LETTER TO THE EDITOR

Discovery of H$_2$CCCH$^+$ in TMC-1

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1. Introduction

Molecular ions are important intermediates in the chemistry of the interstellar medium (ISM). These charged species can rapidly react with neutral partners or recombine with electrons to form other ionic and neutral molecules under astrophysical conditions (Larsson et al. 2012; Agúndez & Wakelam 2013). Despite their fundamental role in astrochemistry, many ions remain elusive mainly due to their highly reactive character and lack of accurate laboratory data to support astronomical detections (McGuire et al. 2020). Consequently, many ions in astrochemical models and theories await confirmation through spectroscopic detection in the ISM.

One example is the formation of the hydrocarbons C$_3$H$_2$ and C$_3$H, whose cyclic isomers (c-C$_3$H$_2$ and c-C$_3$H) and linear isomers (l-C$_3$H$_2$ and l-C$_3$H, i.e., H$_2$CCCH and HCCCH, respectively) were both detected in the ISM (Thaddeus et al. 1985a,b; Yamamoto et al. 1987; Cernicharo et al. 1991), and even deuterated versions were observed (Bell et al. 1986; Spezzano et al. 2013, 2016; Agúndez et al. 2019). The synthesis of the cyclic and linear forms of C$_3$H$_2$ and C$_3$H is thought to occur via the dissociative recombination of the respective isomers of C$_3$H$_2^+$, c-C$_3$H$_3^+$ and H$_2$CCCH$^+$, with electrons (Maluendes et al. 1993).

In turn, the two isomers of C$_3$H$_3^+$ are thought to be produced through the radiative association of C$_3$H$_2^+$ and H$_2$ (Savić & Gerlich 2005). The proof of this chemical pathway for the cyclic variants is difficult because c-C$_3$H$_3^+$ is a symmetric molecule and can only be detected based on its vibrational fingerprints in the infrared (Zhao et al. 2014), which might be feasible with the James Webb Space Telescope (JWST) in the near future. While the singly deuterated version c-C$_3$H$_2$D$^+$ could be probed by radio astronomy, it has a predicted low dipole moment and low column densities (Gupta et al. 2023). This leaves only H$_2$CCCH$^+$ as a good candidate for radio astronomical searches.

In this Letter, based on a novel experimental method, we report the first laboratory millimeter-wave data of H$_2$CCCH$^+$ and its radio-astronomical detection toward the cold dark core TMC-1. We derive its column density toward TMC-1 and discuss these results in the context of state-of-the-art chemical models.

2. Laboratory work

H$_2$CCCH$^+$ is a closed-shell, planar, and near-prolate asymmetric top molecular ion (see sketch in Fig. 1). H$_2$CCCH$^+$ ions were generated in the Cologne laboratory in a storage ion source via electron impact ionization ($E_e \approx 30$ eV) of the...
precursor gas allene (C$_3$H$_4$). By applying a novel trap-based technique called leak-out spectroscopy (LOS; Schmid et al. 2022) in the cryogenic ion trap machine COLTRAP (Asvany et al. 2010, 2014), the vibrational bands $\nu_1$ and $\nu_3 + \nu_5$ were measured in the range 3180–3240 cm$^{-1}$ in high resolution. The vibrational measurements, whose details will be described in a forthcoming publication, enabled the ground state spectroscopic parameters of H$_2$CCCH$^+$ to be determined. Subsequently, pure rotational lines were detected using a vibrational-rotational double resonance (DR) method. Such methods have been reviewed by Asvany & Schlemmer (2021), and the particular scheme involving LOS has only recently been demonstrated by Asvany et al. (2023). An example measurement for H$_2$CCCH$^+$ is shown in Fig. 1.

Double resonance spectra were recorded in multiple individual measurements in which the millimeter-wave frequency (blue arrow in Fig. 1) was stepped in an up-and-down manner several times. Selected rovibrational lines from the $\nu_1$ or the $\nu_3 + \nu_5$ combination band were used for the IR excitation (red arrow in Fig. 1). The frequency steps of the millimeter-wave radiation were kept constant in individual experiments, and varied between 3 and 50 kHz; the larger steps were typically used to search for new lines. The spectroscopic data were normalized employing a frequency switching procedure, in which the H$_2$CCCH$^+$ counts monitored while scanning the spectral range of interest are divided by the counts at an off-resonant millimeter-wave reference frequency. Therefore, the baseline in Fig. 1 is close to unity. The on-resonance signal enhancement is on the order of 1.4, indicating somewhat optimistic uncertainties of our measurements.

