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Lamb-dip spectrum of methylacetylene and methyldiacetylene: precise rotational transition frequencies and parameters of the main isotopic species

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ABSTRACT

Context. Methylacetylene and methyldiacetylene are the first members of the methylpolyynes series, $CH_3C_{2n}H$ (n = 1, 2). Their astrophysical relevance has motivated this spectroscopic study.
Aims. The aim of this investigation is to provide very accurate rest frequencies, as well as to improve the spectroscopic parameters available in the literature for these molecules.
Methods. The Lamb-dip technique was exploited in order to record the rotational spectra of CH_3CCH and CH_3CCCCH at sub-Doppler resolution in the millimeter- and submillimeter-wave frequency ranges. In addition, for CH_3CCH rotational transitions in the THz region were recorded at Doppler resolution.
Results. We report the most accurate ground-state rotational parameters known at the moment for the main isotopic species of methylacetylene, as well as of methyldiacetylene.
Conclusions. Since both molecules are known to be of astrophysical relevance, we are confident that the improvement in the accuracy of the ground-state rotational parameters as well as of the rest frequencies of rotational transitions could be useful for future observations purposes.

Key words. techniques: spectroscopic – molecular data – methods: laboratory – ISM: molecules – radio lines: ISM

1. Introduction

Acetylenic chains, cyanopolyynes, and methylpolyynes are known to be molecules of astrophysical interest as a great deal of them has been detected in the interstellar medium. In particular, symmetric-top molecules are ideal probes for determining the kinetic temperature of the interstellar medium (ISM) because of the K-structure of the rotational transitions, which provides the quite unique opportunity of observing closely spaced lines with different excitation energies (i.e., temperature) simultaneously (Solomon et al. 1971, 1973).

Among methylpolyynes, $CH_3C_{2n}H$ (n = 1, 2, ...), methylacetylene and methyldiacetylene are the first (n = 1) and second (n = 2) members of the series, respectively, and they have been widely observed in the ISM. Concerning the former, its first detection in the ISM was reported by Snyder & Buhl (1973) towards the galactic center source Sgr B2. Moreover, it was observed in extragalactic sources by Mauersberger et al. (1991). Since then, other observations took place (see, for example, Pratap et al. 1997; Agundez et al. 2008). Methyldiacetylene was first observed in the Taurus molecular cloud (TMC-1) in 1984 (MacLeod et al. 1984; Walmsley et al. 1984; Loren et al. 1984). After its first detection, more observations were reported in the literature (see, for example, Cernicharo et al. 2001). Furthermore, the recent detection of interstellar CH_3C_6H toward the TMC-1 cloud (Remijan et al. 2006) deserves to be mentioned.

In response to the need for more precise laboratory rest frequencies and, therefore, to improve the spectroscopic data set available, the ground-state rotational spectrum of methylacetylene was investigated in the submillimeter-wave region by Müller et al. (2002), whereas that of methyldiacetylene was accurately measured in the 8−224 GHz frequency range by Bester et al. (1984). To our knowledge, the latter are the most recent laboratory investigations carried out for the main isotopic species of

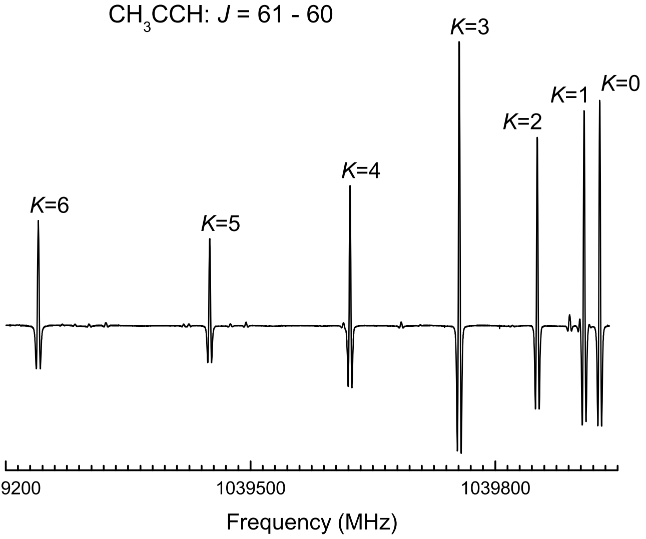

Fig. 1. The K-structure, with K ranging from 0 to 6, of the $J = 61 \leftarrow 60$ transition of CH_3CCH.

