First detection of doubly deuterated methyl acetylene
(CHD₂CCH and CH₂DCCD)*

M. Agúndez¹, E. Roueff², C. Cabezas¹, J. Cernicharo¹, and N. Marcelino¹

¹ Instituto de Física Fundamental, CSIC, C/ Serrano 123, 28006 Madrid, Spain
  e-mail: marcelino.agunde@csic.es
² LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Université, 92190 Meudon, France

Received 22 March 2021 / Accepted 9 April 2021

ABSTRACT

We report the first detection in space of the two doubly deuterated isotopologues of methyl acetylene. The species CHD₂CCH and CH₂DCCD were identified in the dense core L483 through, respectively, nine and eight rotational lines in the 72–116 GHz range using the 30 m telescope of the Institut de Radioastronomie Millimétrique (IRAM). We combined the astronomical frequencies observed here with laboratory frequencies from the literature measured in the 29–47 GHz range to derive more accurate spectroscopic parameters for the two isotopologues. We derive beam-averaged column densities of (2.7 ± 0.5) × 10¹⁴ cm⁻² for CHD₂CCH and (2.2 ± 0.4) × 10¹⁴ cm⁻² for CH₂DCCD, which translate to abundance ratios of CH₃CCH/CHD₂CCH = 34 ± 10 and CH₃CCH/CH₂DCCD = 42 ± 13. The doubly deuterated isotopologues of methyl acetylene are only a few times less abundant than the singly deuterated ones, specifically around 2.4 times less abundant than CH₃CCH. The abundances of the different deuterated isotopologues with respect to CH₃CCH are reasonably accounted for by a gas-phase chemical model in which deuteration occurs from the precursor ions C₆H₅D⁺ and C₆H₅D⁺, when the ortho-to-para ratio of molecular hydrogen is sufficiently low. This points to gas-phase chemical reactions, rather than grain-surface processes, as being responsible for the formation and deuteration fractionation of CH₃CCH in L483. The abundance ratios CH₃DCCD/CH₃CCH = 3.0 ± 0.9 and CH₂DCCD/CH₃CCH = 1.25 ± 0.37 observed in L483 are consistent with the statistically expected values of three and one, respectively, with the slight overabundance of CHD₂CCH compared to CH₂DCCD being well explained by the chemical model.

Key words. astrochemistry – line: identification – molecular processes – ISM: molecules – radio lines: ISM

1. Introduction

Deuterium fractionation is an extraordinary tool to study the early stages of star formation. It can shed particular light on the pre-stellar core phase, during which the cold temperatures and high CO depletion offer optimal conditions to enrich molecules in deuterium, and on the protostellar Class 0 phase, when the gas displays some of the largest levels of deuteration observed as a consequence of the inheritance of gas and ice molecules enriched in deuterium during the pre-stellar core phase (Cecarelli et al. 2014). The cosmic D/H ratio is 1.5 × 10⁻⁵ (Linsky 2003), but deuterium fractionation is so efficient in these environments that deuterated molecules can reach abundances as high as 30–40% relative to the parent hydrogenated species, as occurs for HDCS (Marcelino et al. 2005) and CH₃DOH (Parise et al. 2006). Moreover, for abundant molecules containing more than one hydrogen atom, multiply deuterated forms have been observed with abundance enhancements of many orders of magnitude over the statistically expected value.

Molecules with two deuterium atoms observed to date comprise D₂CO (Turner 1990; Cecarelli et al. 1998), NHD₂ (Roueff et al. 2000), CHD₂OH (Parise et al. 2002), D₂S (Vastel et al. 2003), D₂H⁺ (Vastel et al. 2004; Parise et al. 2011), D₂CS (Marcelino et al. 2005), D₂O (Butner et al. 2007), c-C₃D₂ (Spezzano et al. 2013), CHD₂CN (Calcutt et al. 2018), HCOOCHD₂ (Manigand et al. 2019), and ND₂ (Melosso et al. 2020; Bacmann et al. 2020). Even two triply deuterated molecules have been detected: ND₃ (Lis et al. 2002; van der Tak et al. 2002; Roueff et al. 2005) and CD₂OH (Parise et al. 2004). Multiply deuterated molecules have abundances relative to the hydrogenated species ranging from 5 × 10⁻³ to, in the case of D₂O for hot corino conditions (Butner et al. 2007), to values of the order of 10% in cold dark cloud environments, which may become comparable to those of the corresponding singly deuterated species, as occurs for D₂CS (Marcelino et al. 2005; Vastel et al. 2018; Agúndez et al. 2019) and D₂CO (Parise et al. 2006). It is remarkable that in the case of the ion H₃⁺, whose deuterated species drive most of the deuterium fractionation in the gas phase, the doubly deuterated form (first detected unambiguously by Parise et al. 2011) has an abundance similar to that of the singly deuterated species. Moreover, chemical models predict that the different deuterated species H₂D⁺, D₂H⁺, and D₃⁺ become occasionally more abundant than H₃⁺ itself for some time intervals and specific physical conditions (Roberts et al. 2004; Sipilä et al. 2017).