3. Quantum chemical calculations

The H$_2$CCCH$^+$ molecular ion has been the subject of several quantum-chemical investigations in the past (e.g., Botschwina et al. 1993, 2011; Huang et al. 2011; Marimuthu et al. 2020, and references therein). In the present study, complementary high-level calculations were performed at the CCSD(T) level of theory (Raghavachari et al. 1989) together with correlation consistent (augmented) polarized valence basis sets (Kendall et al. 1992; Peterson & Dunning 2002) and atomic natural orbital basis sets (Almlöf & Taylor 1987). All calculations were performed using the CFOUR program suite (Matthews et al. 2020; Harding et al. 2008). Equilibrium rotational constants were calculated at the all-electron (ae)-CCSD(T)/cc-pwCVQZ level of theory that is known to yield molecular equilibrium structural parameters of very high quality for molecules comprising first- and second-row elements (e.g., Coriani et al. 2005).

Zero-point vibrational contributions $\sum_i \theta_{iA,B,C}^{A,B,C,\text{calc}} = (\Delta A_0, \Delta R_0, \Delta C_0)$ to the equilibrium rotational constants and centrifugal distortion parameters were calculated at the frozen core (fc)-CCSD(T)/ANO1 level. Best estimate (BE, Tables 2 and A.1) rotational and centrifugal distortion constants were finally obtained through empirical scaling of the calculated rotational parameters using factors (i.e., the ratios $X_{\text{exp}}/X_{\text{calc}}$ of a given parameter) derived from isoelectronic propadienylidene, H$_2$CCC, the pure rotational spectrum of which is known well from a previous study (Vrštek et al. 1990). The technique of empirical scaling using structurally closely related
Table 2. Spectroscopic parameters of H$_2$CCCH$^+$ (in MHz) obtained by fitting Watson’s S-reduced Hamiltonian to the rotational transitions from Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This study</th>
<th>Huang et al. (2011)</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>281 856.2(247)</td>
<td>281 911.9</td>
<td>283 318.43</td>
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<tr>
<td>$B_0$</td>
<td>9675.841(1)</td>
<td>9580.2</td>
<td>9670.18</td>
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<td>$C_0$</td>
<td>9342.877(1)</td>
<td>9251.9</td>
<td>9337.82</td>
</tr>
<tr>
<td>$D_J \times 10^3$</td>
<td>2.942(4)</td>
<td>3.0</td>
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<tr>
<td>$D_J$</td>
<td>0.43889(9)</td>
<td>0.479</td>
<td>0.479</td>
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<tr>
<td>$D_K$</td>
<td>20.678 (c)</td>
<td>20.862</td>
<td>20.678</td>
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<td>0.00</td>
<td>-0.097</td>
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<td>0.00</td>
<td>-0.037</td>
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<td>$\mu_A$ / Debye</td>
<td>...</td>
<td>0.524 (d)</td>
<td>0.55</td>
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</table>

Notes. Western’s PGOPHER program (Western 2017) was used for the fit. The experimental uncertainties are given in parentheses. (a) From equilibrium structure and force field calculated at the ae-CCSD(T)/cc-pwCVQZ and fc-CCSD(T)/ANO1 levels, respectively. (b) Best estimate (BE) values, obtained through scaling of calculated values via isoelectronic propadienylidene, H$_2$CCC (see text for details). (c) Fixed to BE value. (d) From Huang & Lee (2011).

4. Observations

New receivers, built within the Nanocosmos project and installed at the Yebes 40 m radio telescope, were used for the observations of TMC-1 ($\alpha_{2000} = 4^h41^m41.9^s$ and $\delta_{2000} = 25^\circ41^\prime27.0^\prime$). The observations of TMC-1 belong to the ongoing QUIJOTE line survey (Cernicharo et al. 2021a, 2023). A detailed description of the telescope, receivers, and backends is given by Tercero et al. (2021). Briefly, the receiver consists of two cold high electron mobility transistor amplifiers covering the 31.0–50.3 GHz band with horizontal and vertical polarizations. The backends are 2 $\times$ 8.25 GHz fast Fourier transform spectrometers with a spectral resolution of 38.15 kHz providing the coverage of the whole Q-band in both polarizations.

