The Submillimeter-wave Spectrum of Propyne, CH_3CCH

Holger S. P. Müller, Sven Thorwirth, Luca Bizzocchi[a], and Gisbert Winnewisser
I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Köln
[a] On leave from Dipartimento di Chimica “G. Ciamician”, Università di Bologna,
Via F. Selmi 2, 40126 Bologna, Italy

Reprint requests to Prof. G. W. or Dr. H. S. P. M.; Fax: +49 221 470 5162;
E-mail: winnewisser@ph1.uni-koeln.de or hspm@zeus.ph1.uni-koeln.de

Z. Naturforsch. **55 a,** 491–494 (2000); received March 16, 2000

The ground state rotational spectrum of propyne has been studied in selected regions between 509 and 820 GHz spanning the quantum numbers $29 \leq J \leq 48$ and $0 \leq K \leq 21$. The accurate new line frequencies were fit together with previously published data to obtain greatly improved spectroscopic constants.

Key words: Rotational Spectroscopy; Interstellar Molecule; Astrophysics; Astrochemistry.

1. Introduction

Propyne, CH_3CCH, also known as methylacetylene, is a symmetric top molecule with a carbon chain at its backbone. Therefore, it is of great astrophysical and astrochemical importance. Its first detection in the interstellar medium (ISM) was reported by Snyder and Buhl towards the galactic center source Sgr B2 in 1973 [1]. Moreover, it was observed in extragalactic sources by Mauersberger et al. [2]. Symmetric top molecules are ideal probes to determine the kinetic temperature of the ISM because each K component of a given rotational transition represents a different excitation energy, i. e. temperature, which increases with K. Furthermore, the low K components occur in fairly narrow frequency ranges so that they can be observed simultaneously. This method was introduced by Solomon et al. using observations of methylcyanide, CH_3CN [3, 4]. Because of propyne's lower dipole moment, 0.78 D [5] *vs.* 3.9 D for CH_3CN [6], it is more easily thermalized, and thus even better suited as a temperature probe [7 - 9].

Propyne has been subjected to several spectroscopic studies. The first microwave (MW) investigation dates back 50 years when Trambarulo and Gordy recorded $J = 2 - 1$ and $3 - 2$ transitions [10]. Later, the ground state rotational spectrum of CH_3CCH was investigated by Ware and Roberts in the MW region [11], and by Dubrulle et al. [12] and Wlodarczak et al. [13] in the millimeter and submillimeter wave regions, respectively. Most recently, R. Bocquet et al. used a far infrared (FIR) laser sideband system to obtain transition frequencies between 0.768 and 1.277 THz [14]. For the sake of completeness, it should be mentioned that pure rotational spectra of CH_3CCH have been recorded in several excited vibrational states, as can be seen in [10, 11, 13, 14], and references therein.

For symmetric top molecules, the purely K-dependent parameters, such as $A - B$ (or $C - B$ for oblate tops), D_K, etc., usually cannot be determined from rotational spectroscopy because of the $\Delta K = 0$ selection rule. $\Delta K = 3$ transitions may be observed due to centrifugal distortion effects, but these transitions are very weak in general. Urban et al. have determined purely K-dependent parameters through the analysis of perturbations in the IR spectrum of propyne using a Padé approximant [15].

Recently, we have studied the submillimeter spectrum of HCCCP, for which CH_3CCH was used as a precursor [16]. In the course of this investigation it was found that high K transitions of propyne were displaced from their predicted line frequencies based on the spectroscopic constants of [14]. In order to improve the data set of this astrophysically important molecule we have investigated its rotational spectrum in the submillimeter region accessing much higher K quantum numbers than before.

0932–0784 / 00 / 0500–0491 $ 06.00

Table 1. Assignments, frequencies (MHz), uncertainties, and residuals[a] (kHz) of rotational transitions of propyne.