Multiply deuterated molecules enable us to put constraints on the deuteration mechanism, either in the gas phase or on the surface of dust grains, and by extension on the formation process of the precursor hydrogenated molecule. If deuterium fractionation occurs in the gas phase, the resulting abundance ratios between singly, doubly, and even triply deuterated forms of a given molecule vary depending on the abundances of H₂D⁺, D₂H⁺, and D₃⁺ and the efficiency of the reactions of deuteron transfer from these ions, which in turn depend on parameters such as the gas kinetic temperature, the level of CO.
depletion, and the ortho-to-para ratio of H₂ (Roberts et al. 2004; Roueff et al. 2005; Flower et al. 2006). If deuteration occurs on grains surfaces, the relative abundances of the different deuterated forms of a molecule are expected to follow a statistical pattern as they should basically depend on the relative arrival rates on grains of D and H atoms from the gas phase, and thus on the abundance ratio between atomic D and H in the gas phase (Brown & Millar 1989).

For molecules with various hydrogen atoms among which some are equivalent, the relative abundances of the different deuterated variants can also give clues to the formation of the molecule. For example, for methanol (CH₃OH) deuteration on the methyl group is three times more probable than on the hydroxyl group, but observed CH₃DOH/CH₃OD ratios differ significantly from the statistical value of three, with values well above or below depending on the source (Parise et al. 2006; Ratajczak et al. 2011; Agúndez et al. 2019). The case of methyl acetylene (CH₃CCH) is also interesting as, similarly to methanol, it contains a methyl group with three equivalent H atoms and one non-equivalent H atom in the terminal CCH group. The two singly deuterated forms of CH₃CCH, CH₂DCCH and CH₂CCD, were first detected in the interstellar medium by Gerin et al. (1992) and Markwick et al. (2005), respectively. Using the Arizona Radio Observatory (ARO) 12 m telescope, Markwick et al. (2005) reported CH₂DCCH/CH₂CCD ratios in the range 1.20–2.04 along the TMC-1 ridge, significantly different from the statistical value of three, although in L483 the observed ratio is consistent with the statistical value (Agúndez et al. 2019).

Here, we report the first identification in space of the two forms of doubly deuterated methyl acetylene: CHD₂CCH and CH₂DCCD. These species were detected toward the dense core L483 using the 30 m telescope of the Institut de Radioastronomie Millimétrique (IRAM). Following observation of the two singly and two doubly deuterated forms of methyl acetylene, we built a gas-phase chemical model, including multiply deuterated species, to investigate the mechanisms of deuteration of CH₃CCH in L483.

2. Observations

The target of the observations, L483, is a dark cloud core located in the Aquila Rift star-forming region, which hosts an embedded infrared source, IRAS 18148–0440, classified as a Class 0 object. The observations were carried out with the IRAM 30 m telescope in the frame of a λ 3 mm line survey covering the 80–116 GHz range (Agúndez et al. 2019). Additional observations in the 72–80 GHz range were taken with the IRAM 30 m telescope in December 2018. Weather conditions were good during this observing run, with 4–5 mm of precipitable water vapor.

We briefly describe the observations. For more details, we refer the reader to Agúndez et al. (2019). We used the Eight MIxer Receiver (EMIR) E090 connected to a fast Fourier transform spectrometer that provided a spectral resolution of 50 kHz. All observations were carried out using the frequency-switching technique, with a frequency throw of 7.2 MHz. Intensities are expressed in terms of TS, the antenna temperature corrected for atmospheric absorption and for antenna ohmic and spillover losses. The uncertainty in TS is estimated to be 10%. The antenna temperature TS can be converted to main beam brightness temperature Tmb by dividing by Beff/Fσ, where Beff = 0.871 exp[–(ν(GHz)/359)²] and Fσ = 0.95¹. Pointing errors were typically 2–3″ and the half power beam width of the IRAM 30 m telescope ranges between 34″ at 72 GHz and 21″ at 116 GHz. All data were reduced using the program CLASS of the GILDAS software package².

