center region [21, 26, 27, 28], increases to about 68 in the Solar neighborhood and even further in the outskirts of the Milky Way [21, 29, 30]. Much lower ^{12}C/^{13}C ratios than 20 were found in the envelopes of some late-type stars, for example ∼10 for CRL618 [12, 31], ∼4 for CK Vulpécula [32], and ∼2 for K4−47 [14, 33].

A recent observational study of the protostellar binary IRAS 16293−2422 with ALMA [34] found only evidence for propyne in the hot corinos, the warmer and denser parts of the molecular clouds surrounding the protostars. The rotational temperatures of ∼100 K appear to be typical for propyne and several other molecules in such environments. Comparison with single dish observations, however, suggest that about half of the propyne must occur on larger scales in these molecular clouds such that interferometric observations (here with ALMA) filter out this part of propyne. Concurrent astrochemical modeling results suggest that both grain as well as gas phase chemistry

*Corresponding author.
Email address: hspm@ph1.uni-koeln.de (Holger S.P. Müller)

needs to be invoked to explain the levels of propyne observed in that study [34].

It is necessary to know rest frequencies of a certain molecule with sufficient accuracy to be able to identify it in space. Such rest frequencies are usually based on laboratory spectroscopic investigations and are frequently provided in databases such as the Cologne Database for Molecular Spectroscopy, CDMS[1] [35]. Recent investigations of ^{13}C-containing isotopologs of molecules detected in space include for example dimethyl ether with one and two ^{13}C [36], the acetaldehyde isotopomers with one ^{13}C [37], $^{13}CH_3NH_2$ [38], isotopic acetone with emphasis on $CH_3{}^{13}C(O)CH_3$ [39], isotopic c-C_3H_2 with several doubly substituted species [40], and isotopic methyl cyanide in the $v_8 = 1$ excited state [41].

The rotational spectrum of propyne was reported as early as 1950. Trambarulo and Gordy recorded the spectra of several isotopic species up to 52 GHz and determined a ground state effective (r_0) structure [42]. Thomas et al. revisited the r_0 structure on the basis of additional isotopologs and additional measurements for some of the earlier studied isotopologs [43]. The latest investigation into the experimental structural parameters of propyne was carried out by Le Guennec et al. [44]. They employed isotopically enriched samples of CH_2DCCH and CH_3CCD to record not only extensive spectra of these two isotopic variants, but also of the respective isotopomers with one ^{13}C between 144 and 471 GHz.

Dubrulle et al. extended the measurements of CH_3CCH and its isotopomers with one ^{13}C to 240 GHz [45]. Further investigations of the main isotopic species reached quantum numbers of $K = 21$ and $J' = 70$ at frequencies up to 1.2 THz [46, 47, 48]. Furthermore, the rotational spectroscopy of CH_3CCH in low-lying excited vibrational states was decisive to untangle rotation-vibration interactions between different polyads of propyne, e.g., between the lowest excited state $v_{10} = 1$ on one hand and $v_{10} = 2$ and $v_9 = 1$ on the other [47, 49, 50]. Similar interactions were analyzed for CH_3NC [51] and for CH_3CN [52]. The dipole moments [53, 54], molecular g values [55], hyperfine structure parameters [56] and other properties of differently deuterated isotopic species of propyne were also studied.

The strongest transitions of propyne at $T = 100$ K occur around 325 GHz, but the lines are still quite strong above 500 GHz. The transition frequencies of propyne isotopomers with one ^{13}C become increasingly uncertain at such frequencies because earlier measurements only reached ~240 GHz [42, 45]. Therefore, we have extended the measurements of these isotopic species up to 785 GHz. The resulting spectroscopic parameters permit reasonable extrapolation to about 1.5 THz, which is probably beyond the needs of radio astronomers. In addition, we carried out quantum-chemical calculations to determine semi-empirical structural parameters and spectroscopic parameters of propyne isotopomers with two ^{13}C, which have not yet been studied in the laboratory.

[1] See https://cdms.astro.uni-koeln.de/.

2. Experimental details

The rotational spectra were recorded at room temperature in static mode employing Pyrex glass cells ~4 m in length and with an inner diameter of 100 mm. A commercial sample of propyne was used in natural isotopic composition and at pressures of mostly 1 Pa, raised up to 4 Pa for weaker transitions in the submillimeter region. The window material was Teflon at lower frequencies, whereas high-density polyethylene was used at higher frequencies. Frequency modulation was used throughout with demodulation at $2f$, causing an isolated line to appear close to a second derivative of a Gaussian.