K_a	frequency	unc.	o – c	K_a	frequency	unc.	o – c
J = 29:							
18	509322.145	80	13.2	17	509655.422	50	19.8
16	509970.291	20	8.2	15	510266.648	10	–15.0
14	510544.437	20	–0.4	13	510803.499	15	–7.3
12	511043.777	10	1.4				
J = 30:							
18	526279.491	50	23.6	16	526948.778	50	3.8
13	527809.190	20	–3.1	12	528057.299	10	–5.2
11	528285.906	10	–5.1	10	528494.929	10	–0.2
9	528684.283	10	2.3	8	528853.896	10	1.5
7	529003.707	10	0.4	6	529133.666	10	6.0
5	529243.716	10	10.8	4	529333.808	10	7.9
3	529403.919	10	9.1	2	529454.010	10	2.3
1	529484.078	10	3.8	0	529494.102	10	4.4
J = 31:							
18	543234.842	50	16.2	16	543925.254	50	9.1
15	544240.963	20	10.6	12	545068.739	10	–0.8
3	546457.822	10	5.3	2	546509.502	10	7.4
1	546540.519	10	9.7	0	546550.854	20	5.2
J = 32:							
15	561224.974	10	4.1	12	562078.011	10	–3.7
J = 33:							
17	577516.023	50	23.3	16	577871.873	40	11.5
15	578206.818	20	3.7	12	579085.057	10	–4.0
J = 34:							
18	594088.391	50	–3.3	17	594475.830	30	4.9
15	595186.432	30	12.6	12	596089.807	10	–4.0
J = 35:							
19	610615.189	80	15.5	18	611035.210	50	9.8
17	611433.417	50	26.2	16	611809.621	50	13.5
15	612163.721	30	2.2	14	612495.588	30	–11.0
13	612805.127	20	–2.7	12	613092.196	15	–0.9
11	613356.698	10	0.5	10	613598.537	10	3.9
9	613817.625	10	11.1	8	614013.871	10	13.2
7	614187.204	10	13.3	6	614337.554	10	7.1
5	614464.875	10	5.8	4	614569.115	10	6.2
3	614650.230	10	4.3	2	614708.196	10	7.2
1	614742.983	10	7.4	0	614754.576	10	3.4
J = 41:							
21	711127.345	100	–156.4	20	711665.173	80	–59.8
19	712177.986	50	33.5	18	712665.490	30	0.6
17	713127.668	20	–9.7	16	713564.369	15	10.7
15	713975.381	10	2.3	14	714360.594	20	0.4
13	714719.865	10	–0.3	12	715053.063	10	–0.7
11	715360.066	10	–1.4	10	715640.763	10	–0.3
9	715895.045	10	–2.2	8	716122.798	20	–26.0
7	716324.009	10	1.0	6	716498.518	10	–5.2
5	716646.303	10	–0.2	4	716767.294	10	2.5
3	716861.442	10	0.2	2	716928.718	10	0.1
1	716969.095	10	1.0	0	716982.553	10	–1.4
J = 44:							
12	765996.077	10	–2.5	11	766324.075	10	–0.6
10	766623.962	10	–2.4	9	766895.635	10	0.2
8	767138.984	10	–1.5	7	767353.922	10	–2.9
6	767540.371	10	–0.9	5	767698.261	10	5.5
4	767827.511	10	–4.7	3	767928.099	10	–3.9
2	767999.974	10	–4.6	1	768043.111	10	–4.0
0	768057.493	10	–2.7				
J = 47:							
18	814199.025	30	6.2	16	815220.296	15	2.4
15	815687.273	20	–8.7	14	816124.943	15	–5.1
13	816533.139	10	2.3	12	816911.702	10	1.5
11	817260.502	10	0.3	10	817579.411	10	–1.3
9	817868.312	10	–2.1	8	818127.097	10	–2.4
7	818355.668	10	–3.3	6	818553.943	10	–0.3
5	818721.838	10	–2.2	4	818859.293	10	–5.3
3	818966.259	10	–5.8	2	819042.685	15	–13.8
1	819088.564	10	–7.0	0	819103.855	10	–8.7

[a] Observed minus calculated frequency.

2. Experimental Details

Selected transitions between 509 and 820 GHz have been recorded with the Cologne Terahertz Spectrometer using phase-locked BWOs (backward wave oscillators) as sources and a magnetically tuned hot electron InSb bolometer as detector. Further details of the spectrometer are given in [17]. A commercial propyne sample was used without further purification. The pressure inside the absorption cell varied between about 1 Pa for most lines and up to 4 Pa for the weaker, high *K* transitions.

