A Study of the c-C_3HD/c-C_3H_2 Ratio in Low-mass Star-forming Regions

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Abstract
We use the deuteration of c-C_3H_2 to probe the physical parameters of starless and protostellar cores, related to their evolutionary states, and compare it to the N_2H^+ deuteriation in order to study possible differences between the deuteration of C- and N-bearing species. We observed the main species c-C_3H_2, the singly and doubly deuterated species c-C_3HD and c-C_3D_2, as well as the isotopologue c-H^3CC_3H toward 10 starless cores and five protostars in the Taurus and Perseus complexes. We examined the correlation between the N(c-C_3HD)/N(c-C_3H_2) ratio and the dust temperature along with the H_2 column density and the CO depletion factor. The resulting N(c-C_3HD)/N(c-C_3H_2) ratio is, within error bars, consistent with 10% in all starless cores with detected c-C_3HD. This also accounts for the protostars except for the source HH211, where we measure a high deuterium level of 23%. The deuterium of N_2H^+ follows the same trend but is considerably higher in the dynamically evolved core L1544. We find no significant correlation between the deuteration of c-C_3H_2 and the CO depletion factor among the starless and protostellar cores. Toward the latter the coolest objects show the largest deuterium fraction in c-C_3H_2. We show that the deuteration of c-C_3H_2 can trace the early phases of star formation and is comparable to that of N_2H^+. However, the largest c-C_3H_2 deuteration level is found toward protostellar cores, suggesting that while c-C_3H_2 is mainly frozen onto dust grains in the central regions of starless cores, active deuteriation is taking place on ice.

Key words: astrochemistry – ISM: clouds – ISM: molecules – line: identification

1. Introduction

During the early stages of star formation, self-gravitating starless cores begin to contract (ν_H > 10^4 cm s^{-1}) and to cool down to a few kelvin (T < 10 K). Under these conditions, the deuteration of molecules is considerably increasing. H_2D^+ is the main deuterium provider for most molecules in dense cores and is formed from the following deuteron–proton reaction (Millar et al. 1989):

\[ \text{H}_2^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2 + 230 \text{ K}. \]  

This reaction is exothermic and proceeds mostly in the forward direction at temperatures lower than 30 K, increasing the abundance of H_2D^+. The abundance of H_2D^+ also depends on the ortho-to-para-H_2 ratio. The backward direction of Reaction (1) is endothermic if the reactants H_2D^+ and H_2 are mostly in the para-form (Pagani et al. 1992). An important process in these environments is the freeze-out of molecules onto dust grains. Previous studies have shown that CO depletes heavily toward the center of cores (Willacy et al. 1998; Caselli et al. 1999; Bacmann et al. 2003; Crapsi et al. 2005; Pagani et al. 2007). Since CO destroys H_2^+ and H_2D^+, its depletion from the gas phase leads to a further enhancement of the total deuteration level (Dalgaro & Lepp 1984). As the starless core continues to contract, it eventually becomes a pre-stellar core, defined as being a self-gravitating core (Ward-Thompson et al. 1999) with signs of contraction motions and high levels of CO freeze-out and deuteration (Crapsi et al. 2005). Pre-stellar cores are a sub-sample of starless cores, i.e., the most dynamically evolved and destined to form one or more protostars. Once the protostar is formed, the central regions of the contracting core warm up and the whole core starts to become affected by the outflow driven by the young stellar object. This causes CO to desorb and also increases the backward rate of Reaction (1), leading finally to a decrease of the total deuteration degree. In summary, the increase and decrease of molecular deuteration is sensitive to the evolutionary stage in the star formation process and is an excellent tool to trace the early stages of star formation.

Species that can be used as evolutionary tracers of high-density and low-temperature gas must have the possibility of deuteriation and should be abundant in space. One molecule that has been proven to be a very good evolutionary tracer is diazenylium, N_2H^+ (Crapsi et al. 2005; Emprechtinger et al. 2009; Friesen et al. 2013; Punanova et al. 2016). It has been shown that the deuteration of N_2H^+ correlates tightly with important evolutionary indicators, such as the dust temperature, the CO depletion factor, and the central column density of H_2. In addition, the emission maps of N_2H^+ strongly follow the dust emission maps, indicating that N_2H^+ is less depleted than C-bearing molecules at higher densities (Bergin et al. 2001; Taffalla et al. 2002). This makes N_2H^+ a very good tracer of the deuteration level in central regions of dense cores. The resistance of N_2H^+ to depletion has been ascribed by previous studies (Flower et al. 2006; Le Gal et al. 2014) to the fact that nitrogen in the interstellar medium (ISM) is mainly in atomic form, and N atoms can stay in the gas phase longer because of their lower sticking probabilities and the slow process which transforms N into N_2.