Measurements between 426 and 785 GHz were carried out with the Cologne Terahertz Spectrometer [57] employing three different phase-locked backward wave oscillators (BWOs) as sources and a liquid helium cooled InSb hot-electron bolometer (QMC) as detector. Accuracies of 10 kHz and better can be achieved for isolated lines with good signal-to-noise ratio and very symmetric line shape, e.g., [58]. Additional recordings near 100 GHz were performed with a BWO based 3 mm synthesizer AM-MSP 2 (Analytik & Meßtechnik GmbH, Chemnitz, Germany) as source and a Schottky-diode as detector. Uncertainties as low as 1 kHz can be reached with this setup under favorable conditions [59]. Only indivial lines were recorded in most instances.

3. Quantum-chemical calculations

Coupled cluster calculations with singles and doubles excitations augmented by a perturbative correction for triple excitations, CCSD(T) [60] were carried out with the CFOUR suite of programs [61, 62]. The correlation consistent basis sets cc-pVXZ (X = T, Q), abbreviated XZ, were used for frozen core calculations [63], and weighted core-valence basis sets were employed for calculation correlating all electrons (ae), these are the cc-pwCVXZ (X = T, Q, 5) basis sets, abbreviated wCXZ [64]. All calculations were carried out at the Regionales Rechenzentrum der Universität zu Köln (RRZK).

Equilibrium geometries were determined by analytic gradient techniques, harmonic force fields by analytic second derivatives, and anharmonic force fields by numerical differentiation of the analytically evaluated second derivatives of the energy. The main goal of these anharmonic force field calculations was to evaluate first order vibration-rotation parameters [65], see also Sect. 5. Core electrons were kept frozen unless "ae" indicates that all electrons were correlated.

4. Observed spectra and determination of spectroscopic parameters

The $J = 7 - 6$ transitions of $CH_3C^{13}CH$ and $^{13}CH_3CCH$ were recorded near 116 GHz. The corresponding transitions of $CH_3^{13}CCH$ occur above the upper limit of the instrument at 118.2 GHz, and so the $J = 6 - 5$ transitions were measured instead for this isotopolog. For transitions with $0 \le K \le 3$, these transitions had been reported before [45], albeit with larger uncertainties of about 40 kHz, which were between 3 and 10 kHz

Table 1: Ground state spectroscopic parameters[a] (MHz) of propyne isotopologs and of methyl cyanide.

Parameter	$CH_3C^{13}CH$	$CH_3^{13}CCH$	$^{13}CH_3CCH$	CH_3CCH[b]	CH_3CN[c]
$(A-B)$	150850.15	150598.07	150827.15	150594.52 (46)	148900.103 (66)
B	8290.246538 (71)	8542.322556 (72)	8313.248883 (49)	8545.876998 (6)	9198.899167 (11)
$D_K \times 10^3$	2916.	2916.	2916.	2915.6 (122)	2830.6 (18)
$D_{JK} \times 10^3$	155.49161 (282)	162.78978 (218)	155.21707 (197)	163.41706 (20)	177.40787 (25)
$D_J \times 10^6$	2754.725 (23)	2940.771 (43)	2809.959 (20)	2939.320 (4)	3807.576 (8)
$H_K \times 10^6$	180.	180.	180.	180.	164.6 (66)
$H_{KJ} \times 10^6$	4.9825 (202)	5.2404 (126)	5.0202 (194)	5.2990 (17)	6.0620 (14)
$H_{JK} \times 10^9$	849.74 (70)	911.42 (111)	832.13 (78)	915.69 (13)	1 025.69 (15)
$H_J \times 10^{12}$	−46.7	−51.2	−47.1	−51.2 (9)	−237.4 (21)
$L_{KKJ} \times 10^{12}$	−360.	−379.	−363.	−385.3 (50)	−444.3 (25)
$L_{JK} \times 10^{12}$	−40.1	−43.0	−41.1	−43.44 (47)	−52.75 (51)
$L_{JJK} \times 10^{12}$	−6.07	−6.65	−6.12	−6.648 (51)	−7.901 (32)
$L_J \times 10^{15}$					−3.10 (17)
$P_{JK} \times 10^{15}$					0.552 (68)
$P_{JJK} \times 10^{18}$	27.	30.	27.	30.4 (55)	55.3 (22)