3. Results

3.1. Detection of CHD₂CCH and CH₂DCCD in L483

In the data of L483 covering the 72–116 GHz frequency range, there are several lines that could not be assigned to any known molecule after inspection of the Cologne Database for Molecular Spectroscopy (CDMS) catalog³ (Müller et al. 2005) and the Jet Propulsion Laboratory (JPL) catalog⁴ (Pickett et al. 1998). Several of these unidentified lines could be grouped in sets of three lines with harmonic relations 5/6/7 and with rotational constants around either 7700 MHz or 7400 MHz. These values are close to the rotational constants B or (B + C)/2 of the isotopologues of methyl acetylene. For example, for CH₂CCD the rotational constant B is 7788 MHz and for CH₂DCCH the value of (B + C)/2 is 8091 MHz (Le Guennec et al. 1993). A closer inspection of the private catalog of J. Cernicharo generated from the MADEX code⁵ (Cernicharo 2012) revealed that the observed frequencies of these sets of harmonically related lines differ by 0.9–2.7 MHz and 0.2–1.7 MHz from the frequencies predicted for rotational transitions of CH₂CCH and CH₂DCCD, respectively. The rotational spectrum of these two molecules has been measured in the laboratory in the frequency range 29–47 GHz with uncertainties of 0.1 MHz in the frequencies (Thomas et al. 1955). Using these data, the frequencies predicted for the 72–116 GHz range have errors of a few megahertz, and this is the reason why some of the unidentified lines seen in the 80–116 GHz range were not properly assigned to CH₂CCH and CH₂DCCH by Agúndez et al. (2019). In fact, the identification of these two molecules drastically reduces the number of lines pending identification in the λ 3 mm line survey of L483 (see Table A.2 of Agúndez et al. 2019). The parameters derived for the lines assigned to the two doubly deuterated isotopologues of methyl acetylene are given in Table 1 and the observed line profiles are shown in Fig. 1 for CH₂CCH and in Fig. 2 for CH₂DCCD. We note that the line at 91971.307 MHz, assigned to the 61,6–51,5 transition of CH₂CCH, was incorrectly assigned to the transition 53–43 F = 6–5 of CH₂CN by Agúndez et al. (2019).

The astronomical frequencies observed in the 72–116 GHz range (see Table 1) and the laboratory frequencies measured in the 29–47 GHz range (Thomas et al. 1955) were used to derive more accurate spectroscopic parameters for CH₂CCH and CH₂DCCD (see Table 2). These constants are a considerable improvement on those reported by Thomas et al. (1955) and enable us to predict the rotational spectrum of the two molecules with an accuracy better than 0.1 MHz up to 200 GHz. Since the lines of doubly deuterated CH₂CCH are relatively bright in L483, it would not be surprising to detect the triply deuterated species CH₂CCD, which should be three times more abundant than CH₂CCH. However, the rotational spectrum has only been measured in the 28–43 GHz range with modest accuracy (Thomas et al. 1955), which may translate to frequency errors of a few megahertz for lines lying above 72 GHz. It would therefore be interesting to measure the

¹ http://www.iram.es/IRAMES/mainWiki/Iram30mmEfficiencies
² http://www.iram.fr/IRAMFR/GILDAS
³ https://cdms.astro.uni-koeln.de/
⁴ https://spec.jpl.nasa.gov/
⁵ https://nanocosmos.iff.csic.es/?page_id=1619
We derived beam-averaged column densities for methyl acetylene, CH$_3$CCH, and its singly and doubly deuterated isotopologues in L483 assuming local thermodynamic equilibrium. Values for CH$_3$CCH and the two singly deuterated forms were already reported by Agúndez et al. (2019). Here we have revised some of these values including new lines observed in the 72–80 GHz range and using new values for the electric dipole moments.

The dipole moment of CH$_3$CCH was experimentally measured by Burrell et al. (1980) to be 0.7839 D. For CH$_3$CCH, the dipole moment was measured by Muenter & Laurie (1966). Here, we adopt the value measured by these latter authors corrected by using a more accurate value of the dipole moment of OCS, which is used as reference (see Burrell et al. 1980). The dipole moment of CH$_3$CCH turns out to be only ~2% lower than that of CH$_3$CCH (see Table 3). For CH$_3$DCCH, CH$_3$DCC, and CH$_3$DCCD, all of which are asymmetric rotors, dipole moments are not known, and we thus evaluated them using quantum chemical calculations. Since for these species the dipole moment is only due to vibrational effects connected to isotopic substitution, anharmonic force field calculations were required. All the calculations were done using the orbital-dependent functional (dubbed B2PLYP; Grimme 2006) with the Becke-Johnson D3(BJ) damping function (Risthaus & Grimme 2013) and the Dunning’s basis set cc-pVTZ (Dunning 1989). In order to obtain more reliable values, we also calculated the dipole moments for CH$_3$CCH, CD$_3$CCH, CH$_3$CCD, and CD$_3$CDD, whose dipole moments are experimentally known (Muenter & Laurie 1966; Burrell et al. 1980). In this manner, we obtained an experimental/theoretical ratio that was used to correct the theoretical values for CH$_3$DCCH, CH$_3$DCC, and CH$_3$DCCD. The calculated dipole moments along the principal axis $a$, which is the relevant parameter since the observed lines are of $a$-type, are given in Table 3. We found they differ only slightly, up to ~2%, from that of CH$_3$CCH.