Following the detection of cyclopropenylidene (c-C_3H_2) in the laboratory (Thaddeus et al. 1985), a number of U-lines observed by Thaddeus et al. (1981) were able to be identified as c-C_3H_2 transitions. After its first detection, it was observed in various sources, like cold dark clouds, diffuse clouds, circumstellar envelopes, planetary nebulae, etc. (e.g., Benson et al. 1998; Spezzano et al. 2013, and references therein). Due to the high abundance of the normal species, the singly deuterated species c-C_3HD and the isotopologue c-H^3CC_3H
have also been observed in various sources over the past 30 years. For example, c-C$_3$H$_2$ was detected toward L1498 (Bell et al. 1988), TMC-1C and L1544 (Spezzano et al. 2013), as well as TMC-1 (Turner 2001) in the Taurus Molecular Cloud.

After the first laboratory measurement of the doubly deuterated species by Spezzano et al. (2012), c-C$_3$D$_2$ was detected in the ISM for the first time toward the starless cores TMC-1C and L1544 with a high signal-to-noise-ratio (S/N) (Spezzano et al. 2013). The observed single and double deuterium in these two sources could be reproduced by a chemical model including only gas-phase reactions (Aikawa et al. 2012). The possibility of double deuterium and its gas-phase chemistry makes c-C$_3$H$_2$ a useful probe for the deuteration processes taking place only in the gas phase. A study of the c-C$_3$H$_2$-deuteration as an evolutionary indicator will give complementary information to the deuteriation of N$_2$H$^+$, and reveal possible differences between the deuteration of C- and N-bearing species in the gas phase. In fact, unlike N$_2$H$^+$, c-C$_3$H$_2$ is believed to be an early-type molecule (Herbst & Leung 1989) in terms of cloud evolution and can therefore trace the early stages of star formation; in particular, in L1544, c-C$_3$H$_2$ preferentially traces the side of the core more exposed to the interstellar radiation field, where the chemistry is continually rejuvenated by the photodissociation of CO (Spezzano et al. 2016). However, c-C$_3$H$_2$ is also affected by freeze-out or chemical depletion, as it does not trace the central regions of starless cores (e.g., Spezzano et al. 2017). It is therefore important to compare the deuteriation of this molecule in starless and protostellar cores in order to investigate the level of deuteration in different stages of low-mass star formation. This can give us insights on possible deuteration processes taking place on grain surfaces during the cold and dense phases just before the switch-on of the protostar.

In this work we present single-pointing observations of c-C$_3$H$_2$, the singly and doubly deuterated species c-C$_3$HD and c-C$_3$D$_2$, as well as the isotopologue c-H$^{13}$CC$_2$H toward 10 starless cores and five protostars in the Taurus and Perseus Molecular Cloud complexes. In Section 2 we summarize the details concerning the observations. Section 3 describes the calculation of the single and double deuteration of c-C$_3$H$_2$ as well as the comparison between the deuterium fraction of N$_2$H$^+$ and c-C$_3$H$_2$. In Section 4 we also describe the correlation between the deuteration level of c-C$_3$H$_2$ and important evolutionary indicators (dust temperature, CO depletion level, and central column density of H$_2$). The conclusions are summarized in Section 4.

2. Observations

The observations were done at the IRAM 30 m telescope located at Pico Veleta (Spain) toward 10 starless cores and five protostellar cores in Taurus and Perseus. A summary of the observed objects, their coordinates, and their distances is reported in Table 1. These sources all lie in our Galactic vicinity and represent different stages of star formation, from starless cores to more evolved pre-stellar cores and young Class 0 protostars. Previous observations of these sources showed a significant deuteration of N$_2$H$^+$ which correlates with evolutionary indicators, such as the dust temperature, CO depletion, and central column density of H$_2$ (Crapsi et al. 2005; Emprechtinger et al. 2009). A special case in our sample is L1521F. Even though some studies (Crapsi et al. 2005) describe this source as an evolved pre-stellar core, successive work (Bourke et al. 2006; Takahashi et al. 2013) has proven that L1521F shows an infrared source and a compact continuum millimeter emission, which indicates the existence of a protostar. The detection of a small outflow and a low bolometric luminosity (0.034–0.07 L$_\odot$) suggests that this source is a so-called Very Low Luminosity Object (hereafter VeLLO) which could be a very young protostellar source or a protostar at its minimum of activity, if episodic accretion is at work (e.g., Visser et al. 2015).