[a] Numbers in parentheses are one standard deviation in units of the least significant figures. Parameters without quoted uncertainties have been estimated from the main isotopic species and were kept fixed in the fits; see section 4.
[b] The CH_3CCH parameters are also from this work; the value of H_K was estimated from the CH_3CN value, the remaining values were obtained from a fit of previous data [46, 47, 48]; see also section 4.
[c] Ref. [52].

in the present study. The quantum numbers of recorded transitions were also very similar for $CH_3C^{13}CH$ and $^{13}CH_3CCH$ in the submillimeter region and covered sufficiently strong transitions with $J = 26-25$, $35-34$, $45-44$, and $46-45$ between about 430 GHz and 763 GHz. The quantum numbers differed again somewhat for $CH_3^{13}CCH$; the transitions occured in sections between 426 and 785 GHz. The K quantum numbers reached between 12 and 14, and the uncertainties were between 3 and 10 kHz for very good lines, up to 100 kHz for weaker or less symmetric lines. The experimental data employed in the fits are provided as supplementary material with quantum numbers, uncertainties and residuals between observed frequencies and those calculated from the final set of spectroscopic parameters.

Pickett's versatile programs SPFIT and SPCAT [66] were utilized for fitting and prediction of the rotational spectra. The purely axial parameters A (or $A-B$), D_K, H_K, etc. of a prolate symmetric top can usually not be determined directly by rotational or rovibrational spectroscopy. One possibility to obtain these parameters involves $\Delta K = 3$ ground state loops generated from a doubly degenerate fundamental vibration and its combination and hot band associated with another doubly degenerate fundamental. The available data in the case of propyne were sufficient to determine A and D_K significantly [47]. The similarity of the spectroscopic parameters of CH_3CCH with those of CH_3CN, in particular for the purely axial parameters, see Table 1, enabled us to estimate a value for H_K of CH_3CCH. The value of H_K of CH_3CN was scaled by the D_K ratio of CH_3CCH and CH_3CN to the power of three which appeared to reflect better the trends observed in higher order parameters than scaling by that ratio to the power of three half. The remaining parameters were redetermined from earlier data [46, 47, 48], but differ only slightly from those of an earlier combined fit [48].

The purely axial parameters A, D_K, and H_K of the propyne isotopomers with one ^{13}C were fixed to values of the main isotopolog because substitution of an atom on the symmetry axis does not change A_e, and potential changes in D_K and H_K should be very small. Several higher order parameters were scaled to appropriate powers of the isotopic ratios of the B values in a first step. Trends in the small deviations observed for quartic and some sextic distortion parameters were taken into account in a second step. Such empirically scaled parameters are usually much better than fixing these higher order parameters to zero and often also better than fixing the values to those of the main isotopic species, as also shown for isotopic species of methyl cyanide [41]. The relations hold strictly for the Dunham parameters of a diatomic molecule. The empirical scaling is more complex for asymmetric rotors of the prolate type for which appropriate powers of $A-(B+C)/2$, $B+C$ and $B-C$ would be used, see the examples of vinyl cyanide [26] or thioformaldehyde [68]. The resulting spectroscopic parameters of the singly ^{13}C substituted propyne isotopomers are given in Table 1 together with those of CH_3CCH and CH_3CN. The uncertainties of a particular parameter are of the same order of magnitude among the three ^{13}C species, and differences reflect variations in the data sets. As the propyne and methyl cyanide

Table 2: Ground state rotational parameters B_0^i (MHz) of propyne isotopologs, semi-empirical equilibrium rotational parameters B_e^i (MHz) according to two quantum-chemical models, residuals O−C (MHz) between B_e^i and values from the structure calculations, and references[a] Refs. from which the B_0^i were derived.