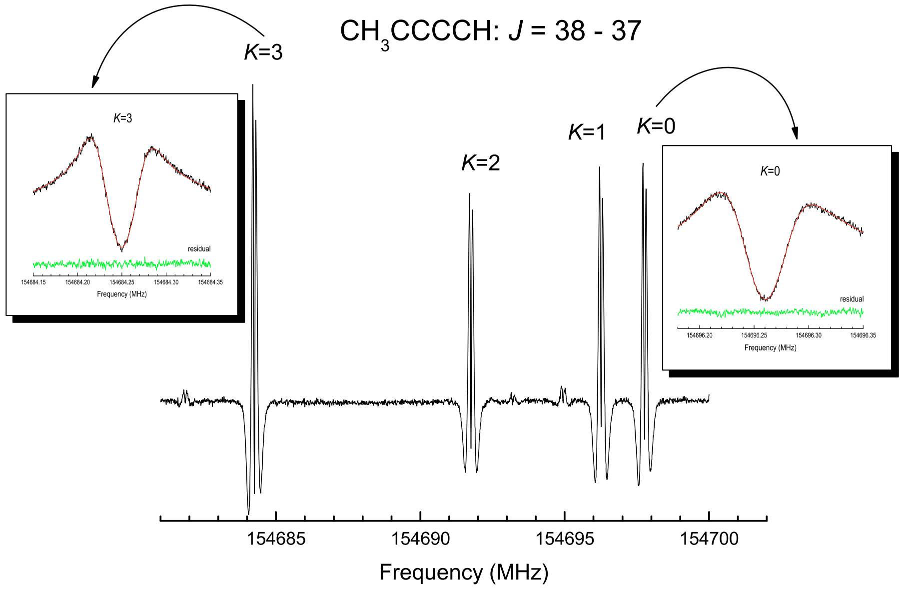

Fig. 2. The $J = 38 \leftarrow 37$, $K = 0$–3, transition of CH$_3$CCCCH recorded at sub-Doppler resolution. In the insets: the line profile analyzes performed for the $K = 0$ and $K = 3$ components.

CH$_3$CCH and CH$_3$CCCCH, respectively. As far as methylacetylene is concerned, it should be noted that this molecule was extensively studied in the past, and we refer the reader to Müller et al. (2002) for a comprehensive summary. Here, we only recall that Wlodarczak et al. (1988) performed the first investigation of the submillimeter-wave rotational spectrum of methylacetylene, Graner et al. (1989) carried out the first precise determination of the A_0 rotational constant, and Urban et al. (1995) obtained reliable ground-state rotational energies by means of conventional, as well as Padé approximant approaches.

To improve even more the spectroscopic parameters of methylacetylene and methyldiacetylene and to provide accurate rest frequencies for both of them, for the first time in the present investigation we performed precise Lamb-dip laboratory spectroscopy, which allows transition frequencies to be obtained with an accuracy as good as 0.5−1 kHz. In addition, measurements in the THz frequency region were also carried out for CH$_3$CCH.

2. Experimental details and spectra analysis

In the present investigation, Lamb-dip measurements were performed employing a frequency-modulated, computer-controlled spectrometer in conjunction with a conventional free space cell, as shown in Cazzoli & Dore (1990a). To increase the sensitivity of the spectrometer as well as of the Lamb-dip effect the radiation path has been doubled (Dore et al. 1999). A detailed description of the spectrometer is given in Cazzoli & Dore (1990b), whereas our experimental set up for performing sub-Doppler resolution spectroscopy has been described in some previous papers (see for examples, Cazzoli et al. 2002a,b, 2003). Therefore, here, we only report the main details related to the present investigation. The millimeter and submillimeter-wave sources employed are either frequency multipliers driven by gunn diode oscillators or gunn diodes themselves covering, on the whole, the 80−750 GHz frequency range. The frequency modulation is obtained by sine-wave modulating the 73 MHz local oscillator of the synchronization loop at 1.666 kHz. A liquid He-cooled InSb detector was used, and its output was processed by means of a Lock-in amplifier tuned at twice the modulation frequency, so that the second derivative of the natural line profile was recorded.