The observations, carried out during different observing runs, were performed using the frequency-switching mode with a frequency throw of 10 MHz in the very first observing runs, during November 2019 and February 2020, 8 MHz during the observations of January–November 2021, and alternating these frequency throws in the last observing runs between October 2021 and February 2023. The total on-source telescope time is 850 h in each polarization (385 and 465 h for the 8 MHz and 10 MHz frequency throws, respectively). The sensitivity of the QUIJOTE line survey varies between 0.17 and 0.25 mK in the 31–50.3 GHz domain. The intensity scale used in this work, antenna temperature ($T_A^*$), was calibrated using two absorbers at different temperatures and the atmospheric transmission model ATM (Cernicharo 1985; Pardo et al. 2001). The calibration uncertainties adopted were 10%. The beam efficiency of the Yebes 40 m telescope in the Q-band is given as a function of frequency by $B_{eff} = 0.797 \exp[-(v(GHz)/71.1)^2]$. The forward telescope efficiency is 0.97. The telescope beam size varies from 56.7″ at 31 GHz to 35.6″ at 49.5 GHz.

The data of TMC-1 taken with the IRAM 30 m telescope consist of a 3 mm line survey obtained with the old ABCD receivers connected to an autocorrelator that provided a spectral resolution of 40 kHz (Marcelino et al. 2007; Cernicharo et al. 2012). Some additional high-sensitivity frequency windows observed in 2021 used the new 3 mm EMIR dual polarization receiver connected to four fast Fourier transform spectrometers providing a spectral resolution of 49 kHz (Agúndez et al. 2022; Cabezas et al. 2022a). All the observations were performed using the frequency switching method. The final 3 mm line survey has a sensitivity of 2–10 mK. However, at some selected frequencies the sensitivity is as low as 0.6 mK.

5. Detection of H$_2$CCCH$^+$ in TMC-1

We searched for one para (2$_{02}$-1$_{01}$) and two ortho (2$_{12}$-1$_{11}$, 2$_{11}$-1$_{10}$) lines of H$_2$CCCH$^+$ within the QUIJOTE line survey. The three lines were clearly detected and are shown in Fig. 2. In the data at 3 mm we covered the frequencies of three para and four ortho lines, with upper levels $J = 4, 5, 6$ and energies below 30 K. Only one line, the $J = 5_{14}$–$4_{13}$, falls in one of the high-sensitivity windows ($\sigma = 0.6$ mK) of our line survey, and it was also clearly detected (see Fig. 2). Two other lines are within frequency ranges with $\sigma$ below 2 mK, and were marginally detected. The derived line parameters for all searched transitions of H$_2$CCCH$^+$ are given in Table B.1. We checked that the detected lines cannot be assigned to lines of other species or isotopologs by exploring the spectral catalogs MADEX (Cernicharo 2012), CDMS (Müller et al. 2005), and JPL (Pickett et al. 1998).

To estimate the column density of H$_2$CCCH$^+$, we considered the ortho and para levels as belonging to two different species. For the dipole moment we used the value of 0.55 D calculated in this work. No collisional rates are available for this molecule. However, Khalifa et al. (2019) computed the

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1 ERC grant ERC-2013-Syg-610256-NANOCOSMOS. [https://nanocosmos.iff.csic.es/](https://nanocosmos.iff.csic.es/)

2 Q-band Ultrasp rivals Inspection Journey to the Obscure TMC-1 Environment
collisional rates between He and H$_2$CCC. This cumulenic species is isoelectronic with our molecule and has a very similar structure. We therefore adopted these rates, correcting for the abundance of He with respect to H$_2$, to estimate the excitation temperatures of the observed transitions of H$_2$CCC$^+$. Assuming a volume density of (1–3)$\times$10$^8$ cm$^{-3}$ (Fossé 2001; Lique et al. 2006; Pratap et al. 1997), we derive excitation temperatures close to 10 K for the $J = 2$–1 lines, and ~8–10 K for the lines in the 3 mm domain, the largest value corresponding to $n$(H$_2$) = 3$\times$10$^{10}$ cm$^{-3}$. These excitation temperatures are considerably larger than those obtained for H$_2$CCC, which are between 4 and 5 K, due to the larger dipole moment of this species (4.1 vs. 0.55 D). From the adopted rotational temperatures of 9 K, and assuming a source of uniform brightness temperature with a radius of 40" (Fossé 2001), we derive a column density for ortho-H$_2$CCC$^+$ of (5.4±1)$\times$10$^{14}$ cm$^{-2}$. For the para species the estimated column density is (1.6±0.5)$\times$10$^{14}$ cm$^{-2}$, a value that is consistent with the expected ortho to para ratio of 3/1. The computed synthetic spectra show excellent agreement with the observed line intensities (see Fig. 2). Hence, the total column density of H$_2$CCC$^+$ in TMC-1 is (7.0±1.5)$\times$10$^{11}$ cm$^{-2}$.