We now include two new lines for CH$_3$CDD, the 5$_0$–4$_1$ and 5$_1$–4$_1$, observed in the 72–80 GHz range. For CH$_3$CCH, we observed lines with $K = 0, 1, 2, 3$, and thus the column density includes these four $K$ ladders, although the $K = 0$ and $K = 1$ levels account for most of the column density (92%). For CH$_3$DCCD, only $K = 0$ and $K = 1$ lines were observed. Among all isotopologues of methyl acetylene, CH$_3$DCCH has the most precise determination of the rotational temperature, $10.2 \pm 0.7$ K, due to the higher number of lines observed and the wider range of upper level energies involved. We therefore adopted this value for all other isotopologues when deriving column densities. We note that if the rotational temperature is not fixed, the values obtained are consistent with the rotational temperature of 10.2 K adopted. For example, for CH$_3$DCCH we obtain a rotational temperature of $9.3 \pm 1.3$ K while for CH$_3$DCCD we get $11.4 \pm 2.0$ K. The rotational partition function was computed by summation including energy levels up to $J = 100$. For guidance, in Table 4 we give rotational partition functions for CH$_3$DCCH and CH$_3$DCCD at different temperatures. The column densities derived in L483 for CH$_3$CCH and its singly and doubly deuterated forms are given in Table 3. Deuteration ratios for various molecules in L483 have been discussed by Agúndez et al. (2019). Regarding doubly deuterated methyl acetylene, the two forms show a deuteration enrichment comparable to H$_2$O and HCS, which show the largest levels of deuteration in L483 (H$_2$CO/D$_2$CO = 31.3 and H$_2$S/D$_2$S = 21.7; Agúndez et al. 2019), and are significantly more enriched in deuterium than CH$_3$OH and c-C$_3$H$_2$, for which CH$_3$OH/CH$_3$D$_2$OH = 357 and c-C$_3$H$_7$/c-C$_3$D$_7$ = 103 (Agúndez et al. 2019).
Fig. 1. Observed lines of CH$_2$CCH in L483 in the 72–116 GHz range. The systemic velocity of L483 (5.30 km s$^{-1}$) is indicated by a vertical dotted blue line. Green lines are Gaussian fits to each line profile. Frequencies and line parameters are given in Table 1.

Fig. 2. Observed lines of CH$_2$DCCD in L483 in the 72–116 GHz range. The systemic velocity of L483 (5.30 km s$^{-1}$) is indicated by a vertical dotted blue line. Green lines are Gaussian fits to each line profile. Frequencies and line parameters are given in Table 1. The $6_{0,5}$–$5_{0,5}$ line is not detected because it overlaps with the strong HCN $J = 1$–0 line.
Table 2. Spectroscopic parameters of CHD$_2$CCH and CH$_2$DCCD.

| Parameter | CHD$_2$CCH | CH$_2$DCCD |
|-----------|------------|------------|
| $A_0$ (MHz) | 95746(533) | 11968.0(170) |
| $B_0$ (MHz) | 7765.71927(255) | 7440.77759(341) |
| $C_0$ (MHz) | 7630.99013(254) | 7332.00345(340) |
| $\Delta J$ (kHz) | 2.3807(270) | 2.0759(347) |
| $\Delta J_{K}$ (kHz) | 123.83(224) | 118.93(295) |

Notes. Numbers in parentheses are 1σ uncertainties in units of the last digit. $^{(a)}$Number of lines included in the fit. For CHD$_2$CCH, $J_{\text{max}}$ = 7, $K_{\text{max}}$ = 2, and $V_{\text{max}}$ = 108.241 GHz, and for CH$_2$DCCD, $J_{\text{max}}$ = 5, $K_{\text{max}}$ = 2, and $V_{\text{max}}$ = 103.784 GHz. $^{(b)}$Root mean square of the fit.

CHD$_2$CCH, CH$_3$DCCD, CD$_3$CCH, and CH$_2$DCCD. The final chemical network comprises 394 species linked through more than 14,000 reactions. When no experimental information is available, we assume that the total rate coefficient of reactions involving deuterium atoms is identical to that with hydrogenated compounds. The derivation of branching ratios is principally based on statistical considerations.

However, for deuterated methyl acetylene, we consider that the external CH and CCH (or CD and CCD) groups are much more mobile than the methyl group. Then, we assume that for reactions involving the ejection of CH and CCH (or CD and CCD), only the terminal group is implied in the reaction. As an example:

$$ C^+ + CHDCCCH \rightarrow C_2H_2D^+ + CH $$

(1a)

$$ C^+ + CHDCCCH \rightarrow C_2H_2D^+ + C_2H $$

(1b)

$$ C^+ + CHDCCCD \rightarrow C_3H_3^+ + CD $$

(2a)

$$ C^+ + CHDCCCD \rightarrow C_3H_3^+ + C_2D. $$

(2b)

For reactions of dissociative recombination, we consider that atomic hydrogen is ejected twice as efficiently as deuterium, as found in some experiments (e.g., Jensen et al. 1999). We include the findings of Savić & Gerlich (2005) and Savić et al. (2005), who showed that the rate coefficients of reactions of $C$ with HD and $D_2$ are different from those with $H_2$. In Table 5, we also report the corresponding rate coefficients used in our network. These values are still subject to some uncertainties as discussed in Savić & Gerlich (2005) and Savić et al. (2005).

