

*Letter to the Editor***Submillimeter-wave spectrum of the ethynyl radical, CCH, up to 1 THz****H.S.P. Müller, T. Klaus, and G. Winnewisser**

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Abstract. The $N = 7 \leftarrow 6$ to $11 \leftarrow 10$ pure rotational transitions of CCH, $X^2\Sigma^+$, were measured in the laboratory between 611 and 961 GHz. The radical was produced in a dc glow discharge of a mixture of helium and acetylene. The electron spin-rotation splitting was resolved. The new line frequencies were fit together with previously published data, providing greatly improved spectroscopic constants, such as $B = 43\,647.529\,01$ (115) MHz, as well as precise rest frequencies well beyond 1 THz.

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

1. Introduction

The ethynyl radical is an important astrochemical and astrophysical molecule, and it also plays a vital role in combustion processes. Its rotational spectrum in the region of the $N = 1 - 0$ transition was identified in the interstellar medium (ISM) by Tucker et al. (1974). Since the laboratory spectrum had not been observed at that time, the hyperfine (hf) constants obtained in matrix ESR studies (Cochran et al. 1964, Graham et al. 1974) were instrumental in the identification of the emission features. Its prevalence in the ISM is comparable to that of methanol, which means that it is among the most abundant polyatomic molecules (Tucker et al. 1974). Several further reports exist on the occurrence of ethynyl in the ISM which utilized the $N = 1 \rightarrow 0$ transition for the most part, but some studies used others, up to the $N = 4 \rightarrow 3$ transition near 349 GHz until very recently. Moreover, CCH was observed in external galaxies (Henkel et al. 1988). Not surprisingly, the isotopic species CCD (Combes et al. 1985), ^{13}CCH , and C^{13}CH (Saleck et al. 1995) were detected in the ISM as well. Furthermore, it was found to be among the few suitable molecules to determine magnetic fields in molecular clouds (Bel and Leroy 1998).

Even with the knowledge of precise transition frequencies, about seven more years elapsed before the CCH rotational spec-

trum was observed in the laboratory by Sastry et al. (1981). Subsequently, the spectroscopic constants have been improved further by a combined analysis of laboratory and astrophysical data (Gottlieb et al. 1983).

For the extension of radioastronomy to higher frequencies, not only by radiotelescopes, but also by missions such as SOFIA (Stratospheric Observatory For Infrared Astronomy) and FIRST (Far InfraRed Space Telescope), the knowledge of precise rest frequencies is required to unambiguously identify the carriers of spectral features. Therefore, we have recorded the rotational spectrum of the ethynyl radical in the laboratory between 611 and 961 GHz. Very recently, we learned about the detection of the $7 \leftarrow 6$ and $8 \leftarrow 7$ transitions by Schilke et al. (2000) towards Orion KL using the Caltech Submillimeter Observatory. This finding clearly demonstrates the observability of ethynyl beyond the lower submillimeter region and thus the need for accurate spectroscopic data.

2. Experiment

The CCH radical was produced in a dc glow discharge of a mixture of 10 Pa helium and 3 – 5 Pa acetylene. The absorption cell was 2 m long with an inner diameter of 10 cm. Cooling of the cell increased the signal intensity. The voltage and current applied were about 1 kV and 150 mA, respectively. Phase-locked backward wave oscillators and a liquid He-cooled hot-electron InSb bolometer were used as sources and detector, respectively. Further details of the spectrometer are given by Winnewisser (1995) and Winnewisser et al. (1995).