In addition, Doppler-limited measurements were also carried out for methylacetylene in the 1.0−1.2 THz frequency range. In particular, the THz frequency source is actually a tripler followed by another tripler (RPG GmbH), whose radiation power is on the whole 10 to 40 μW. A liquid He-cooled Ge bolometer was employed as a detector in the THz region. Another difference concerns the radiation path. In fact, in the THz region parabolic mirrors, instead of high density polyethylene lenses, were used for collimating and focalizing the radiation. The frequency modulation has been obtained by sine-wave modulating the 73 MHz local oscillator of the synchronization loop at 333 Hz. For both Lamb-dip and THz measurements, the frequency sources are phase-locked to a Rubidium frequency standard.

The Lamb-dip measurements were carried out at pressures of 0.3−1 mTorr. Such low values of working pressure were chosen to minimize the dip widths as much as possible, as well as to avoid pressure frequency shift effects. In addition, the source power was adequately reduced to have narrow and not distorted dips. The modulation depth used was adjusted in the ranges of 16 to 32 kHz according to the experimental conditions and the transitions under consideration. As far as the Doppler-limited measurements are concerned, higher values of pressure (i.e., 25−90 mTorr) and modulation depth (i.e., 450−1800 kHz) were used. All measurements have been carried out at room temperature. A commercial sample of methylacetylene was used without any further purifications, whereas methyldiacetylene was synthesized by following the procedure reported in Verkruijsse & Brandsma (1991), as described in Cazzoli et al. (2008).

Going into more detail, the K structures, with K ranging from 0 to 15, of the $J + 1 \leftarrow J$ rotational transitions, with J = 8, 9, 11, 26, 29, 39, 41, 60−62, 65, 67, 69 for methylacetylene and J = 19, 24, 37, 42, 50, 74, 84, 95, 113, 125 for methyldiacetylene, were recorded with an accuracy of about 1 kHz for the Lamb-dip measurements and 10−20 kHz for the Doppler-limited ones.

Figure 1 presents an example of THz measurements: the K-components, with K ranging from 0 to 6, of the $J = 61 \leftarrow 60$ transition of CH$_3$CCH. It is evident that the $K = 3n$ lines are more intense than the $K \neq 3n$ ones due to the hydrogen nuclear statistics. It is also worthwhile noting the extremely good signal-to-noise ratio of the recorded spectrum that actually allowed a frequency accuracy as good as 20 kHz. In Fig. 2 the $J = 38 \leftarrow 37$, $K = 0$–3, transition of CH$_3$CCCCH is depicted providing an example of rotational spectrum recorded at

Table 1. Rotational J', $K' \leftarrow J''$, K'' transitions (MHz) of CH_3CCH with the corresponding observed-calculated (o-c) differences (kHz) (second fit: see text).