The observations were carried out with the EMIR receiver using the E090 configuration (3 mm atmospheric window). Each sub-band covered a frequency range of 1.8 GHz, leading to a total spectral coverage of 7.2 GHz. All four EMIR sub-bands were connected to the Fast Fourier Transform Spectrometer with a frequency resolution of 50 kHz. Frequency switching was performed with a frequency throw of ±3.9 MHz. Telescope pointing was checked every 2 hr on Mercury and was accurate to 3". The intensity of the obtained spectra was given in antenna temperature units, $T_A^*$. The antenna temperature $T_A^*$ was converted to the main beam temperature $T_{MB}$ using the relation $T_{MB} = \frac{b_{MB}}{b_{eff}} \cdot T_A^*$.

In both samples we observed the main isotopologue c-C$_3$H$_2$, the singly and doubly deuterated species c-C$_3$HD and c-C$_3$D$_2$, as well as the isotopologue c-$^{13}$CC$_2$H, with one $^{13}$C being off the principal axis of the molecule. Table 2 summarizes the observed species, the spectroscopic parameters, and telescope settings at the corresponding frequencies: $E_{up}$ describes the upper state energy and $A_{up}$ is the Einstein coefficient of the corresponding transition. The upper state degeneracy is given by $g_{uv}$. The parameters $B_{eff}$ and $b_{MB}$ describe the main beam efficiency and the main beam size of the telescope at a given frequency, respectively. The system temperature $T_{sys}$ is given in K. The forward efficiency, $F_{eff}$, is in the observing frequency range equal to 95%.

3. Results

In the Appendix A we show the observed spectra toward all sources. The $^{3}_2–^{3}_1$ transition of c-C$_3$H$_2$ at 84.727 GHz was detected in all starless and pre-stellar cores except for L1400K, L1517B, and L1512. The same line of c-C$_3$H$_2$ was also detected in all protostars except for L1448IRS2. The c-C$_3$H$_4$ ($^{3}_0–^{3}_2$) and c-$^{13}$CC$_2$H ($^{2}_1–1_{0,1}$) emission was detected in all starless, pre-stellar, and protostellar cores with a high S/N; the strongest lines have an S/N of 25 and 40, respectively. The $^{3}_1–^{2}_0$ transition of c-C$_3$D$_2$ at 97.761 GHz was found at a high S/N level (the strongest line was detected at a 27σ level) in the following starless and pre-stellar cores: L1495AN, L1512, L1517B, TMC2, and L1544. In the case of the protostellar cores, c-C$_3$D$_2$ was detected in four sources: Per5, HH211, L1521F, and IRAS16293-2422 with S/N levels ranging from 7.8 to 13.5.

3.1. Calculation of the Column Densities and the Deuteration Level

The data reduction and analysis was carried out using the GILDAS$^1$ software (Pety 2005). In order to subtract the baseline caused mainly by the frequency switching mode, high-order polynomials were fitted. Each line was fitted by using the standard CLASS Gaussian fitting method. The total column density was calculated by using the expression for optically

$\text{http://www.iram.fr/IRAMFR/GILDAS}$
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Chantzos et al.

Table 1

| Source | Object | R.A. | Decl. | Distance (pc) | References |
|--------|--------|------|-------|--------------|------------|
| L1495  | starless core | 04 14 08.2 | +28 08 16 | 140 | 2 |
| L1495B | starless core | 04 18 05.1 | +28 22 22 | 140 | 1 |
| L1495AN | starless core | 04 18 31.8 | +28 27 30 | 140 | 1 |
| L1495AS | starless core | 04 18 41.8 | +28 23 50 | 140 | 1 |
| L1400K | starless core | 04 30 52.1 | +54 51 55 | 140 | 2 |
| L1400A | starless core | 04 30 56.8 | +54 52 36 | 140 | 1 |
| CB23   | starless core | 04 43 27.7 | +29 39 11 | 140 | 1 |
| L1517B | starless core | 04 55 18.8 | +30 38 04 | 140 | 1 |
| L1512  | starless core | 05 04 09.7 | +32 43 09 | 140 | 1 |
| TMC2   | pre-stellar core | 04 32 48.7 | +24 25 12 | 140 | 1 |
| L1544  | pre-stellar core | 05 04 17.2 | +25 10 43 | 140 | 3 |
| L1521F | protostellar core | 04 28 39.8 | +26 51 35 | 140 | 1 |
| Per 5  | protostellar core | 03 29 51.6 | +31 39 03 | 220 | 4 |
| IRAS03282 | protostellar core | 03 31 21.0 | +30 45 30 | 220 | 4 |
| HH211  | protostellar core | 03 45 56.8 | +32 00 50 | 220 | 4 |
| L1448IRS2 | protostellar core | 03 25 22.4 | +30 45 12 | 220 | 4 |
| IRAS16293 | protostellar core | 16 32 22.6 | −24 28 33 | 120 | 5 |

Note. Here we also include the well studied objects L1544 and IRAS16293-2422.