			CCSD(T)/cc-pVTZ		CCSD(T)/cc-pwCVTZ		
Isotopolog	Axis i	B_0^i	B_e^i	O−C	B_e^i	O−C	Refs.
CH_3CCH	b	8545.877	8573.176	−0.0286	8573.231	−0.0316	TW
$CH_3C^{13}CH$	b	8290.247	8316.680	−0.0197	8316.741	−0.0215	TW
$CH_3^{13}CCH$	b	8542.333	8569.651	0.0099	8569.707	0.0083	TW
$^{13}CH_3CCH$	b	8313.249	8338.960	−0.0248	8339.016	−0.0278	TW
CH_3CCD	b	7788.169	7808.965	−0.0065	7808.999	−0.0070	[44]; [42, 43, 56]
$CH_3C^{13}CD$	b	7592.916	7613.230	0.0021	7613.267	−0.0004	[44]
$CH_3^{13}CCD$	b	7787.026	7807.844	0.0260	7807.879	0.0267	[44]
$^{13}CH_3CCD$	b	7576.800	7596.329	−0.0023	7596.364	−0.0033	[44]
CH_2DCCH	b	8155.686	8180.361	0.0027	8180.412	0.0053	[44]; [43, 67]
	c	8025.476	8053.941	−0.0011	8053.949	−0.0011	
$CH_2DC^{13}CH$	b	7908.447	7932.379	0.0122	7932.435	0.0151	[44]
	c	7785.911	7813.422	0.0079	7813.437	0.0081	
$CH_2D^{13}CCH$	b	8150.513	8175.206	0.0408	8175.258	0.0450	[44]
	c	8020.426	8048.895	0.0327	8048.904	0.0343	
$^{13}CH_2DCCH$	b	7956.786	7980.122	0.0026	7980.174	0.0047	[44]
	c	7832.349	7859.325	−0.0014	7859.335	−0.0025	
CH_2DCCD	b	7440.765	7459.582	0.0041	7459.613	0.0075	[43]
	c	7331.974	7354.098	−0.0056	7354.093	−0.0049	
CHD_2CCH	b	7765.701	7789.873	−0.0264	7789.896	−0.0288	[43]
	c	7630.949	7658.396	−0.0089	7658.383	−0.0056	
CD_3CCH	b	7355.701	7380.982	0.0004	7380.963	−0.0035	[43]; [54, 56]
CHD_2CCD	b	7095.074	7113.693	−0.0152	7113.701	−0.0165	[43]
	c	6982.554	7004.047	−0.0059	7004.026	−0.0018	
CD_3CCD	b	6734.340	6754.068	0.0065	6754.041	0.0030	[43]; [42]

[a] TW stands for this work. The primary source is given for data not from this work. Additional references, as far as applicable, are separated from the primary one by a semi-colon.

molecules are isoelectronic, they share very similar structures. The A rotational parameters are very similar, 159.1 GHz versus 158.1 GHz, and so are the D_K parameters. The structural changes caused by the CH group in propyne versus the N atom in methyl cyanide can account for the slightly larger differences in the B rotational parameters, and the differences increase further with increasing J dependence (increasing power of $J(J+1)$) of a given parameter.

5. Structural parameters of propyne

The equilibrium structure is the best and easiest defined structure of a molecule. It requires to calculate equilibrium rotational parameter(s), for example, B_e from the ground state rotational parameter(s) B_0 as follows

$$B_e = B_0 + \frac{1}{2}\sum_j \alpha_j^B - \frac{1}{4}\sum_{j\leq k} \gamma_{jk}^B - ... \qquad (1)$$

where the α_j^B are first order vibration-rotation interaction parameters, the γ_{jk}^B are second order vibration-rotation interaction parameters, and so on. Doubly degenerate modes occur two times in the sum. Equivalent formulations hold for A_e (and C_e in the case of asymmetric rotor isotopic species). The general n-atomic asymmetric rotor molecule has three different rotational parameters A, B, and C, $3n-6$ first order vibrational corrections, $(3n-6)(3n-5)/2$ second order vibrational corrections, and so on. The situation is slightly better for symmetric top molecules. In addition, data for more than one isotopic species need to be known to determine all independent structural parameters, unless the molecule is a symmetric triatomic of the type AB_2, where atoms A and B may be the same. Complete sets even of first order vibration-rotation parameters for a sufficiently large ensemble of isotopic species are available from experiment only in rare cases. Moreover, these parameters are not identical to the α_j^B because of effects of the γ_{jk}^B etc. and possibly because of vibration-rotation interactions such as Fermi or Coriolis resonances.

An alternative, lately very common, approach is to calculate $\sum_j \alpha_j^B$ by quantum-chemical means to derive semi-empirical equilibrium rotational parameters $B_{i,e}$ from the experimental ground state values [79, 80]. Second and higher order vibrational contributions are neglected. Numerous quantum-chemical programs are available to carry out such calculations.