As in our previous studies of isotopic fractionation (Roueff et al. 2015), we do not solve the full para/ortho chemistry of hydrogen compounds but rather introduce the ortho-to-para ratio of $H_2$, OPR, as a free parameter. This factor impacts the reverse reactions of the deuteron exchanges of HD with $H_2^+$, $H_2D^+$, and $D_2H^+$ and the reaction $N^+ + H_2$ (DiSalvo et al. 2012), as shown in Table 6, where $n(OH_2) = \frac{n(OH_2^+)}{\text{OPR}} n(H_2)$. The exponential terms, $\gamma$, were obtained by subtracting the energy of the $J = 1$ level of $OH_2$, 170.5 K, from the endothermicity of the reaction with reactants and products in their ground states. We did not introduce the similar reactions $CH_3D_2^+ (n = 0, 1, 2, 3) + OH_2$, $C_2H_2D_2^+ (n = 0, 1, 2) + OH_2$, and $C_3D^+ + OH_2$ since the corresponding endothermicities are much larger (Roueff et al. 2013; Nyman & Yu 2019) and the reactions do not take place in the present low temperature, $\sim 10^4$ K, conditions.

Table 7 displays the deuteron ratios of various carbon-containing molecules observed in L483, including present methyl acetylene detections, and three steady-state model results corresponding to the physical conditions, $n(H_2) = 3 \times 10^4$ cm$^{-3}$ and $T = 10$ K, prevailing in L483 (Agúndez et al. 2019). Model 1 represents a fiducial model with OPR = 10$^{-3}$ and $\zeta = 1.3 \times 10^{-17}$ s$^{-1}$, which corresponds to typical values for dark clouds. We notice that this choice overestimates the H/D ratio of methyl acetylene by about a factor of two, a feature that we already noticed in our previous study of TMC-1 (Cabezas et al. 2021). Decreasing the ortho-to-para ratio of $H_2$ by a factor of ten, as done in model 2, allows us to decrease reasonably the H/D ratios of the various C-containing molecules. This trend is further strengthened in model 3, where the cosmic-ray ionization rate is reduced down to $5 \times 10^{-18}$ s$^{-1}$, which results in H/D ratios for singly and doubly deuterated methyl acetylene close to the observed values.

While a more detailed study is highly desirable, we can make some comments. The abundance ratio between the two singly deuterated forms of methyl acetylene, CH$_3$DCCCH/CH$_3$CCD, is close to three according to the observations and this fact is reproduced by the models. This feature results directly from the statistical considerations for the insertion of deuterium in the CH$_2$ group and in the terminal CCH group. For example, in the dissociative recombination of $C_3H_2D^+$ and $C_3H_2D_2^+$, which are the principal formation routes of deuterated methyl acetylene, we explicitly account for this statistical factor in the reaction rate coefficients. The doubly deuterated forms, on the other hand, are assumed to be produced in equal amounts from the dissociative recombinations of $C_3H_2D^+$ and $C_3H_2D_2^+$, following statistical arguments as well. The difference between the abundances of CH$_3$DCCD and CH$_2$DCCD results then from the destruction rates, for which we assume that the possible ejection of $H$ or $D$ occurs from the terminal CCH or CCD group. As an example, CH$_3$DCCD+ $\rightarrow$ CH$_3H_2D^+$ + $H_2$ + HD, whereas CH$_2$DCCH + $H_2^+$ $\rightarrow$ CH$_2$D$_2^+$ + $H_2$ + HD. Then, CH$_2$DCC is more easily recycled in a doubly deuterated form and its abundance is somewhat larger than that of CH$_2$DCCD, as derived from the observations. A low ortho-to-para ratio of $H_2$ significantly favors the deuterium enhancement of methyl acetylene, which reflects the role of deuteron transfer in ion-molecule reactions. We note that the range 10$^{-3}$–10$^{-4}$ is within the OPR $H_2$ values derived for typical conditions of dark clouds (Le Bourlot 1991; Furuya et al. 2015). In a similar way, lowering the cosmic-ray ionization rate leads to a decrease in the ionization fraction, which enhances the abundance of molecular ions and decreases the H/D ratio of the various molecular species.