3. Observed Spectra, Analysis, and Discussion

The spectroscopic constants presented in [14] lead to very good predictions for the transitions with $K < 10$. They were found within 100 kHz of the predictions, generally at slightly lower frequencies; at higher *J*, this was also true for the lowest *K* transitions. The deviations between observed and calculated frequencies increased for higher values of *K*, but with 4.5 MHz for $K = 21$ they were still fairly small. This *K* value is substantially higher than $K = 13$, which has been accessed in previous investigations of the rotational spectrum of CH_3CCH [14]. The transitions from the present study, their frequencies, uncertainties and residuals from the fit are given in Table 1. The complete line list as well as new predictions of

Table 2. Present spectroscopic constants (MHz) of CH_3CCH in comparsion to previous values and values of CH_3CN.

	Fit 1[a]	Fit 2[b]	[14][c]	[15][d]	CH_3CN[e]
$(A - B) \cdot 10^{-3}$				150.594 36 (32)	148.900 164 (78)
B	8 545.876 883 1 (220)	8 545.876 861 8 (223)	8 545.876 890 (17)	8 545.876 757 (36)	9 198.899 485 (64)
$D_J \cdot 10^3$	2.939 344 3 (316)	2.939 227 5 (377)	2.939 352 (55)	2.939 081 (90)	3.807 622 (110)
$D_{JK} \cdot 10^3$	163.413 06 (227)	163.416 09 (233)	163.419 2 (46)	163.402 3 (76)	177.410 4 (45)
D_K				2.905 0 (108)	2.831 8 (35)
$H_J \cdot 10^{12}$	–29.6 (95)	–68.1 (116)		–70.5 (150)	–261.1 (147)
$H_{JK} \cdot 10^9$	914.51 (113)	915.07 (115)	913.5 (39)	894.35 (208)	1023.54 (290)
$H_{KJ} \cdot 10^6$	5.291 4 (116)	5.303 1 (118)	5.248 (46)	5.257 (63)	6.104 (49)
$H_K \cdot 10^6$					156. (72)
$L_{JJK} \cdot 10^{12}$	–6.588 (232)	–6.499 (238)	–6.200 (79)		–7.12 (31)
$L_{JK} \cdot 10^{12}$	–39.15 (223)	–42.14 (231)			–54.0 (141)
$L_{KKJ} \cdot 10^{12}$	–417.1 (214)	–419.8 (214)			–497. (100)
rms[f]	17.9	16.9			
wrms[f]	0.511	0.413			
wrms[g]	0.755	0.644			

[a] Present data used together with those of [11 - 14]. [b] Present data used together with those of [11 - 13]. [c] Rotational data. [d] Rotational and IR data. [e] [19], except purely K dependent parameters from [20]. [f] (Weighted) standard deviation for present data. [g] Weighted standard deviation for all lines used in the fit.

the pure rotational spectrum are available online from the Cologne Database for Molecular Spectroscopy via http://www.ph1.uni-koeln.de/vorhersagen/.

The new transitions frequencies have been subjected to a weighted least-squares fit together with the previously published data [11 - 14] employing Pickett's program SPFIT [18]. Uncertainties were explicitely stated in [12, 14]; 30 kHz was adopted for the transitions from [11, 13]. The resulting spectroscopic constants are presented in Table 2 under the heading Fit 1. In order to test the effects of the FIR laser sideband lines on the fit, another fit has been performed in which these lines were not used in the fit. The constants are given in Table 2 under the heading Fit 2. Table 2 also contains spectroscopic constants of propyne from [14, 15] along with values for the related methylcyanide molecule [19, 20].

The uncertainties of the present spectroscopic constants are probably conservative because the weighted standard deviation for the new transition frequencies is close to 0.5, and overall it is still much smaller than 1.0. As might be expected, the overall agreement between the present constants and those from [14, 15] is quite good. The larger uncertainty of L_{JJK} compared to the value from [14] and some small, but significant deviations between the present constants and those from [14, 15] are caused to a large extent by the greater number of J-dependent parameters determined in the current work. The spectroscopic constants of propyne are also quite close to those of methyl cyanide which is obtained from the former by replacing the CH group by an N atom. The main difference between the two new fits is in the H_J values. Omitting the data from [14], a value in perfect agreement with that from [15] is obtained. Inclusion of these lines reduces the magnitude of H_J, which suggests that they are slightly biased towards higher frequencies. In fact, on the average the lines are too high by 317 and 428 kHz for fits 1 and 2, respectively, while the standard deviation of the FIR laser sideband lines increases from 479 kHz in Fit 1 to 590 kHz in Fit 2, still close to the estimated uncertainty of 500 kHz. In a trial fit, an H_J value of 29 (20) $\cdot 10^{-12}$ MHz was obtained in [14]. Even though the constant is not significantly determined, the absolute uncertainty is only slightly worse than those of [15] or of the present fits. Since in all instances the uncertainties of H_J are fairly large with respect to its value, it appears that even more data would have to be included in the fits to obtain a well-determined value for this constant.