It is interesting to compare the abundance of H$_2$CCC$^+$ to that of H$_2$CCC. For the latter species we detected, with an excellent signal-to-noise ratio, all its ortho and para lines in the frequency range of our line surveys. The derived line parameters are summarized in Table B.2 and the lines are shown in Fig. B.1. The decline of the line intensity between the $J_u = 2$ and $J_u = 5$ lines is obvious in Fig. B.1, which indicates that the lines are not thermalized to the kinetic temperature of the cloud for this species. Using the collisional rates of Khalifa et al. (2019), and adopting the same assumptions on the source size as for H$_2$CCC$^+$, we derive a column density for the ortho and para species of (1.5±0.1)$\times$10$^{12}$ and (0.45±0.05)$\times$10$^{12}$ cm$^{-2}$, respectively. The best fit is obtained for a density of $n$(H$_2$) = 8$\times$10$^9$ cm$^{-3}$. The total column density of H$_2$CCC is (1.95±0.15)$\times$10$^{12}$ cm$^{-2}$ and the ortho-to-para ratio for this species is 3.3±0.6. The H$_2$CCC/H$_2$CCC$^+$ abundance ratio is 2.8±0.7 which is on the order of that found for C$_3$O/H$_2$O$^+$ (Cernicharo et al. 2020b), but much lower than the abundance ratio found in TMC-1 for other neutral species and their protonated forms (Marcelino et al. 2020; Cernicharo et al. 2021b,c; Cabezas et al. 2022b; Agúndez et al. 2022).

6. Discussion

To describe the chemistry of H$_2$CCC$^+$, we used the Nautilus code (Ruaud et al. 2016), a three-phase (gas, dust grain ice surface, and dust grain ice mantle) time-dependent chemical model with a chemical network for C$_3$H$^+$ species very similar to that presented in Loison et al. (2017). To describe the physical conditions in TMC-1, we used a homogeneous cloud with a density equal to 2.5$\times$10$^9$ cm$^{-3}$, a temperature equal to 10 K for both the gas and the dust, a visual extinction of 30 mag, and a cosmic-ray ionization rate of 1.3$\times$10$^{-17}$ s$^{-1}$. All elements are assumed to be initially in atomic form, except for hydrogen, which is entirely molecular (Hincelin et al. 2011). The calculated abundances relative to H$_2$ for H$_2$CCC and H$_2$CCC$^+$, and also for C$_3$ and C$_3$H$^+$, which are strongly linked to H$_2$CCC$^+$, are shown in Fig. 3.

As can be seen in Fig. 3, the H$_2$CCC and H$_2$CCC$^+$ abundances observed are relatively well reproduced by the model for a relatively early molecular cloud age of around 2$\times$10$^6$ years, however, with a lower H$_2$CCC/H$_2$CCC$^+$ ratio than the one observed. Looking in more detail at the chemistry of H$_2$CCC$^+$ and H$_2$CCC (see Fig. 3 of Loison et al. 2017), it appears that H$_2$CCC$^+$ is a product of H$_2$CCC$^+$ (and also of c-C$_3$H$_2^+$), but that the flow of protonation of H$_2$CCC toward H$_2$CCC$^+$ is a very minor pathway for the formation of H$_2$CCC$^+$, which is almost essentially produced by the reaction C$_3$H$^+$ + H$_2$. This inverted link between H$_2$CCC and H$_2$CCC$^+$ explains the unusually high MH$^+$/M ratio compared to those cases in which the protonated form comes from the protonation of the neutral form (Agúndez et al. 2022).