3. Analysis and discussion

The ground electronic state of the ethynyl radical is $^2\Sigma^+$, giving rise to electron spin-rotation splitting. Thus, ten lines were recorded for the five rotational transitions investigated in the present study. The lines were found quite close to the positions that were predicted using the spectroscopic constants of Gottlieb et al. (1983). The deviations from the predicted positions ranged from 1.7 and 2.0 MHz, respectively, for the two fine structure components of the $7 \leftarrow 6$ transition to 7.3 and 8.0 MHz, respectively, for the $11 \leftarrow 10$ transition. The ^1H hyperfine splitting

Table 1. Assignments, frequencies (MHz), uncertainties, and residuals $o-c$ (kHz) of CCH

N'	J'	F'	\leftarrow	N''	J''	F''	frequency	unc.	$o-c$
1	1.5	1	\leftarrow	0	0.5	1	87 284.156 ^a	30	27
1	1.5	2	\leftarrow	0	0.5	1	87 316.925 ^a	4	7
1	1.5	1	\leftarrow	0	0.5	0	87 328.624 ^a	6	3
1	0.5	1	\leftarrow	0	0.5	1	87 402.004 ^a	5	2
1	0.5	0	\leftarrow	0	0.5	1	87 407.165 ^a	11	3
1	0.5	1	\leftarrow	0	0.5	0	87 446.512 ^a	23	18
2	2.5	3	\leftarrow	1	1.5	2	174 663.222 ^a	8	-13
2	2.5	2	\leftarrow	1	1.5	1	174 667.685 ^a	17	-14
2	1.5	2	\leftarrow	1	0.5	1	174 721.777 ^a	26	-19
2	1.5	1	\leftarrow	1	0.5	0	174 728.074 ^{a,b}	30	-4
3	3.5	4	\leftarrow	2	2.5	3	262 004.260 ^b	50	-57
3	3.5	3	\leftarrow	2	2.5	2	262 006.482 ^b	50	-54
3	2.5	3	\leftarrow	2	1.5	2	262 064.986 ^b	50	-37
3	2.5	2	\leftarrow	2	1.5	1	262 067.469 ^b	50	-18
4	4.5	5	\leftarrow	3	3.5	4	(349 337.741) ^c	13	
4	4.5	4	\leftarrow	3	3.5	3	(349 339.067) ^c	16	
4	3.5	4	\leftarrow	3	2.5	3	(349 399.342) ^c	14	
4	3.5	3	\leftarrow	3	2.5	2	(349 400.692) ^c	14	
5	5.5	6	\leftarrow	4	4.5	5	(436 660.999) ^c	21	
5	5.5	5	\leftarrow	4	4.5	4	(436 661.893) ^c	24	
5	4.5	5	\leftarrow	4	3.5	4	(436 723.078) ^c	21	
5	4.5	4	\leftarrow	4	3.5	3	(436 723.915) ^c	21	
6	6.5	7	\leftarrow	5	5.5	6	(523 971.565) ^c	31	
6	6.5	6	\leftarrow	5	5.5	5	(523 972.222) ^c	33	
6	5.5	6	\leftarrow	5	4.5	5	(524 033.955) ^c	30	
6	5.5	5	\leftarrow	5	4.5	4	(524 034.510) ^c	30	
7	7.5		\leftarrow	6	6.5		611 267.201 ^d	80	51
7	6.5		\leftarrow	6	5.5		611 329.708 ^d	80	-5
8	8.5		\leftarrow	7	7.5		698 544.778 ^d	150	76
8	7.5		\leftarrow	7	6.5		698 607.457 ^d	100	-0
9	9.5		\leftarrow	8	8.5		785 802.090 ^d	120	102
9	8.5		\leftarrow	8	7.5		785 864.969 ^d	80	48
10	10.5		\leftarrow	9	9.5		873 036.391 ^d	80	-82
10	9.5		\leftarrow	9	8.5		873 099.537 ^d	150	-45
11	11.5		\leftarrow	10	10.5		960 245.718 ^d	120	88
11	10.5		\leftarrow	10	9.5		960 308.867 ^d	120	-50

^a Gottlieb *et al.* (1983).^b Sastry *et al.* (1981).^c Frequency and uncertainty calculated from the spectroscopic constants in Table 2.^d This work, hyperfine splitting not resolved.