We evaluated $\sum_j \alpha_j^B$ employing CCSD(T)/TZ and ae-CCSD(T)/wCTZ calculations for all available isotopologs; the corresponding data are summarized in Table 2. The ground state rotational parameters, the vibrational corrections calculated at two different levels, and the resulting semi-empirical equilibrium rotational parameters are available as supplementary material. The rotational parameters obtained in earlier studies were refit in the present study taking into account estimates of (higher order) centrifugal distortion parameters in order to reduce effects from omission or truncation of these parameters. Furthermore, we used the S reduction for all asymmetric rotor isotopologs.

Structural parameter were determined using the program STRFIT [81]. The semi-empirical equilibrium moments of inertia derived from the respective rotational parameters in Table 2 were adjusted. Data pertainting to the a-axis were omitted because of lack of accuracy. The resulting structural parameters $r_e^{\rm SE}$ are given in Table 3 together with values from quantum-chemical calculations and from previous structure determinations. The $r_e^{\rm SE}$ equilibrium structural parameters of propyne are compared with values of related molecules in Table 4.

The CCSD(T)/XZ bond lengths are longer than the ae-CCSD(T)/wCXZ values, and both display the usual bond shortening upon increase in basis set size. The bond angles are quite similar throughout. The ae-CCSD(T)/wC5Z structural parameters are very close to our semi-empirical structures, and both models yield virtually the same values with the exception of the methylenic CH bond, for which the values differ by slightly more than two times the combined uncertainties. The CEPA-1/TZ structural parameters agree quite well with our $r_e^{\rm SE}$ values, except for the CC single bond. CEPA stands for coupled electron pair approximation. It is a quantum-chemical method described in Ref. [69]. The agreement is better after empirical refining of the CC bond lengths. The correction was based on a comparison between CEPA-1/TZ and experimental CC bond lengths of diacetylene [70]. The ground state effective r_0 structure agrees modestly well with our $r_e^{\rm SE}$ values. The agreement improves somewhat for the $r_{I,\epsilon}$ values and more so for the r_m^ρ values. The $r_{I,\epsilon}$ structure model assumes $I_{i,0} - I_{i,e}$ to be isotopic independent for a given axis i; it is equivalent to the substitution structure r_s, as investigated in Ref. [82]. The r_m^ρ structure model assumes a more complex isotopic scaling of these differences, see Ref. [83] for more details.

The CC triple bond in acetylene has a length of 120.29 pm [75, 76]; delocalization of π electrons between the two CC triple bonds and the CC single bond in diacetylene lengthens the triple bonds to 120.85 pm and shortens the single bond considerably to 137.27 pm [74] from 152.2 pm in ethane [78]. Only the methyl group in propyne can be involved in the delocalization of the π electrons of the CC triple bond, which leads to a triple bond length of 120.46 pm, between the acetylene and diacetylene values, and to a single bond length of 145.88 pm, between the diacetylene and the ethane values. The degree of delocalization is larger in vinyl acetylene than in propyne, leading to CC triple and single bond lengths closer to those of diacetylene [73]. The acetylenic CH bond lengths in Table 4 are all very close to 106.15 pm; slightly larger scatter exists for the given methylenic CH bond lengths. The structural parameters of the CH_3C unit in methyl cyanide [71] are quite similar to those of the isoelectronic propyne. In addition, the parameters of the CH_3C unit in pentadiyne [72] and propyne are quite similar also. The CC triple bond lengths of 120.91 ± 0.16 pm and 120.85 ± 0.06 pm and the length of the CC single bond between them (137.34 ± 0.14 pm) are very close to the corresponding diacetylene values, as may be expected.

Table 3: Quantum-chemical and experimental bond lengths (pm) and bond angle (deg) of propyne.[a]

Method[b]	$r(C_mH)$	r(C−C)	∠(HCC)	r(C≡C)	$r(C_aH)$
CCSD(T)/TZ	109.087	146.653	110.577	121.114	106.276
CCSD(T)/QZ	108.979	146.366	110.580	120.810	106.290
ae-CCSD(T)/wCTZ	108.908	146.242	110.602	120.706	106.244
ae-CCSD(T)/wCQZ	108.824	146.003	110.611	120.504	106.156
ae-CCSD(T)/wC5Z	108.790	145.935	110.602	120.450	106.128
CEPA-1/TZ[c]	108.77	147.06	110.50	120.65	106.17
dito, refined[d]	108.77	145.84	110.50	120.53	106.17
r_0[e]	109.40 (4)	145.95 (5)	110.6 (2)	120.88 (6)	105.48 (3)
$r_{I,\epsilon}$[e]	109.27 (3)	145.74 (1)	110.8 (1)	120.75 (1)	105.62 (1)
r_m^{ρ}[e]	108.85 (5)	145.52 (5)	111.12 (6)	120.37 (6)	105.89 (3)
r_e^{SE}(CCSD(T))	108.836 (3)	145.884 (6)	110.593 (2)	120.463 (6)	106.141 (3)
r_e^{SE}(ae-CCSD(T))	108.852 (4)	145.884 (6)	110.591 (2)	120.460 (7)	106.146 (3)