*References.* (1) Lee et al. (2001), (2) Tafalla et al. (2002), (3) Ward-Thompson et al. (1999), (4) Cernis (1990), (5) Caux et al. (2011).

Table 2

| Species | Transitions $J_{K_a}K_c$ | Frequency (GHz) | References | $E_{up}$ (K) | $A_{ul}$ $(10^{-5}$ s$^{-1}$ | $g_a$ | $B_{eff}$ (%) | $\theta_{MB}$ (″) | $T_{sys}$ (K) |
|---------|--------------------------|-----------------|------------|--------------|----------------|--------|--------------|----------------|--------------|
| $c$-C$_3$H$_2$ | $3_{1,2} - 3_{1,3}$ | 84.727 | 1 | 16.14 | 1.04 | 7 | 81 | 29 | 80–120 |
| $c$-C$_3$HD | $3_{0,3} - 2_{1,2}$ | 104.187 | 2 | 10.85 | 3.95 | 21 | 79 | 25 | 90–151 |
| $c$-C$_3$HD | $2_{1,1} - 1_{1,0}$ | 95.994 | 2 | 7.56 | 0.45 | 15 | 80 | 27 | 99–114 |
| $c$-H$_2^{13}$C$_2$H | $2_{1,2} - 1_{0,1}$ | 84.185 | 2 | 6.33 | 2.17 | 10 | 81 | 29 | 80–116 |
| $c$-C$_3$D$_2$ | $3_{0,3} - 2_{1,2}$ | 94.371 | 3 | 9.88 | 3.37 | 21 | 80 | 27 | 82–123 |
| $c$-C$_3$D$_2$ | $3_{1,3} - 2_{0,2}$ | 97.761 | 3 | 9.88 | 3.37 | 42 | 80 | 26 | 79–119 |
| $c$-C$_3$D$_2$ | $2_{2,1} - 1_{1,0}$ | 108.654 | 3 | 7.90 | 4.79 | 15 | 78 | 24 | 96–105 |

References. (1) Thaddeus et al. (1984), (2) Bogey et al. (1987), (3) Spezzano et al. (2012).

thin transitions:

$$N_{rot} = \frac{8\pi k_B W/\nu^2}{A_{ul} c^3} J(T_{ex}) \frac{J(T_{ex})}{J(T_{bg})} \frac{Q_{rot}(T_{ex})}{g_a e^{-\frac{E_{rot}}{k_BT_{ex}}}}.$$ (2)

where $W = \frac{\Delta \nu T_{bg}^2}{2(\ln 2)^2}$ is the integrated intensity of the line, with $\Delta \nu$ being the linewidth (FWHM), $k_B$ is the Boltzmann constant, $\nu$ is the transition frequency, $c$ is the speed of light, and $h$ is the Planck constant. The partition function of a molecule at a given excitation temperature $T_{ex}$ is given by $Q_{rot}$. $T_{bg}$ is the cosmic background temperature (2.7 K). For a further extension of our sample we also included in this study the pre-stellar core L1544 (Spezzano et al. 2013) as well as the Class 0 protostar IRAS16293-2422 (hereafter IRAS16293) (Caux et al. 2011). In Tables 3 and 4 we summarize the detected lines in every source and the line properties derived from Gaussian fits. The sources CB23, L1495AN, L1495B, Per5, HH211, L1448IRS2, IRAS03282, and IRAS16293 show differences in the linewidth between the main isotopologue and the isotopic variants ranging in the 0.1–0.5 km s$^{-1}$ interval. These differences do not exhibit any clear trend and are poorly constrained with errors varying from 36% to 94%. Such discrepancies are likely to be produced by the high noise levels of these latter observations and by the coarse sampling of the line profiles (channel spacing is 0.167 km s$^{-1}$).