Considering the link between C$_3$H$^+$, H$_2$CCC$^+$, and C$_3$, it is interesting to see if the observations of H$_2$CCC$^+$ (this work) combined to the observation of C$_3$H$^+$ (Cernicharo et al. 2022) allow us to estimate the abundance of C$_3$, which in our dense cloud model is the second carbon reservoir, accounting for up to 15% of carbon. If C$_3$ does not react with atomic oxygen, as calculated by Woon & Herbst (1996), the protonation reactions of C$_3$ producing C$_3$H$^+$ are by far the main reactions of destruction of C$_3$ and of production of C$_3$H$^+$. As these protonation reactions control the destruction of C$_3$, the uncertainties on the rates affect the abundance of C$_3$, but do not change...
the flux of these reactions. The underestimation of \( \text{C}_3 \) in the model is therefore not related to these protonation rates, but to the rate of the reaction \( \text{C}_3 \text{H}^+ + \text{H}_2 \rightarrow 3 \text{H}_2 \) at 10 K by a factor of 3 allows us to reproduce the abundance of \( \text{C}_3 \text{H}^+ \) observed by Cernicharo et al. (2022), as shown in Fig. 3. This change in the rate coefficient does not affect the flux of the \( \text{C}_3 \text{H}^+ + \text{H}_2 \) reaction, and therefore does not affect the abundance of \( \text{H}_2 \text{CCC}^+ \), as long as the branching ratios to \( \text{H}_2 \text{CCC}^+ \) and \( \text{c-C}_3 \text{H}^+ \) are not varied. Since \( \text{H}_2 \text{CCC}^+ \) is mainly destroyed by the reaction with electrons, its abundance is controlled by the rate of this reaction, which is known only over the temperature range 172–489 K (McLain et al. 2005) with a temperature dependency inconsistent with theory. An increase in this rate at 10 K by a factor of 5, which is not impossible given the uncertainties, allows us to reproduce the observation for \( \text{H}_2 \text{CCC}^+ \) with a ratio between \( \text{H}_2 \text{CCC}/\text{H}_2 \text{CCC}^+ \) that is very close to the observed value. Considering the uncertainties of the different chemical reactions linking \( \text{C}_3 \) to \( \text{C}_3 \text{H}^+ \) and \( \text{H}_2 \text{CCC}^+ \), the observations of \( \text{C}_3 \text{H}^+ \) (Cernicharo et al. 2022) and \( \text{H}_2 \text{CCC}^+ \) (this work) validate the chemical scheme controlling the formation of cyclic and linear \( \text{C}_3 \text{H}_2 \) and \( \text{C}_3 \text{H}_3 \) and the high gas-phase abundance of \( \text{C}_3 \) in TMC-1, around \( 10^{-5} \) relative to \( \text{H}_2 \).

It would also be very interesting to know the abundance of the more stable cyclic isomer \( \text{c-C}_3 \text{H}_3^+ \), which in the chemical model is predicted to be slightly more abundant (by a factor of three) than \( \text{H}_2 \text{CCC}^+ \). This species has no dipole moment, but its deuterated version, \( \text{c-C}_3 \text{H}_2 \text{D}^+ \), has a low dipole moment of 0.225 D (Huang & Lee 2011) and its rotational spectrum has been recently measured in the 90–230 GHz frequency range in Cologne (Gupta et al. 2023). We searched for \( \text{c-C}_3 \text{H}_2 \text{D}^+ \) in the QUIJOTE line survey but at the current level of sensitivity, this species is not detected and we derive an upper limit to its column density of \( 4 \times 10^{12} \) \( \text{cm}^{-3} \). Assuming that the \( \text{C}_3 \text{H}_2^+ / \text{c-C}_3 \text{H}_2 \text{D}^+ \) ratio is 10, as found for the analog case of \( \text{CH}_3 \text{CH}_3 \) with three equivalent H nuclei (Cabezas et al. 2021), the column density of \( \text{c-C}_3 \text{H}_3^+ \) is \( <4 \times 10^{12} \) \( \text{cm}^{-2} \), which is not very meaningful.

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Appendix A: Structural calculations, internal coordinates

Bond lengths are given in Å; angles are given in degrees.

A.1. $\text{H}_2\text{CCCH}^+$

$\text{H}_2\text{CCH}^+$, CCSD(T)/cc-pwCVQZ

\begin{align*}
\text{H} & \\
\text{C} & 1 \ r_1 \\
\text{X} & 2 \ r_d \ 1 \ \text{a}90 \\
\text{C} & 2 \ r_2 \ 3 \ \text{a}90 \ 1 \ \text{d}180 \\
\text{X} & 4 \ r_d \ 2 \ \text{a}90 \ 3 \ \text{d}0 \\
\text{C} & 4 \ r_3 \ 5 \ \text{a}90 \ 2 \ \text{d}180 \\
\text{H} & 6 \ r_4 \ 4 \ \text{a}1 \ 5 \ \text{d}0 \\
\text{H} & 6 \ r_4 \ 4 \ \text{a}1 \ 5 \ \text{d}180 \\
\text{r}_1 & = 1.073118130747218 \\
\text{r}_d & = 1.000000818629780 \\
\text{a}90 & = 90.000000000000000 \\
\text{r}_2 & = 1.228490857165352 \\
\text{d}180 & = 180.000000000000000 \\
\text{d}0 & = 0.000000000000000 \\
\text{r}_3 & = 1.346565030012042 \\
\text{r}_4 & = 1.086025065701484 \\
\text{a}1 & = 120.382476682815607 \\
\end{align*}