We plan to further investigate the dependence of deuteron fractionation on various parameters in a dedicated study but these first results show that the gas-phase ion-molecule scheme can explain the formation of methyl acetylene and its singly and doubly deuterated substitutes. Moreover, if deuteration occurs on grain surfaces and deuterated ratios are governed by the D/H ratio in the gas phase, then it would hold that CH$_3$DCCD/CH$_3$CCD = 3 CH$_2$CCD/CH$_3$CCD. That is, CH$_3$DCCD/CH$_3$CCD should be 0.19, while the observed value is 0.37, meaning that doubly deuterated species are twice as abundant than expected if deuteration occurs on grain surfaces following a statistical scheme. This fact further strengthens the gas-phase origin of deuteration for methyl acetylene. It is interesting to note that our models also predict the deuteration of allene (CH$_3$CCH$_2$) at similar levels as methyl acetylene. However, the dipole moment of the fully hydrogenated form of allene is zero and that resulting from deuteration inclusion is probably too small to permit the detection of any deuteron isotope.
Table 3. Column densities and ratios for CH$_3$CCH and its singly and doubly deuterated species in L483.

| Species           | $\mu$ (D) | $N_{\text{lines}}$ | $E_{\text{up}}$ (K) | $T_{\text{rot}}$ (K) | $N$ (cm$^{-2}$) | Column density ratio |
|------------------|-----------|---------------------|----------------------|----------------------|----------------|---------------------|
| CH$_3$CCH        | 0.7839    | 8                   | 11.5–82.3            | 10.2                  | 9.10 × 10$^{13}$ | CH$_3$CCH/CH$_2$DCCH 5.2 ± 1.6 |
| CH$_3$DCCH       | 0.7850    | 15                  | 11.6–43.6            | 10.2 ± 0.7            | (1.76 ± 0.34) × 10$^{13}$ | CH$_3$CCH/CH$_2$DCCH |
| CH$_3$CCD        | 0.7698    | 6                   | 10.5–20.9            | 10.2                  | 5.79 × 10$^{12}$ | CH$_3$CCH/CH$_2$CCD 15.7 ± 4.7 |
| CH$_2$DCCD       | 0.7870    | 9                   | 11.1–25.0            | 10.2                  | 2.69 × 10$^{12}$ | CH$_3$CCH/CHD$_2$CCCH 33.8 ± 10.1 |
| CH$_2$DCCD       | 0.7711    | 8                   | 10.6–25.3            | 10.2                  | 2.16 × 10$^{12}$ | CH$_3$CCH/CH$_2$DCCD 42.1 ± 12.6 |

Notes. (a) Dipole moments along the principal axis $a$. (b) Experimental value from Burrell et al. (1980). (c) Calculated value (this work). Errors in the column densities are estimated to be 20%. Errors in the column density ratios are estimated to be 30%.

Table 4. Rotational partition functions for CHD$_2$CCH and CH$_2$DCCD.

| Temperature (K) | $Q_{\text{rot}}$ (D) CHD$_2$CCH | CH$_2$DCCD |
|-----------------|----------------------------------|-----------|
| 300.0           | 11646.9629                       | 10855.0235 |
| 225.0           | 7563.8563                        | 7049.8187 |
| 150.0           | 4117.1979                        | 3837.5133 |
| 75.00           | 1456.4144                        | 1357.4949 |
| 37.50           | 515.6773                         | 480.6346 |
| 18.75           | 182.8944                         | 170.4479 |
| 9.375           | 65.0786                          | 60.6361 |
| 5.000           | 25.6362                          | 23.8844 |
| 2.725           | 10.5863                          | 9.9782|

Notes. (a) Computed including energy levels up to $J = 100$.

Table 6. Reactions involving ortho H$_2$.

| Reaction | $\alpha$ (cm$^3$ s$^{-1}$) | $\gamma$ (K) Ref. |
|----------|---------------------------|-------------------|
| $\text{C}_3\text{H}^+$ + HD $\leftrightarrow$ C$_2$D$^+$ + H$_2$ | $5.6 \times 10^{-11}$ | 500–375 (1) |
| $\text{C}_3\text{H}^+$ + D$_2$ $\leftrightarrow$ C$_2$D$^+$ + HD | $3.0 \times 10^{-13}$ | 420–320 (1) |
| $\text{C}_2\text{H}^+$ + H$_2$ $\leftrightarrow$ C$_2$H$_2^+$ + H | $1.7 \times 10^{-9}$ | (1) |
| $\text{C}_2\text{H}^+$ + HD $\leftrightarrow$ C$_2$H$_2^+$ + D | $9.3 \times 10^{-10}$ | (1) |
| $\text{C}_2\text{H}^+$ + HD $\leftrightarrow$ C$_2$H$_2^+$ + D | $7.6 \times 10^{-10}$ | (1) |
| $\text{C}_2\text{H}^+$ + D$_2$ $\leftrightarrow$ C$_2$D$_2^+$ + D | $1.3 \times 10^{-9}$ | (1) |
| $\text{C}_2\text{H}^+$ + H$_2$ $\leftrightarrow$ c-C$_3$H$_3^+$ + H | $1.0 \times 10^{-12}$ | (2) |
| $\text{C}_3\text{H}^+$ + H$_2$ $\leftrightarrow$ C$_3$HD$^+$ + H | $4.6 \times 10^{-10}$ | (1) |
| $\text{C}_3\text{H}^+$ + HD $\leftrightarrow$ C$_3$HD$^+$ + D | $3.0 \times 10^{-12}$ | (1) |
| $\text{C}_3\text{H}^+$ + D$_2$ $\leftrightarrow$ C$_3$D$_2^+$ + D | $1.0 \times 10^{-11}$ | (1) |
| $\text{C}_3\text{H}^+$ + D$_2$ $\leftrightarrow$ C$_3$D$_2^+$ + H | $2.7 \times 10^{-11}$ | (1) |
| $\text{C}_3\text{D}^+$ + H$_2$ $\leftrightarrow$ C$_3$HD$^+$ + H | $1.0 \times 10^{-12}$ | (3) |
| $\text{C}_3\text{D}^+$ + HD $\leftrightarrow$ C$_3$D$^+$ + H | $1.0 \times 10^{-10}$ | (1) |
| $\text{C}_3\text{D}^+$ + HD $\leftrightarrow$ C$_3$D$_2^+$ + H | $8.3 \times 10^{-11}$ | (1) |
| $\text{C}_3\text{D}^+$ + D$_2$ $\leftrightarrow$ C$_3$D$_2^+$ + D | $1.7 \times 10^{-10}$ | (1) |