It is worthwhile mentioning that in [15] an approximate value was obtained for H_K using a Padé approximant: –93 (111) $\cdot 10^{-6}$ MHz. This value agrees fairly well with that of CH_3CN, 156 (72) $\cdot 10^{-6}$ MHz, even though one has to keep in mind that both values are not significantly determined. Nevertheless, the uncertainties put limits to the values of H_K. The value of 3.34 (121) $\cdot 10^{-6}$ MHz, obtained from a fit using a conventional Hamiltonian, appears to be too large, but its relatively large uncertainty allows for much smaller values.

4. Conclusion

The present study provides greatly improved *J*-dependent spectroscopic constants for propyne in the vibrational ground state, permitting even highly excited rotational transitions to be identified unambigously in the ISM. The constants should also be of use for the analysis of infrared spectra.

Acknowledgements

We acknowledge support by the DFG via Grants SFB 301 and SFB 494 and by special funding from the Science and Research Ministry of the Land Nordrhein-Westfalen.

[1] L. E. Snyder and D. Buhl, Nature Phys. Sci. **243,** 45 (1973).
[2] R. Mauersberger, C. Henkel, C. M. Walmsley, L. J. Sage, and T. Wiklind, Astron. Astrophys. **247,** 307 (1991).
[3] P. M. Solomon, K. B. Jefferts, A. A. Penzias, and R. W. Wilson, Astrophys. J. **168,** L107 (1971).
[4] P. M. Solomon, A. A. Penzias, K. B. Jefferts, and R. W. Wilson, Astrophys. J. **185,** L63 (1973).
[5] P. M. Burrell, E. Bjarnov, and R. H. Schwendeman, J. Mol. Spectrosc. **82,** 193 (1980).
[6] J. Gadhi, A. Lahrouni, J. Legrand, and J. Demaison, J. Chim. Phys. **92,** 1984 (1995).
[7] E. Churchwell and J. M. Hollis, Astrophys. J. **272,** 591 (1983).
[8] T. B. H. Kuiper, E. N. Rodriguez Kuiper, D. F. Dickinson, B. E. Turner, and B. Zuckerman, Astrophys. J. **276,** 211 (1984).
[9] J. Askne, B. Höglund, Å. Hjalmarson, and W. M. Irvine, Astron. Astrophys. **130,** 311 (1984).
[10] R. Trambarulo and W. Gordy, J. Chem. Phys. **18,** 1613 (1950).
[11] J. M. Ware and J. A. Roberts, J. Chem. Phys. **81,** 1215 (1984).
[12] A. Dubrulle, D. Boucher, J. Burie, and J. Demaison, J. Mol. Spectrosc. **72,** 158 (1978).
[13] G. Wlodarczak, R. Bocquet, A. Bauer, and J. Demaison, J. Mol. Spectrosc. **129,** 371 (1988).
[14] R. Bocquet, W. D. Chen, D. Papoušek, G. Wlodarczak, and J. Demaison, J. Mol. Spectrosc. **164,** 456 (1994).
[15] Š. Urban, P. Pracna, and G. Graner, J. Mol. Spectrosc. **169,** 185 (1995).
[16] L. Bizzocchi, S. Thorwirth, and G. Winnewisser, manuscript in preparation.
[17] G. Winnewisser, A. F. Krupnov, M. Yu. Tretyakov, M. Liedtke, F. Lewen, A. A. Saleck, R. Schieder, A. P. Shkaev, and S. V. Volokhov, J. Mol. Spectrosc. **165,** 294 (1994).
[18] H. M. Pickett, J. Mol. Spectrosc. **148,** 371 (1991).
[19] J. C. Pearson and H. S. P. Müller, Astrophys. J. **471,** 1067 (1996).
[20] R. Antilla, V.-M. Hornemann, M. Koivussari, and R. Paso, J. Mol. Spectrosc. **157,** 198 (1993).