Transition				Freq.	o-c	Transition				Freq.	o-c
J'	K'	J''	K''	(MHz)	(kHz)	J'	K'	J''	K''	(MHz)	(kHz)
9	8	8	8	153 629.5158(5)	0.5	42	9	41	9	715 895.0461(5)	0.1
9	7	8	7	153 673.4387(5)	0.0	42	8	41	8	716 122.8242(5)	0.9
9	6	8	6	153 711.5389(5)	0.4	42	6	41	6	716 498.5235(5)	0.3
9	5	8	5	153 743.8027(5)	–0.1	42	5	41	5	716 646.3035(5)	0.3
9	4	8	4	153 770.2187(5)	0.0	42	4	41	4	716 767.2919(5)	0.4
9	3	8	3	153 790.7720(5)	0.9	42	3	41	3	716 861.4423(5)	0.6
9	2	8	2	153 805.4627(5)	1.0	42	2	41	2	716 928.7179(5)	0.1
9	1	8	1	153 814.2764(5)	0.8	42	1	41	1	716 969.0939(5)	0.2
9	0	8	0	153 817.2147(5)	0.3	42	0	41	0	716 982.5547(5)	0.6
10	9	9	9	170 642.0339(5)	0.0	61	12	60	12	1 037 184.554(20)	10.4
10	8	9	8	170 697.2742(5)	0.1	61	9	60	9	1 038 381.782(20)	9.7
10	7	9	7	170 746.0668(5)	0.2	61	8	60	8	1 038 705.667(20)	3.6
10	6	9	6	170 788.3907(5)	–0.9	61	7	60	7	1 038 991.745(20)	4.8
10	5	9	5	170 824.2315(5)	–1.0	61	3	60	3	1 039 755.868(20)	–13.8
10	4	9	4	170 853.5757(5)	0.2	61	2	60	2	1 039 851.520(20)	–17.5
10	3	9	3	170 876.4101(5)	0.8	61	1	60	1	1 039 908.920(20)	–2.1
10	2	9	2	170 892.7264(5)	0.4	61	0	60	0	1 039 928.059(20)	21.5
10	1	9	1	170 902.5184(5)	1.0	62	15	61	15	1 052 546.059(20)	10.9
10	0	9	0	170 905.7826(5)	0.2	62	14	61	14	1 053 102.081(20)	–1.4
12	11	11	11	204 608.7740(5)	–0.3	62	13	61	13	1 053 620.666(20)	7.7
12	10	11	10	204 690.4219(5)	0.7	62	12	61	12	1 054 101.576(20)	–14.0
12	9	11	9	204 764.3869(5)	0.9	62	9	61	9	1 055 316.849(20)	1.7
12	8	11	8	204 830.6433(5)	–1.6	62	6	61	6	1 056 187.810(20)	–9.6
12	7	11	7	204 889.1662(5)	–0.9	62	5	61	5	1 056 401.104(20)	4.9
12	6	11	6	204 939.9313(5)	–0.8	62	4	61	4	1 056 575.711(20)	0.5
12	5	11	5	204 982.9186(5)	–0.6	62	3	61	3	1 056 711.590(20)	1.9
12	4	11	4	205 018.1137(5)	0.9	62	2	61	2	1 056 808.679(20)	–1.3
12	3	11	3	205 045.5006(5)	–1.0	62	1	61	1	1 056 866.942(20)	–8.4
12	2	11	2	205 065.0702(5)	1.6	62	0	61	0	1 056 886.392(20)	15.7
12	1	11	1	205 076.8164(5)	0.2	63	15	62	15	1 069 435.901(20)	22.4
12	0	11	0	205 080.7322(5)	–0.1	63	14	62	14	1 070 000.134(20)	3.9
27	12	26	12	459 991.3044(5)	0.8	63	12	62	12	1 071 014.381(20)	–24.8