Notes. Reaction rate coefficient is given by $k(T) = \alpha \left(\frac{T}{10^8}\right)^\beta \exp(-\gamma/T)$.

Table 7. H/D ratios of C-containing molecules observed in L483 and steady-state values calculated with our gas-phase chemical model.

| Molecular ratio | OPR H$_2$ | L483 | Model 1 | Model 2 | Model 3 |
|-----------------|-----------|-------|---------|---------|---------|
| CH$_3$CCH/CH$_2$DCCH | 5.2$^{(b)}$ | 10.1 | 7.6 | 6.3 |
| CH$_3$CCH/CH$_2$CCD | 15.7$^{(b)}$ | 27.3 | 20.4 | 17.1 |
| CH$_3$CCH/CHD$_2$CCH | 33.8$^{(b)}$ | 91.1 | 56.0 | 38.0 |
| CH$_3$CCH/CH$_2$DCDD | 42.1$^{(b)}$ | 131.5 | 78.4 | 54.5 |

Notes. See text for the assumed physical conditions. We adopted the elemental abundance ratios O/H = 8 × 10$^{-6}$, D/H = 1.5 × 10$^{-5}$, C/O = 0.5, and C/N = 1. (a) Cosmic-ray ionization rate of H$_2$. (b) Observed values in this work (see Table 3). (c) Observed values from Agúndez et al. (2019).

5. Conclusions

We have presented the first detection in space of the two doubly deuterated isomers of methyl acetylene, CH$_2$DCCH and CH$_2$DCCD, toward the dark cloud core L483. The frequencies predicted for these two species from laboratory data have significant errors when compared with those derived from astronomical observations. We have therefore derived new
spectroscopic parameters for the two deuterium isotopologues. These parameters have the accuracy needed to observe these species in cold interstellar clouds showing narrow lines. We derive abundance ratios of CH$_3$CCH/CH$_2$DCH$_2$CCH $= 34 \pm 10$ and CH$_2$CCH/CH$_3$DCCD $= 42 \pm 13$. Doubly deuterated methyl acetylene is found to be only a few times less abundant than the singly deuterated forms. We have constructed a gas-phase chemical model including multiply deuterated molecules, which is able to reproduce the abundance ratios of the different deuterated isotopologues with respect to CH$_3$CCH observed in L483. In particular, the fact that CHD$_2$CCH is slightly more abundant than CH$_3$DCCD is well accounted for by the chemical model. This favors a scenario in which deuteriation of methyl acetylene occurs in the gas phase, rather than on the surface of dust grains.

Acknowledgements. We acknowledge funding support from Spanish MICIU through grants AYA2016-75066-C2-1-P, PID2019-10610GB-I00, and PID2019-107115GB-C21 and from the European Research Council (ERC Grant 610256: NANOCOSMOS). M.A. also acknowledges funding support from the Ramón y Cajal programme of Spanish MICIU (grant RyC-2014-16277). C.C. thanks Prof. Cristina Puzzarini (Università di Bologna) for her advices and comments about the quantum chemical calculations.