$\text{H}_2\text{CCH}^+$, CCSD(T)/ANO1

\begin{align*}
\text{H} & \\
\text{C} & 1 \ r_1 \\
\text{X} & 2 \ r_d \ 1 \ \text{a}90 \\
\text{C} & 2 \ r_2 \ 3 \ \text{a}90 \ 1 \ \text{d}180 \\
\text{X} & 4 \ r_d \ 2 \ \text{a}90 \ 3 \ \text{d}0 \\
\text{C} & 4 \ r_3 \ 5 \ \text{a}90 \ 2 \ \text{d}180 \\
\text{H} & 6 \ r_4 \ 4 \ \text{a}1 \ 5 \ \text{d}0 \\
\text{H} & 6 \ r_4 \ 4 \ \text{a}1 \ 5 \ \text{d}180 \\
\text{r}_1 & = 1.074705266639338 \\
\text{r}_d & = 1.000000204657382 \\
\text{a}90 & = 90.000000000000000 \\
\text{r}_2 & = 1.234261558515133 \\
\text{d}180 & = 180.000000000000000 \\
\text{d}0 & = 0.000000000000000 \\
\text{r}_3 & = 1.351397370372584 \\
\text{r}_4 & = 1.088292080166718 \\
\text{a}1 & = 120.373581553220575 \\
\end{align*}

A.2. $\text{H}_2\text{CCC}$

$\text{H}_2\text{CCC}$, CCSD(T)/cc-pwCVQZ

\begin{align*}
\text{C} & \\
\text{C} & 1 \ r_1 \\
\text{X} & 2 \ r_d \ 1 \ \text{a}90 \\
\text{C} & 2 \ r_2 \ 3 \ \text{a}90 \ 1 \ \text{d}180 \\
\text{H} & 4 \ r_3 \ 2 \ \text{a}1 \ 3 \ \text{d}0 \\
\text{H} & 4 \ r_3 \ 2 \ \text{a}1 \ 5 \ \text{d}180 \\
\text{r}_1 & = 1.287645153115967 \\
\text{r}_d & = 1.000000000000000 \\
\text{a}90 & = 90.000000000000000 \\
\text{r}_2 & = 1.327897213723068 \\
\text{d}180 & = 180.000000000000000 \\
\text{r}_3 & = 1.083584615827809 \\
\text{a}1 & = 121.271597504509145 \\
\text{d}0 & = 0.000000000000000 \\
\end{align*}

$\text{H}_2\text{CCC}$, CCSD(T)/ANO1

\begin{align*}
\text{C} & \\
\text{C} & 1 \ r_1 \\
\text{X} & 2 \ r_d \ 1 \ \text{a}90 \\
\text{C} & 2 \ r_2 \ 3 \ \text{a}90 \ 1 \ \text{d}180 \\
\text{H} & 4 \ r_3 \ 2 \ \text{a}1 \ 3 \ \text{d}0 \\
\text{H} & 4 \ r_3 \ 2 \ \text{a}1 \ 5 \ \text{d}180 \\
\text{r}_1 & = 1.294632885150227 \\
\text{r}_d & = 1.000000204657382 \\
\text{a}90 & = 90.000000000000000 \\
\text{r}_2 & = 1.33303062830918 \\
\text{d}180 & = 180.000000000000000 \\
\text{r}_3 & = 1.085894615830395 \\
\text{a}1 & = 121.302559724582778 \\
\text{d}0 & = 0.000000000000000 \\
\end{align*}
Table A.1. Calculated and experimental spectroscopic parameters of H$_2$CCC and H$_2$CCCH$^+$ (in MHz). Equilibrium rotational constants calculated at the ae-CCSD(T)/cc-pwCVQZ level of theory; zero-point vibrational corrections $\Delta A_0$, $\Delta B_0$, $\Delta C_0$; and centrifugal distortion constants calculated at the fc-CCSD(T)/ANO1 level. Best theoretical estimates for the rotational and centrifugal distortion constants $X$ of H$_2$CCCH$^+$ are estimated as $X_{\text{scaled}} = \frac{X_{\text{H}_2\text{CCC}}}{X_{\text{H}_2\text{CCC}}} \times X_{\text{H}_2\text{CCCH}^+}$ (i.e., using isoelectronic H$_2$CCC as a calibrator).