27	10	26	10	460 373.4414(5)	–0.1	63	9	62	9	1 072 247.600(20)	–15.1
27	9	26	9	460 538.7862(5)	0.2	63	6	62	6	1 073 131.464(20)	12.9
27	8	26	8	460 686.8956(5)	0.0	63	3	62	3	1 073 662.955(20)	0.9
27	7	26	7	460 817.7142(5)	–0.2	63	2	62	2	1 073 761.500(20)	20.0
27	6	26	6	460 931.1924(5)	0.0	63	1	62	1	1 073 820.627(20)	16.5
27	5	26	5	461 027.2859(5)	–0.4	63	0	62	0	1 073 840.335(20)	11.8
27	4	26	4	461 105.9587(5)	–0.5	66	15	65	15	1 120 080.104(20)	85.2
27	3	26	3	461 167.1808(5)	0.0	66	14	65	14	1 120 668.720(20)	3.2
27	2	26	2	461 210.9275(5)	0.1	66	12	65	12	1 121 726.916(20)	–12.6
27	1	26	1	461 237.1825(5)	0.3	66	9	65	9	1 123 013.530(20)	–14.3
27	0	26	0	461 245.9347(5)	–0.1	66	6	65	6	1 123 935.641(20)	–6.6
30	12	29	12	511 043.7708(5)	0.2	66	3	65	3	1 124 490.150(20)	–9.6
30	9	29	9	511 650.9347(5)	0.5	66	2	65	2	1 124 592.962(20)	11.4
30	6	29	6	512 086.1146(5)	–0.7	66	1	65	1	1 124 654.668(20)	27.3
30	5	29	5	512 192.6838(5)	–0.1	66	0	65	0	1 124 675.193(20)	–13.6
30	4	29	4	512 279.9320(5)	–0.4	68	15	67	15	1 153 821.001(20)	–32.8
30	3	29	3	512 347.8264(5)	–0.8	68	14	67	14	1 154 425.770(20)	14.2
30	2	29	2	512 396.3417(5)	–0.6	68	12	67	12	1 155 512.975(20)	–12.3
30	1	29	1	512 425.4585(5)	–0.4	68	9	67	9	1 156 834.790(20)	–23.6
30	0	29	0	512 435.1651(5)	–0.6	68	6	67	6	1 157 782.140(20)	–16.4
40	15	39	15	680 048.5349(5)	–0.5	68	3	67	3	1 158 351.831(20)	–21.3
40	12	39	12	681 076.7384(5)	–0.1	68	2	67	2	1 158 457.443(20)	–19.2
40	9	39	9	681 880.0715(5)	–0.2	68	1	67	1	1 158 520.829(20)	–26.5
40	6	39	6	682 455.8480(5)	–0.1	68	0	67	0	1 158 541.958(20)	25.8
40	5	39	5	682 596.8450(5)	0.0	70	15	69	15	1 187 543.822(20)	–26.4
40	4	39	4	682 712.2799(5)	0.0	70	12	69	12	1 189 280.580(20)	–10.2
40	3	39	3	682 802.1084(5)	–0.3	70	9	69	9	1 190 637.299(20)	–32.5
40	2	39	2	682 866.2964(5)	–0.5	70	6	69	6	1 191 609.639(20)	–22.5
40	1	39	1	682 904.8193(5)	–0.3	70	3	69	3	1 192 194.370(20)	–17.2
40	0	39	0	682 917.6621(5)	–0.1	70	2	69	2	1 192 302.756(20)	–8.7
42	15	41	15	713 975.3826(5)	0.4	70	1	69	1	1 192 367.809(20)	–0.7
42	12	41	12	715 053.0606(5)	–0.6	70	0	69	0	1 192 389.488(20)	–0.4