For the calculation of the total column densities of $c$-C$_3$H$_2$ and its isotopologues we assumed the same excitation temperature $T_{ex}$ that was used in the same sources by Crapsi et al. (2005) and Emprechtinger et al. (2009) for N$_2$H$^+$. We also used the same excitation temperature for the deuterated and the $^{13}$C species. The effect of underestimating the excitation temperature of the main and the deuterated species by 1 K changes the deuteration level $N(c$-C$_3$HD)/$N(c$-C$_3$H$_2$) by up to 30%. In the case of L1544 we used the $T_{ex}$ derived in Gerin et al. (1987), where detections of $c$-C$_3$H$_2$ and its deuterated counterpart are reported. In particular, there were

The critical density of $c$-C$_3$H$_2$ ($3_{1,3} - 3_{1,1}$) lies a factor of 12.7 higher than the critical density of N$_2$H$^+$(1–0) at 30 K (Chandra & Kegel 2000; Schöier et al. 2005). We cannot compare the critical densities of the above transitions at lower temperatures, since the collisional rate of the $c$-C$_3$H$_2$ ($3_{1,2} - 3_{1,1}$) transition is unknown below 30 K.
three transitions of c-C$_3$H at 19.419, 79.812, and 104.187 GHz detected in L1544, which gave a $T_{ex}$ of 5 ± 2 K. An optically thick transition of c-C$_3$H$_2$ detected at 85.339 GHz provided a $T_{ex}$ of 6 K. This excitation temperature is, within the errors, equal to that found in N$_2$H$^+$ (1–0) and N$_2$D$^+$ (2–1) toward the same source (Crapsi et al. 2005). Due to the large error of $T_{ex}$ for c-C$_3$H$_2$, we used for the main and the deuterated species a $T_{ex}$ of 6 K.

Since c-H$^3$C$_2$H was detected in every source, we used the total column density of c-H$^3$C$_2$H to derive N(c-C$_3$H$_2$) by considering a $^{12}$C/$^{13}$C ratio of 77 (Wilson & Rood 1994). This gave us the additional advantage of avoiding ambiguities due to the optical depth of the main species. The carbon isotope ratio was determined in several sources, from different molecular species and can vary up to a factor of 2 (Wilson & Rood 1994). This means that the derived N(c-C$_3$H$_2$) suffers from an uncertainty of a factor of 2. The assumed ortho-to-para ratio of c-C$_3$H$_2$ and c-C$_3$D$_2$ is 3 and 2, respectively. Tables 5 and 6 show the derived column densities for every species in each starless core and protostar, respectively. The error for the column densities was calculated by propagating the uncertainty on the integrated intensity, $W$, including the 1σ statistical error as well as 10% calibration uncertainty. The column densities for the singly and doubly deuterated species were calculated from the c-C$_3$HD ($3_{0,1,3} - 2_{1,2}$) and c-C$_3$D$_2$ ($3_{1,3} - 2_{0,2}$) transitions.

Figure 1 shows the deuterium fraction for each species in every starless core. Here one can clearly see that the deuteration for both c-C$_3$H$_2$ and N$_2$H$^+$ follows a similar trend and is of the same magnitude, except for the most dynamically evolved object, the pre-stellar core L1544. The deuteration of c-C$_3$H$_2$ is in all sources within the 1σ uncertainty consistent with 10%, except for L1400K where the c-C$_3$H$_2$ column density was estimated to be less than 0.26 × 10$^{12}$ cm$^{-2}$, which resulted in a 3σ upper limit for the N(c-C$_3$H$_2$)/N(c-C$_3$H$_2$) ratio of 0.03. All these sources except for TMC2 and L1544 have been identified by Crapsi et al. (2005) as less evolved starless cores having, among other properties, a deuteration degree ≤0.1 which is also in our case fulfilled (in the source L1495B the deuterium fraction can still be within errors less than or equal to 0.1).

L1544 is the only source where the deuteration of N$_2$H$^+$ is larger than that of c-C$_3$H$_2$, showing a significant discrepancy of a factor of 2.6. One possible explanation for this can be found in the formation route of N$_2$H$^+$. The progenitor of N$_2$H$^+$ is N$_2$ which is formed via neutral–neutral reactions: N + C → CN and CN + N → N$_2$ (Pineau des Forêts et al. 1990; Le Gal et al. 2014). Carbon-bearing molecules like c-C$_3$H$_2$ on the other hand are formed faster through sequential ion–neutral reactions. For this reason, N$_2$H$^+$ is believed to be a late-type molecule, becoming highly abundant in evolved cores, such as L1544. Furthermore, N$_2$H$^+$ is more resistant to depletion and survives in the gas phase longer than C-bearing molecules, thus tracing regions where the deuterium fractionation is more efficient because of the large amount of freeze-out of neutral species (such as CO and O) which participate in the destruction of the H$^+$ deuterated isotopologues (Dalgarno & Lepp 1984).