References

Agúndez, M., Marcelino, N., Cernicharo, J., et al. 2019, A&A, 625, A147
Bacmann, A., Fauré, A., Hily-Blant, P., et al. 2020, MNRAS, 499, 1795
Brown, P. D., & Millar, T. J. 1989, MNRAS, 1989, 240, 25
Burrell, P. M., Bjarnov, E., & Schwendeman, R. H. 1980, J. Mol. Spectr., 82, 193
Butner, H. M., Charnley, S. B., Ceccarelli, C., et al. 2007, ApJ, 659, L137
Cabezas, C., Endo, Y., Roueff, E., et al. 2021, A&A, 646, L1
Calcutt, H., Jørgensen, J. K., Müller, H. S. P., et al. 2018, A&A, 616, A90
Ceccarelli, C., Castets, A., Loinard, L., et al. 1998, A&A, 338, L43
Ceccarelli, C., Caselli, P., Bockelée-Morvan, D., et al. 2014, Protostars and Planets VI, 859
Cernicharo, J. 2012, in European Conference on Laboratory Astrophysics, eds. C. Stéhéle, C. Joblin, & L. d’Hendecourt, EAS Pub. Ser., 58, 251
Dislaire, V., Hily-Blant, P., Maret, S., et al. 2012, A&A, 537, A20
Dunning Jr., T. H. 1989, J. Chem. Phys., 90, 1007
Etin, E. E., Akpan, N. I., Adelagun, R. A. O., et al. 2020, Indian J. Phys., https://doi.org/10.1007/s12648-020-01747-x
Flower, D. R., Pineau des Forêts, & Walmsley, C. M. 2006, A&A, 449, 621
Fuzy, K., Aikawa, Y., Hincelin, U., et al. 2015, A&A, 584, A124
Gerin, M., Combes, F., Wlodarczk, G., et al. 1992, A&A, 253, L29
GrImm, S. 2006, J. Chem. Phys., 124, 034108
Hily-Blant, P., Faure, A., Rist, C., et al. 2018, MNRAS, 477, 4454
Jensen, M. J., Bilodeau, R. C., Heber, O., et al. 1999, Phys. Rev. A, 60, 2970
Le Bourlot, J. 1991, A&A, 242, 235
Le Guennec, M., Demaison, J., Wlodarczk, G., & Marsden, C. J. 1993, J. Mol. Spectr., 160, 471
Linsky, J. L. 2003, Space Sci. Rev., 106, 49
Lis, D. C., Roueff, E., Gerin, M., et al. 2002, ApJ, 571, L55
Loison J.-C., Agúndez, M., Wakelam V., et al. 2017, MNRAS, 470, 4075
Marcelino, N., Cernicharo, J., Roueff, E., et al. 2005, ApJ, 620, 308
Markwick, A. J., Charnley, S. B., Butner, H. M., & Millar, T. J. 2005, ApJ, 627, L117
Melosso, M., Bizzocchi, L., Sipilä, O., et al. 2020, A&A, 641, A153
Munter, J. S., & Laurie, V. W. 1966, J. Chem. Phys., 45, 855
Müller, H. S. P., Schröder, F., Stutzki, J., & Winnewisser, G. 2005, J. Mol. Struct., 742, 215
Nynan, G., & Yu, H.-G. 2019, AIP Adv. 9, 095017
Parise, B., Ceccarelli, C., Tielens, A. G. G. M., et al. 2002, A&A, 393, L49
Parise, B., Castets, A., Herbst, E., et al. 2004, A&A, 416, L39
Parise, B., Ceccarelli, C., Tielens, A. G. G. M., et al. 2006, A&A, 453, 949
Parise, B., Belloche, A., Du, F., et al. 2011, A&A, 526, A31
Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, J. Quant. Spectr. Rad. Transf., 60, 883
Rataczak, A., Taquet, V., Kahane, C., et al. 2011, A&A, 528, A13
Risthaus, T., & Grimme, S. 2013, J. Chem. Theory Comput., 9, 1580
Roberts, H., Herbst, E., & Millar, T. J. 2004, A&A, 424, 905
Roueff, E., Tiné, S., Coudert, L. H., et al. 2000, A&A, 354, L63
Roueff, E., Lis, D. C., van der Tak, F. F. S., et al. 2005, A&A, 438, 585
Roueff, E., Gerin, M., Lis, D. C., et al. 2013, J. Phys. Chem. A, 117, 9959
Roueff, E., Loison, J.-C., & Hickson, K. M. 2015, A&A, 576, A99
Savíc, I., & Gerlich, D. 2005, PCCP, 7, 1026
Savíc, I., Schlemmer, S., & Gerlich, D. 2005, ApJ, 621, 1163
Sipilä, O., Harju, J., Caselli, P., & Schlemmer, S. 2015, A&A, 581, A122
Sipilä, O., Harju, J., & Caselli, P. 2017, A&A, 607, A26
Spezzano, S., Brünken, S., Schilke, P., et al. 2013, ApJ, 769, L19
Taquet, V., Ceccarelli, C., & Kahane, C. 2012, ApJ, 748, L3
Thomas, L. F., Sherrard, E. I., & Sheridan, J. 1955, Trans. Faraday Soc., 51, 619
Turner, B. E. 1990, ApJ, 362, L29
Turner, B. E. 2001, ApJS, 136, 579
van der Tak, F. F. S., Schilke, P., Müller, H. S. P., et al. 2002, A&A, 388, L53
Vastel, C., Phillips, T. G., Ceccarelli, C., & Pearson, J. 2003, ApJ, 593, L97
Vastel, C., Phillips, T. G., & Yoshida, H. 2004, ApJ, 606, L127
Vastel, C., Quénard, D., Le Gal, R., et al. 2018, MNRAS, 478, 5514

M. Agúndez et al.: Doubly deuterated methyl acetylene