Table 2. Rotational $J', K' \leftarrow J'', K''$ transitions (MHz) of CH_3CCCCH with the corresponding observed-calculated (o-c) differences (kHz).

Transition				Freq.	o-c
J'	K'	J''	K''	(MHz)	(kHz)
20	10	19	10	81 347.8940(20)	–2.2
20	9	19	9	81 362.9239(20)	–1.8
20	8	19	8	81 376.3845(20)	2.8
20	6	19	6	81 398.5597(10)	–1.7
20	5	19	5	81 407.2797(10)	–1.1
20	4	19	4	81 414.4154(10)	–1.9
20	3	19	3	81 419.9683(10)	–1.1
20	2	19	2	81 423.9357(10)	–0.4
20	1	19	1	81 426.3162(10)	–0.2
20	0	19	0	81 427.1083(10)	–1.6
25	9	24	9	101 701.7729(10)	–1.3
25	8	24	8	101 718.5795(10)	–0.6
25	7	24	7	101 733.4147(10)	–2.3
25	6	24	6	101 746.2812(10)	–0.7
25	5	24	5	101 757.1710(10)	–1.1
25	4	24	4	101 766.0833(10)	–2.1
25	3	24	3	101 773.0196(10)	–0.2
25	2	24	2	101 777.9727(10)	–1.3
25	1	24	1	101 780.9450(10)	–1.9
25	0	24	0	101 781.9362(10)	–1.8
38	12	37	12	154 482.0271(10)	0.3
38	11	37	11	154 516.4115(10)	–0.7
38	9	37	9	154 576.2795(10)	1.0
38	8	37	8	154 601.7462(10)	–0.4
38	7	37	7	154 624.2323(10)	1.3
38	6	37	6	154 643.7276(10)	0.8
38	5	37	5	154 660.2304(10)	0.2
38	4	37	4	154 673.7363(10)	–1.1
38	3	37	3	154 684.2471(10)	0.9
38	2	37	2	154 691.7525(10)	–1.3
38	1	37	1	154 696.2587(10)	–0.3
38	0	37	0	154 697.7624(10)	1.4
43	12	42	12	174 802.9361(10)	–0.9
43	11	42	11	174 841.7894(10)	0.0
43	10	42	10	174 877.2910(10)	0.7
43	9	42	9	174 909.4335(10)	1.2
43	8	42	8	174 938.2106(10)	1.8
43	7	42	7	174 963.6153(10)	1.5
43	6	42	6	174 985.6430(10)	0.8
43	5	42	5	175 004.2895(10)	0.3
43	4	42	4	175 019.5537(10)	2.5
43	3	42	3	175 031.4259(10)	1.0
43	2	42	2	175 039.9090(10)	1.2
43	1	42	1	175 044.9993(10)	1.0
43	0	42	0	175 046.6962(10)	1.0
51	12	50	12	207 311.9202(20)	0.0
51	11	50	11	207 357.8740(20)	–0.5
51	10	50	10	207 399.8637(20)	–0.9
51	9	50	9	207 437.8801(10)	–1.7
51	8	50	8	207 471.9164(10)	–1.9
51	7	50	7	207 501.9661(10)	–0.9
51	6	50	6	207 528.0226(10)	0.7
51	5	50	5	207 550.0766(10)	–0.6
51	4	50	4	207 568.1301(10)	1.2
51	3	50	3	207 582.1736(10)	0.7
51	2	50	2	207 592.2045(10)	–1.8
51	1	50	1	207 598.2263(10)	–0.9
51	0	50	0	207 600.2340(10)	–0.3
75	10	74	10	304 924.4685(10)	1.4
75	9	74	9	304 979.7649(10)	0.9
75	8	74	8	305 029.2716(10)	1.0
75	7	74	7	305 072.9775(10)	0.8
75	6	74	6	305 110.8738(10)	0.4
75	5	74	5	305 142.9538(10)	0.8
75	4	74	4	305 169.2097(10)	0.8
75	3	74	3	305 189.6366(10)	0.9
75	2	74	2	305 204.2301(10)	0.8
75	1	74	1	305 212.9874(10)	0.8
75	0	74	0	305 215.9069(10)	1.0
85	12	84	12	345 391.7325(10)	0.8
85	11	84	11	345 467.0523(10)	0.7
85	10	84	10	345 535.8733(10)	–0.1
85	9	84	9	345 598.1832(10)	0.0
85	8	84	8	345 653.9676(10)	–0.4
85	7	84	7	345 703.2163(10)	–0.5
85	6	84	6	345 745.9192(10)	–0.1
85	5	84	5	345 782.0663(10)	–0.6
85	4	84	4	345 811.6518(10)	–0.4
85	3	84	3	345 834.6691(10)	–0.1
85	2	84	2	345 851.1129(10)	–0.4
85	1	84	1	345 860.9817(10)	0.5
85	0	84	0	345 864.2708(10)	0.1
96	12	95	12	390 027.1125(20)	–0.6
96	11	95	11	390 111.5765(20)	–0.9
96	10	95	10	390 188.7530(10)	–1.3
96	9	95	9	390 258.6272(10)	–1.1
96	8	95	8	390 321.1850(10)	–0.1
96	7	95	7	390 376.4117(10)	–0.3
96	5	95	5	390 464.8311(10)	–2.2
96	4	95	4	390 498.0103(10)	0.5
96	3	95	3	390 523.8210(10)	0.4
96	2	95	2	390 542.2616(10)	0.9
96	1	95	1	390 553.3245(10)	–1.6
96	0	95	0	390 557.0147(10)	–0.1
114	3	113	3	463 598.4658(10)	–0.3
114	2	113	2	463 620.0707(10)	–1.5
114	1	113	1	463 633.0372(10)	–0.3
114	0	113	0	463 637.3598(10)	0.1
126	6	125	6	512 145.6527(10)	1.3
126	3	125	3	512 273.2460(10)	–0.1
126	2	125	2	512 296.8883(10)	1.0
126	1	125	1	512 311.0737(10)	–0.1
126	0	125	0	512 315.8030(10)	0.0