[a] All values from this work unless indicated otherwise. Numbers in parentheses are one standard deviation in units of the least significant figures. The methylenic and acetylenic CH bonds are indicated by C_mH and C_aH, respectively.
[b] Quantum-chemical calculations as detailed in Sect. 3.
[c] Coupled electron pair approximation [69], data from Ref. [70].
[d] CEPA-1/TZ, refined; CC bonds corrected empirically [70].
[e] Ref. [44]; see section 5 for explanation on the structure models.

Table 4: Equilibrium bond lengths (pm) and bond angle (deg) of propyne in comparison to values of related molecules.[a]

Molecule	$r(C_mH)$	r(C−C)	∠(HCC)	r(C≡C)	$r(C_aH)$
CH_3CCH[b]	108.852 (4)	145.884 (6)	110.591 (2)	120.460 (7)	106.146 (3)
CH_3CN[c]	108.65 (1)	145.85 (4)	109.84 (1)		
CH_3C_4H[d]	108.90 (24)	145.69 (8)	110.50 (8)	120.85 (6)	106.13 (3)
C_2H_3CCH[e]		142.67		120.72	106.17
HC_4H[f]		137.27		120.85	106.15
HCCH[g]				120.2958 (7)	106.164 (1)
HCCH[h]				120.2817 (12)	106.167 (14)
CH_3F[i]	108.70 (5)				
C_2H_6[j]	108.9 (1)	152.2 (2)	111.2 (1)		

[a] Numbers in parentheses are one standard deviation in units of the least significant figures, unless stated otherwise. The methylenic and acetylenic CH bonds are indicated by C_mH and C_aH, respectively.
[b] This work; r_e^{SE}, ae-CCSD(T)/wCTZ values.
[c] Ref. [71]; r_e^{SE}, ae-CCSD(T)/wCTZ values with 3σ uncertainties.
[d] Ref. [72]; r_e^{SE}, MP2/TZ values with 3σ uncertainties; see also discussion in section 5.
[e] Ref. [73]; r_e^{SE}, CCSD(T)/TZ values with no uncertainties given.
[f] Ref. [74]; r_e^{SE}, ae-CCSD(T)/CQZ values with no uncertainties given.
[g] Ref. [75]; r_e^{SE}, ae-CCSD(T)/wCQZ values.
[h] Ref. [76]; experimental r_e values.
[i] Ref. [77]; experimental r_e value.
[j] Ref. [78]; r_m^{ρ} values according to the second set of data.

Table 5: Predicted main ground state spectroscopic parameters[a] (MHz) of propyne isotopomers with two ^{13}C.

Parameter	$CH_3^{13}C^{13}CH$	$^{13}CH_3C^{13}CH$	$^{13}CH_3^{13}CCH$
B^b	8288.214	8060.023	8308.459
B^c	8288.234	8060.007	8308.472
$D_{JK} \times 10^3$	155.04	147.53	154.50
$D_J \times 10^6$	2755.4	2630.3	2811.7
$H_{KJ} \times 10^6$	4.93	4.72	4.96
$H_{JK} \times 10^9$	849.	911.	832.

[a] See section 6.
[b] Calculated B_e from the semi-empirical CCSD(T)/cc-pwCVTZ structure and vibrational corrections from the CCSD(T)/cc-pwCVTZ calculation.
[c] As above, but also corrected for the residual of the CH_3CCH isotopolog and for the differences between the main isotopolog and the appropriate ^{13}C isotopomers.

6. Spectroscopic parameters for propyne isotopomers with two ^{13}C atoms

We evaluated spectroscopic parameters for propyne isotopomers containing two ^{13}C, because their rotational spectra have not yet been investigated, but they may be detectable in astronomical sources with very high enrichment in ^{13}C compared to the dominant ^{12}C, such as in the envelope of the planetary nebula K4−47 in which the ^{12}C/^{13}C ratio is as low as 2.2 ± 0.8 and in which all isotopomers of propyne with one ^{13}C were already detected [14].