<table>
<thead>
<tr>
<th>Parameter $^a$</th>
<th>Experiment Vrtilek et al. (1990)</th>
<th>Calculated This study</th>
<th>Calculated This study</th>
<th>Scaled This study, BE</th>
<th>Experiment This study</th>
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<td>$A_e$</td>
<td>$\cdots$</td>
<td>292302 .539</td>
<td>285650 .316</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$B_e$</td>
<td>$\cdots$</td>
<td>10578 .491</td>
<td>9675 .219</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$C_e$</td>
<td>$\cdots$</td>
<td>10209 .024</td>
<td>9358 .247</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\Delta A_0$</td>
<td>$\cdots$</td>
<td>2357 .134</td>
<td>2331 .884</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\Delta B_0$</td>
<td>$\cdots$</td>
<td>$-3$ .807</td>
<td>5 .043</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$\Delta C_0$</td>
<td>$\cdots$</td>
<td>10 .869</td>
<td>20 .431</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$A_0$</td>
<td>288783 (.34)</td>
<td>289945 .405</td>
<td>283318 .432</td>
<td>282182 .595</td>
<td>281856 .247</td>
</tr>
<tr>
<td>$B_0$</td>
<td>10588 .639(2)</td>
<td>10582 .298</td>
<td>9670 .175</td>
<td>9675 .970</td>
<td>9675 .841(1)</td>
</tr>
<tr>
<td>$C_0$</td>
<td>10203 .966(2)</td>
<td>10198 .155</td>
<td>9337 .816</td>
<td>9343 .136</td>
<td>9342 .877(1)</td>
</tr>
<tr>
<td>$D_J \times 10^3$</td>
<td>.4 .248(2)</td>
<td>.722</td>
<td>.684</td>
<td>.606</td>
<td>.942(4)</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>0 .5164(5)</td>
<td>.571</td>
<td>.479</td>
<td>.4328</td>
<td>.4388(9)</td>
</tr>
<tr>
<td>$d_1 \times 10^3$</td>
<td>$-0$ .153(2)</td>
<td>$-0$ .143</td>
<td>$-0$ .996</td>
<td>$-0$ .103</td>
<td>$-0$ .121(3)</td>
</tr>
<tr>
<td>$d_2 \times 10^3$</td>
<td>$-0$ .070(1)</td>
<td>$-0$ .050</td>
<td>$-0$ .037</td>
<td>$-0$ .051</td>
<td>$-0$ .051$^a$</td>
</tr>
</tbody>
</table>

Notes. “Kept fixed in the analysis.”
Appendix B: Line parameters of H₃CCCH⁺ and H₂CCC

The line parameters of H₃CCCH⁺ and H₂CCC were obtained by fitting a Gaussian line profile to the observed data. The results are given in Tables B.1 and B.2, respectively. The observed lines of H₂CCCH⁺ are shown in Fig. 2 and those of H₂CCC in Fig. B.1.

### Table B.1. Line parameters of the observed transitions of H₂CCCH⁺ in TMC-1.

<table>
<thead>
<tr>
<th>Transition</th>
<th>ν_{obs}^a (MHz)</th>
<th>∫ T_A^b dv^b (mK × km s⁻¹)</th>
<th>Δν^c (kms⁻¹)</th>
<th>T_A^d (mK)</th>
<th>σ^f (mK)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_{1,2} - 1_{1,1}</td>
<td>37702.627±0.010</td>
<td>0.38±0.13</td>
<td>0.63±0.20</td>
<td>0.56</td>
<td>0.13</td>
<td>A</td>
</tr>
<tr>
<td>2_{0,2} - 1_{0,1}</td>
<td>38037.044±0.010</td>
<td>0.36±0.09</td>
<td>0.78±0.17</td>
<td>0.43</td>
<td>0.13</td>
<td>B</td>
</tr>
<tr>
<td>2_{1,1} - 1_{1,0}</td>
<td>38368.581±0.010</td>
<td>0.57±0.07</td>
<td>0.77±0.11</td>
<td>0.70</td>
<td>0.13</td>
<td>C</td>
</tr>
<tr>
<td>4_{0,4} - 3_{0,3}</td>
<td>76071.062±0.020</td>
<td>2.28±0.07</td>
<td>0.40±0.10</td>
<td>5.50</td>
<td>1.80</td>
<td>CD</td>
</tr>
<tr>
<td>4_{1,3} - 3_{1,2}</td>
<td>76735.888±0.020</td>
<td>2.04</td>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5_{1,5} - 4_{1,4}</td>
<td>94254.055±0.004</td>
<td>3.27±0.08</td>
<td>0.85±0.23</td>
<td>3.60</td>
<td>1.40</td>
<td>BD</td>
</tr>
<tr>
<td>5_{0,5} - 4_{0,4}</td>
<td>95085.988±0.030</td>
<td>1.04±0.20</td>
<td>0.80±0.10</td>
<td>3.80</td>
<td>0.60</td>
<td>B</td>
</tr>
<tr>
<td>6_{1,6} - 5_{1,5}</td>
<td>111303.272±0.004</td>
<td>1.1</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6_{0,6} - 5_{0,5}</td>
<td>114099.086±0.006</td>
<td>4.90</td>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes.** aObserved frequency assuming a ν_{LSR} of 5.83 km s⁻¹. bIntegrated line intensity in mK × km s⁻¹. cLine width in km s⁻¹. dAntenna temperature in mK. eRoot mean square noise of the data. fBlended with a weak feature at 38638.7 MHz. gFor undetected lines their rest frequencies correspond to the observed frequency in the laboratory (Table 1) or to the predicted value from the molecular constants of Table 2. hThe feature appears too strong. iMarginal detection.