sub-Doppler resolution. This figure, even if recorded with a modulation depth greater than that used for resolving the individual K components (shown as examples in the insets for K = 0 and 3), allows us to point out that transition frequencies can be more accurately retrieved by employing the Lamb-dip technique thanks to the narrower line width.

3. Analysis and results

In analyzing the spectra, we note that in no cases has the hyperfine structure due to the hydrogen nuclei been resolved. The transition frequencies were determined either by fitting the experimental data points to a parabolic function or by a line profile analysis (see Cazzoli & Dore 1990a), with the former mostly employed and the latter mainly used for distorted dips. A graphical example of the line profile analysis performed is given in the insets of Fig. 2. In all cases the reported frequencies are obtained as averages of a set of measurements, which were then very reproducible, i.e., the frequency differences are less (or even much less) than 1 kHz. Therefore, the standard deviation of the mean was used as indicator of the frequency accuracy. Consequently, the derived rest frequencies have an estimated accuracy of 0.5

Table 3. Ground-state rotational and centrifugal distortion constants of CH_3CCH and CH_3CCCCH.

CH_3CCH		This work[a]	This work[b]	This work[c]	Müller et al. (2002)	Müller et al. (2000)
$A_0 - B_0$	(MHz)	–	–	150 594.45(55)	150 594.45(46)	
B_0	(MHz)	8545.8770201(87)	8545.8769958(63)	8545.8769857(60)	8545.8768621(217)	8545.8768831(220)
D_J	(kHz)	2.9393482(86)	2.9393197(40)	2.9393130(32)	2.9392410(251)	2.9393443(316)
D_{JK}	(kHz)	163.41736(25)	163.41699(22)	163.41667(21)	163.41449(209)	163.41306(227)
D_K	(kHz)	–	–	2907.2(140)	2907.2(122)	
H_J	(Hz)	–0.0000429(25)	–0.0000514(10)	–0.00005251(63)	–0.00006320(610)	–0.00002960(950)
H_{JK}	(Hz)	0.91595(16)	0.91573(15)	0.91551(13)	0.91408(89)	0.91451(113)
H_{KJ}	(Hz)	5.2984(22)	5.2974(20)	5.2967(19)	5.3021(114)	5.2914(116)
L_{JJK}	(mHz)	–0.006629(52)	–0.006672(61)	–0.006641(49)	–0.006313(148)	–0.006588(232)
L_{JK}	(mHz)	–0.04405(72)	–0.04341(56)	–0.04228(42)	–0.04181(189)	–0.03915(223)
L_{KKJ}	(mHz)	–0.3770(66)	–0.3802(61)	–0.3899(57)	–0.4194(203)	–0.4171(214)
P_{JJJJK}	(μHz)	–	0.0000340(64)	0.0000297(52)		
rms error[d]	(MHz)	0.00056	0.0126	23.5		

CH_3CCCCH		This work[a]	Bester et al. (1984)
B_0	(MHz)	2035.7470641(46)	2035.74706(8)
D_J	(kHz)	0.08664738(54)	0.086687(40)
D_{JK}	(kHz)	19.86699(20)	19.8630(12)
H_J	(Hz)	0.000004472(18)	0.0000130(66)
H_{JK}	(Hz)	0.036688(21)	0.03568(21)
H_{KJ}	(Hz)	0.3435(13)	0.3278(37)
L_{JJK}	(mHz)	–0.00008561(68)	
L_{JK}	(mHz)	–0.00109(10)	
rms error[d]	(kHz)	1.1	