The abundance of the doubly deuterated species with respect to the normal species is 0.4%–1.5%. These values are comparable to those calculated by Spezzano et al. (2013) in TMC-1C and L1544. The ratios N(c-C$_3$HD)/N(c-C$_3$H$_2$) and N(c-C$_3$D$_2$)/N(c-C$_3$H$_2$) are quite similar in all starless and protostellar cores. This suggests that c-C$_3$H$_2$ and c-C$_3$HD follow the same deuteration route and are not affected by the dynamical evolution of the dense core, as already pointed out in Spezzano et al. (2013). In the source CB23 we find a marginal detection of c-C$_3$D$_2$ and therefore derive a 3σ upper limit for the column density. The abundance ratios N(c-C$_3$HD)/N(c-C$_3$H$_2$), N(c-C$_3$D$_2$)/N(c-C$_3$H$_2$) and N(c-C$_3$D$_2$)/N(c-C$_3$HD) among the starless core sample are listed in Table 7.

Also in the observed protostars the deuteration for both species is similar, as we can clearly see in Figure 2. The deuterium fraction peaks in HH211, reaching 23% in case of c-C$_3$H$_2$ and 27% in case of N$_2$H$^+$ which is also the highest estimated deuteration among all observed protostellar and starless cores. The abundance ratio N(c-C$_3$HD)/N(c-C$_3$H$_2$) is within the error bars equal to 10%, with the exception of HH211, where the average deuteration level is 0.23 ± 0.06. These results are similar to the N(c-C$_3$D$_2$)/N(c-C$_3$HD) ratio, which ranges from 5% to 17%. Finally, the abundance of the doubly deuterated species with respect to the main isotopologue varies between 0.6% and 3.6%. The single and double deuteration level of c-C$_3$H$_2$ in every protostellar core is summarized in Table 8.

In case of IRAS16293, we derived the deuteration of c-C$_3$H$_2$ and its isotopologues, as well as the depletion factor of CO using the publicly available data from TIMASSS (Caux et al. 2011). For the calculation of the c-C$_3$H$_2$ column density and its isotopologues, we assumed a $T_{ex}$ of 8.9 K for the main and the $^{13}$C species, and a $T_{ex}$ of 6.3 K for the deuterated counterparts, as was derived in Majumdar et al. (2017). The N(c-C$_3$HD)/N(c-C$_3$H$_2$) ratio in IRAS16293 calculated in this work is 0.10 ± 0.02. This is comparable to the deuteration of 14% determined in Majumdar et al. (2017) within the uncertainties.

### 3.2. Correlation between Deuteration and CO Depletion Factor

In a cold and dense cloud, molecules in the gas phase tend to collide and freeze-out onto dust grains, leading to a gradual decrease of their gas-phase abundance. Molecules are bound on grains through van der Waals forces (Garrod et al. 2007), meaning that species with a non-zero dipole moment, such as CS and CO, will be strongly bound on grain surfaces at the low temperatures typical of starless cores; thus, they deplete from the gas phase by significant amounts. Deuteration is expected to correlate with the CO depletion factor, since CO destroys H$_2$D$^+$ (Dalgarno & Lepp 1984). Previous studies have proven that the deuteration fraction of N$_2$H$^+$ correlates strongly with the degree of CO depletion (Caselli et al. 2002; Crapsi et al. 2005; Emprechtinger et al. 2009). The level of depletion is usually expressed as the depletion factor $f_d$ and is given by:

$$f_d(CO) = \frac{X_{\text{ref}}(CO)}{X(CO)},$$

where $X_{\text{ref}}(CO)$ is the reference abundance of CO in the local ISM and $X(CO)$ is the observed CO abundance (e.g., Emprechtinger et al. 2009).

Figure 3 shows the N(c-C$_3$HD)/N(c-C$_3$H$_2$) and the N(N$_2$D$^+$)/N(N$_2$H$^+$) ratio versus the CO depletion factor for the starless core sample. The depletion factors for L1544, TMC2, L1495, and L1517B were taken from Crapsi et al. (2005). To search for a statistical correlation between N(c-C$_3$HD)/N(c-C$_3$H$_2$) and $f_d(CO)$ we applied the Kendall’s $\tau$ and Spearman’s $\rho$ rank correlation tests. The Kendall’s test
The values for L1544 were taken from Spezzano et al. (2013).
### Table 4: Observed Lines in the Protostellar Core Sample