### Table B.2. Line parameters of the observed transitions of H₂CCC in TMC-1.

<table>
<thead>
<tr>
<th>Transition</th>
<th>ν_{obs}^a (MHz)</th>
<th>∫ T_A^b dv^b (mK × km s⁻¹)</th>
<th>ν_{LSR}^c (MHz)</th>
<th>Δν^d (kms⁻¹)</th>
<th>T_A^e (mK)</th>
<th>σ^f (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2_{1,2} - 1_{1,1}</td>
<td>41198.335±0.002</td>
<td>82.7±0.1</td>
<td>5.70±0.01</td>
<td>0.65±0.01</td>
<td>120.4</td>
<td>0.1</td>
</tr>
<tr>
<td>2_{0,2} - 1_{0,1}</td>
<td>41584.675±0.001</td>
<td>57.8±0.1</td>
<td>5.76±0.01</td>
<td>0.63±0.01</td>
<td>86.9</td>
<td>0.2</td>
</tr>
<tr>
<td>2_{1,1} - 1_{1,0}</td>
<td>41967.671±0.002</td>
<td>84.6±0.1</td>
<td>5.75±0.01</td>
<td>0.61±0.01</td>
<td>130.8</td>
<td>0.2</td>
</tr>
<tr>
<td>4_{1,4} - 3_{1,3}</td>
<td>82395.089±0.003</td>
<td>61.9±1.3</td>
<td>5.71±0.01</td>
<td>0.47±0.01</td>
<td>124.8</td>
<td>3.0</td>
</tr>
<tr>
<td>4_{0,4} - 3_{0,3}</td>
<td>83165.345±0.003</td>
<td>31.9±0.4</td>
<td>5.77±0.02</td>
<td>0.54±0.01</td>
<td>55.5</td>
<td>0.9</td>
</tr>
<tr>
<td>4_{1,3} - 3_{1,2}</td>
<td>83933.699±0.003</td>
<td>56.6±0.4</td>
<td>5.75±0.02</td>
<td>0.54±0.01</td>
<td>97.9</td>
<td>0.9</td>
</tr>
<tr>
<td>5_{1,5} - 4_{1,4}</td>
<td>102992.379±0.004</td>
<td>25.4±1.2</td>
<td>5.73±0.02</td>
<td>0.47±0.03</td>
<td>51.1</td>
<td>3.1</td>
</tr>
<tr>
<td>5_{0,5} - 4_{0,4}</td>
<td>103952.926±0.003</td>
<td>86.7±1.1</td>
<td>5.71±0.03</td>
<td>0.29±0.05</td>
<td>28.0</td>
<td>3.6</td>
</tr>
<tr>
<td>5_{1,4} - 4_{1,3}</td>
<td>104915.583±0.003</td>
<td>19.0±1.1</td>
<td>5.77±0.03</td>
<td>0.48±0.03</td>
<td>37.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

**Notes.** aAdopted rest frequencies from the CDMS entry for H₂CCC. bIntegrated line intensity in mK × km s⁻¹. cVelocity of the line in km s⁻¹. dLine width in km s⁻¹. eAntenna temperature in mK. fRoot mean square noise of the data.
Fig. B.1. Observed lines of H$_2$CCC in the 31-115 GHz domain toward TMC-1. The abscissa corresponds to the velocity of the cloud with respect to the Local Standard of Rest ($v_{\text{LSR}}$). The ordinate is the antenna temperature corrected for atmospheric and telescope losses in mK. The spectral resolution is 38 kHz below 50 GHz and 48 kHz above. Derived line parameters are given in Table B.2. The red lines show the computed synthetic spectra for the lines of H$_2$CCC (see text). The lines in the left column correspond to para lines of H$_2$CCC, while those of the central and right columns correspond to transitions of the ortho species. The adopted frequencies are those of the CDMS catalog (Müller et al. 2005) and are given in Table B.2.