($I_H = 1/2$) was not resolved for these transitions, because it was about 0.5 MHz or less, smaller than the halfwidth of the lines, 1.0 – 1.7 MHz. The newly measured lines are presented in Table 1 together with previously published data as well as calculated line positions for transitions for which no measured frequencies are available to date.

The experimental lines in Table 1 were fit together employing the program SPFIT (Pickett 1991). The weight of each individual line was inverse proportional to the square of the uncertainty given in Table 1. Intensity weighted averages of the

Table 2. Spectroscopic constants^a (MHz) of CCH

Parameter	present value	Gottlieb <i>et al.</i> (1983)
Rotational and centrifugal distortion constants		
B	43 674.528 94 (115)	43 674.534 (6)
D	0.105 687 (51)	0.107 1 (8)
$H \times 10^6$	0.32 (32)	–
Fine structure constants		
γ	–62.602 9 (43)	–62.606 (4)
$\gamma^D \times 10^3$	–2.313 (255)	–
spin – spin coupling constants		
b_F	44.492 2 (183)	44.511 (17)
b_F^D	–0.011 0 (38)	–
c	12.225 6 (261)	12.254 (26)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

two strong hf components were used for the present data. As in previous studies, the rotational, electron spin, and nuclear spin angular momenta were coupled in the following way: $\mathbf{N} + \mathbf{S} = \mathbf{J}$ and $\mathbf{J} + \mathbf{I}_H = \mathbf{F}$.

The Hamiltonian for the ethynyl radical has the following form:

$$\mathcal{H} = \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{fs}} + \mathcal{H}_{\text{hfs}}. \quad (1)$$

The spectroscopic constants taken into account in the rotational Hamiltonian \mathcal{H}_{rot} are the rotational constant B and the centrifugal distortion constants D and H . In the fine structure Hamiltonian the electron spin-rotation coupling constant γ and its centrifugal distortion correction γ^D were used. Finally, the hyperfine structure is described by the scalar and tensor electron spin-nuclear spin coupling constants b_F and c , respectively, along with the centrifugal distortion correction to the former, b_F^D .

The spectroscopic constants obtained from a least-squares fitting procedure are in Table 2; the values from (Gottlieb *et al.* 1983) are included for comparison purpose.

The constants γ^D and b_F^D have been determined for the first time. Even though b_F^D is just barely determined, and thus should be viewed cautiously, it contributed significantly to the reduction of the standard deviation of the fit. The ratios b_F^D/b_F and γ^D/γ are similar in magnitude, suggesting that b_F^D is of the right order of magnitude. But it should be kept in mind that there is no strict relation between the two ratios.

Since no hyperfine splitting was resolved in the present study and since the uncertainties of the lines from Sastry *et al.* (1981) are larger while the hf splittings are smaller than those of Gottlieb *et al.* (1983), the spin-spin coupling constants b_F , b_F^D , and c are largely determined by the data from the latter study. Taking into account that in previous studies $b = b_F - c/3$ was determined instead of b_F , the agreement between current and previous spectroscopic constants is very good; small differences are due to the larger number of rotational transitions and spectroscopic constants used in the present fit.

A thorough discussion of the ^{13}C and ^1H hf constants has been given by Graham et al. (1974).

The sextic centrifugal distortion constant H is not significantly determined, but its value is of the right order of magnitude. For example, the constants B , D , and H for the related HCN molecule are about 44315.975 MHz, 0.0872 MHz, and $0.0845(19) \times 10^{-6}$ MHz, respectively (e. g., Ahrens and Winnewisser 2000).

The present spectroscopic constants will facilitate the identification of CCH by submillimeter spectroscopy. A prediction of the rotational spectrum of CCH extending to higher frequencies and giving intensities at 300 K is available online from the Cologne Database for Molecular Spectroscopy (<http://www.ph1.uni-koeln.de/vorhersagen/>).

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