| Source/Molecule | Frequency (GHz) | $T_{MB}$ (K) | $ms$ (mK) | $W$ (K km s$^{-1}$) | $v_{LSR}$ (km s$^{-1}$) | $\Delta v$ (km s$^{-1}$) |
|-----------------|-----------------|--------------|-----------|-----------------|----------------------|--------------------|
| Per5            |                 |              |           |                 |                      |                    |
| $c$-$C_3H_2$    | 84.727          | 0.09         | 9         | $0.050 \pm 0.004$ | $8.102 \pm 0.021$  | $0.529 \pm 0.051$  |
| $c$-$C_3HD$     | 104.187         | 0.27         | 21        | $0.116 \pm 0.007$ | $8.174 \pm 0.013$  | $0.401 \pm 0.032$  |
| $H^3$-$C_2H$    | 84.185          | 0.09         | 6         | $0.035 \pm 0.002$ | $8.171 \pm 0.012$  | $0.362 \pm 0.026$  |
| $C_3D_2$        | 97.761          | 0.09         | 11        | $0.029 \pm 0.004$ | $8.215 \pm 0.021$  | $0.318 \pm 0.050$  |
| HH211           |                 |              |           |                 |                      |                    |
| $c$-$C_3H_2$    | 84.727          | 0.10         | 7         | $0.051 \pm 0.002$ | $9.089 \pm 0.013$  | $0.461 \pm 0.029$  |
| $c$-$C_3HD$     | 104.187         | 0.35         | 14        | $0.163 \pm 0.005$ | $9.097 \pm 0.007$  | $0.432 \pm 0.018$  |
| $H^3$-$C_2H$    | 84.185          | 0.05         | 5         | $0.022 \pm 0.002$ | $9.100 \pm 0.019$  | $0.403 \pm 0.045$  |
| $C_3D_2$        | 97.761          | 0.10         | 7         | $0.037 \pm 0.002$ | $9.102 \pm 0.012$  | $0.361 \pm 0.032$  |
| IRAS03282       |                 |              |           |                 |                      |                    |
| $c$-$C_3H_2$    | 84.727          | 0.02         | 5         | $0.020 \pm 0.002$ | $7.002 \pm 0.062$  | $0.933 \pm 0.155$  |
| $c$-$C_3HD$     | 104.187         | 0.12         | 9         | $0.064 \pm 0.004$ | $6.863 \pm 0.015$  | $0.517 \pm 0.034$  |
| $H^3$-$C_2H$    | 84.185          | 0.03         | 12        | $0.077 \pm 0.005$ | $6.365 \pm 0.013$  | $0.404 \pm 0.028$  |
| $C_3D_2$        | 97.761          | 0.05         | 6         | $0.013 \pm 0.002$ | $6.812 \pm 0.035$  | $0.414 \pm 0.072$  |
| IRAS16293       |                 |              |           |                 |                      |                    |
| $c$-$C_3H_2$    | 84.727          | 0.22         | 6         | $0.086 \pm 0.002$ | $6.407 \pm 0.005$  | $0.366 \pm 0.010$  |
| $c$-$C_3HD$     | 104.187         | 0.33         | 17        | $0.144 \pm 0.006$ | $6.433 \pm 0.009$  | $0.410 \pm 0.018$  |
| $H^3$-$C_2H$    | 84.185          | 0.18         | 12        | $0.077 \pm 0.005$ | $6.365 \pm 0.013$  | $0.404 \pm 0.028$  |
| $C_3D_2$        | 97.761          | 0.05         | 6         | $0.018 \pm 0.002$ | $6.477 \pm 0.020$  | $0.360 \pm 0.063$  |

**Note.** The line properties are derived from Gaussian fits.

The excitation temperature of C$^{18}$O was set equal to 43 K which is the dust temperature for IRAS16293 (Schöier et al. 2002). At this temperature no CO depletion is expected. However, the C$^{18}$O column density is an average along the line of sight which, apart from the warm central regions, also includes the cold envelope, where CO can be significantly frozen (e.g., Brünken et al. 2014). The hydrogen column density N(H$_2$) was derived using the Herschel/SPIRE image of IRAS16293 at 250, 350, and 500 µm. These data are publicly available and can be downloaded from the Herschel Science Archive.$^3$ For more information concerning the data reduction, see Section 3.3. The resulting N(H$_2$) of 1.0 × 10$^{23}$ cm$^{-2}$ is the mean value of column densities within a beam of 40$''$. Following Equation (3), the depletion factor for IRAS16293 is equal to

$$ X(C^{18}O) \approx \frac{N_{ref}(C^{18}O) \cdot 560}{N(H_2)} \cdot X(C^{16}O) $$