In a first step, the semi-empirical rotational parameter B_e was calculated for each of the three isotopomers from the ae-CCSD(T)/wCTZ semi-empirical structure. The first order vibrational corrections calculated at the same level were subtracted off to yield the first estimate of the ground state rotational parameter of each of the three isotopomers given in the first row of Table 5. The semi-empirical rotational parameters of the various isotopologs of propyne were not fit perfectly well, but have small residuals on the order of a few tens of kilohertz, as can be seen in Table 2. We sought to improve the estimates of the ground state rotational parameters of the three isotopomers with two ^{13}C atoms by correcting each B value with the residual of the main isotopolog and then by the differences in the residuals between the appropriate isotopologs with one ^{13}C and the main species. This yields the B values given in the second row of Table 5.

The quartic centrifugal distortion parameters D_{JK} and D_J as well as the sextic parameters H_{KJ} and H_{JK} were evaluated in a fairly similar way. The quantum-chemically calculated equilibrium quartic centrifugal distortion parameters for isotopomers with one and two ^{13}C atoms were corrected by the ratio of the experimental ground state D and the calculated equilibrium D. This yields good estimates for the experimental ground state D values of the ^{13}C containing isotopologs. The values of the doubly substituted isotopic species were then corrected with the ratios between the experimentally determined D values of the appropriate singly substituted isotopologs and their first order estimates determined in the previous step. These values should be very good estimates of D_{JK} and D_J for the propyne isotopomers with two ^{13}C. The sextic centrifugal distortion parameters H_{KJ} and H_{JK} were evaluated from the experimental values of the main isotopic species by applying the ratios between the appropriate singly substituted species and the main species. The resulting distortion parameters are also given in Table 5.

7. Conclusions

Our measurements of the rotational spectra of propyne isotopomers containing one ^{13}C increased the upper limit of data from ~240 GHz to ~785 GHz, yielding greatly improved spectroscopic parameters which should allow reasonable extrapolation to about 1.5 THz, beyond the current upper limit of ALMA and possibly well beyond the needs of radio astronomers. This estimate is based on observations that in a-type spectra with good data coverage at the upper frequency limit the calculated uncertainties are still meaningful at about two times the upper frequency limit. The calculated uncertainties at 1.5 THz are ~60 kHz or less at low K up to ~200 kHz at $K = 10$. Thus, we expect that actual transition frequencies will be within ~1 MHz of the calculations at this frequency. The line, parameter and fit files are available in the data section[2] of the CDMS[35]; calculations of the rotational spectra are deposited in its catalog section[3]. Quantum-chemical calculations yielded first order vibration-rotation interaction parameters, which were used to derive semi-empirical equilibrium structural parameters of propyne. These parameters are in very good agreement with quantum-chemical calculations at the highest level employed in the present study. Finally, we estimated the main spectroscopic parameters of propyne isotopomers containing two ^{13}C to facilitate their detection in astronomical source with high levels of ^{13}C or to identify them in laboratory measurements.

Acknowledgments

We are grateful for support by the Deutsche Forschungsgemeinschaft via the collaborative research centers SFB 494, subproject E2, and SFB 956 (project ID 184018867), project B3 and via the Gerätezentrum SCHL 341/15-1 ("Cologne Center for Terahertz Spectroscopy"). We thank the Regionales Rechenzentrum der Universität zu Köln (RRZK) for providing computing time on the DFG funded High Performance Computing System CHEOPS. Our research benefited from NASA's Astrophysics Data System (ADS).

Appendix A. Supplementary Material

The following are the Supplementary data to this article: The part of the fit files which contain all experimental data

[2] See: https://cdms.astro.uni-koeln.de/classic/predictions/daten/CH3CCH/
[3] See: https://cdms.astro.uni-koeln.de/classic/entries/

employed in the fits with quantum numbers, uncertainties and residuals between observed frequencies and those calculated from the final sets of spectroscopic parameters. Also included in these files are the spectroscopic parameters with uncertainties and correlation coefficients. A separate file gives the ground state rotational parameters, the vibrational corrections calculated at two different levels, and the resulting semi-empirical equilibrium rotational parameters of all isotopic species used for the structure evaluations.

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