[a] Fit performed including only Lamb-dip measurements, [b] fit performed including Lamb-dip and THz measurements. The corresponding residuals have been reported in Table 1, [c] fit performed including Lamb-dip, THz, ΔK = 3 (Müller et al. 2002) and other measurements available (see text), [d] root mean square error of the fit as provided by the SPFIT/SPCAT program.

and 1 kHz for methylacetylene and methyldiacetylene, respectively. An uncertainty of 2 kHz has only been assigned to the weaker transitions of CH_3CCCCH. In the case of methylacetylene, the high reproducibility of the Lamb-dip measurements is mainly due to the fact that the dips are particularly narrow, narrower than for methyldiacetylene. This may be ascribed to the different dipole moments: 0.7804(1) D for CH_3CCH (Muenter & Laurie 1966) and 1.2071(10) D (Bester et al. 1984), consequently to a lower relaxation rate for CH_3CCH. Finally, for Doppler-limited measurements, the frequencies were only obtained by fitting the experimental data points to a parabolic function.

On the whole, a total of 128 and 103 distinct frequency lines have been assigned for CH_3CCH and CH_3CCCCH, respectively. They are collected in Tables 1 (methylacetylene) and 2 (methyldiacetylene), together with the corresponding residuals (obs. – calc.) of the fit described below. We may notice that they are lower in almost all cases than the given uncertainties.

For both molecules, the retrieved frequency values were included in least-squares fits in which each line frequency was weighted proportionally to the inverse square of its experimental uncertainty. For CH_3CCH, three different fits were carried out: the first one including only Lamb-dip measurements, the second including both Lamb-dip and THz measurements, and a third one in which, in addition to our transition frequencies, data available in the literature have also been included in the analysis. More precisely, some accurate low-frequency values (i.e., <150 GHz) (Dubrulle et al. 1978; Ware & Roberts 1984), some transitions with K values greater than 15 (Müller et al. 2002), some transitions in the 720−1000 GHz frequency range (Müller et al. 2002) and, finally, $\Delta K = +3$ ground-state combination differences (Müller et al. 2002) have been considered. The last allows determination of the axial A_0 and D_K constants. All these fits were carried out with Pickett's SPCAT/SPFIT suite of programs (Pickett 1991). The results are reported in Table 3 for both methylacetylene and methyldiacetylene. In both cases the present spectroscopic parameters are compared with those available in the literature. From this comparison, one may first note that our results for both species are in overall good agreement with the most recently published studies, but nevertheless the present work reports clear improvements with respect to the literature data.

As far as methylacetylene is concerned, for the first fit, i.e., the one including only Lamb-dip measurements, the small standard deviation has to be noted; in fact, such a small σ (0.56 kHz) points out that the spectroscopic parameters obtained are able to reproduce the rotational frequencies with an accuracy of about 0.5 kHz up to ~700 GHz. Therefore, CH_3CCH might be taken into consideration as secondary frequency standards for the millimeter- and submillimeter-wave (up to 700 GHz) frequency regions. Concerning the second and third fits, the accuracy of almost all the spectroscopic constants (all but A_0 and D_K, in the third fit) has been largely improved by reducing the uncertainties by about one order of magnitude. In addition, our THz measurements allowed us to determine a new centrifugal distortion constant, the P_{JJJJK}. Even larger improvements were obtained for methyldiacetylene, not only were the spectroscopic parameters improved by one or two orders of magnitude, but also two octic centrifugal distortion constants were determined for the first time.

4. Conclusion

Precise Lamb-dip measurements were carried out in the 80−750 GHz frequency range for both methylacetylene and methyldiacetylene. They allowed us to provide very accurate rest frequencies, as well as to improve the spectroscopic parameters available in the literature. In addition, transition frequencies in the THz frequency region (1.0–1.2 THz) were recorded at Doppler resolution for CH_3CCCCH.

On the whole, we present the most accurate ground-state rotational parameters of methylacetylene and methyldiacetylene known at the moment. Since both of them are known to have a strong astrophysical relevance, we think that the improvement in the accuracy of the ground-state rotational parameters and of the rest frequencies obtained in the present investigation could be very useful for future observational purposes.

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