This expression gives $\tau = 0.33$ with a significance $\rho = 0.49$ and the Spearman's test gives $\rho = 0.40$ with $p = 0.60$, indicating that there is no correlation between the $c$-$C_3H_2$ deuteration and the CO depletion factor within the starless core sample. In case of the N$_2$H$^+$ deuteration, however, we note a significant jump toward the pre-stellar core L1544. As already mentioned, this indicates that N$_2$H$^+$ is less affected by depletion than $c$-$C_3H_2$ and traces the deuteration level in the highest-density regions of the core; in fact the N$_2$H$^+$ abundance also increases where CO is significantly frozen, as CO destroys N$_2$H$^+$ to form HCO$^+$. The correlation between $N(c$-$C_3H_2)/N(c$-$C_3H_2)$ and the CO depletion factor in the observed protostars is shown in Figure 4. The depletion factors for the sources HH211, IRAS03282, L1448IRS2, and Per5 were taken from Emprechtinger et al. (2009), while the depletion factor for L1521F was reported in Crapsi et al. (2005). For this depletion level in IRAS16293 we used the spectral properties of the C$^{18}$O (1–0) transition given in Caux et al. (2011) to calculate the column density of C$^{18}$O, as was done in Emprechtinger et al. (2009). Here we use $X_{ref}(C^{18}O) = 9.5 \times 10^{-5}$ (Freking et al. 1982) to allow a fair comparison with Emprechtinger et al. (2009), although other values for $X_{ref}(C^{18}O)$ can be found in the literature (Wannier 1980; Lacy et al. 1994). We use the relation $X(C^{16}O)/X(C^{18}O) = 560$ (Wilson & Rood 1994) such that:

$$ X(C^{16}O) \approx \frac{N_{ref}(C^{18}O) \cdot 560}{N(H_2)} \cdot X(C^{16}O) $$

This value is consistent with the low $f_d$(CO) values measured by Punanova et al. (2016) in various sources toward ρ Ophiuchus. The fact that $f_d$(CO) is lower than 1 suggests that

http://www.cosmos.esa.int/web/herschel/science-archive
### Table 5

| Starless Core | \(N(\text{c-C}_3\text{H}_2)\) \((10^{12} \text{ cm}^{-2})\) | \(N(\text{c-C}_3\text{H}_2)\) \((10^{13} \text{ cm}^{-2})\) | \(N(\text{c-H}_3\text{C}_2\text{H})\) \((10^{13} \text{ cm}^{-2})\) | \(N(\text{c-C}_3\text{D}_2)\) \((10^{12} \text{ cm}^{-2})\) |
|--------------|------------------|------------------|------------------|------------------|
| CB23         | 10.9 ± 1.2       | 1.15 ± 0.13      | 0.28 ± 0.03      | <0.07            |
| L1400A       | 9.1 ± 1.1        | 0.74 ± 0.09      | 0.24 ± 0.03      | <0.07            |
| L1400K       | 8.0 ± 1.3        | <0.26            | 0.21 ± 0.03      | <0.07            |
| L1495        | 8.6 ± 2.1        | 0.66 ± 0.08      | 0.22 ± 0.06      | <0.07            |
| L1495AN      | 31.7 ± 3.5       | 2.50 ± 0.28      | 0.82 ± 0.09      | 0.13 ± 0.02      |
| L1495AS      | 11.4 ± 1.6       | 0.94 ± 0.11      | 0.30 ± 0.04      | <0.07            |
| L1495B       | 7.5 ± 1.2        | 0.94 ± 0.14      | 0.20 ± 0.03      | <0.07            |
| L1512        | 13.2 ± 1.6       | 1.09 ± 0.13      | 0.34 ± 0.04      | 0.08 ± 0.02      |
| L1517B       | 12.2 ± 1.9       | 1.23 ± 0.14      | 0.32 ± 0.05      | 0.16 ± 0.03      |
| TMC2         | 25.9 ± 2.9       | 2.94 ± 0.32      | 0.67 ± 0.08      | 0.31 ± 0.03      |
| L1544        | 34.9 ± 3.7       | 3.18 ± 0.32      | 0.91 ± 0.10      | 0.53 ± 0.06      |

Note.  
* No data available.

### Table 6

| Protostellar Core | \(N(\text{c-C}_3\text{H}_2)\) \((10^{12} \text{ cm}^{-2})\) | \(N(\text{c-C}_3\text{H}_2)\) \((10^{13} \text{ cm}^{-2})\) | \(N(\text{c-H}_3\text{C}_2\text{H})\) \((10^{13} \text{ cm}^{-2})\) | \(N(\text{c-C}_3\text{D}_2)\) \((10^{12} \text{ cm}^{-2})\) |
|------------------|------------------|------------------|------------------|------------------|
| Per5             | 14.2 ± 1.7       | 1.4 ± 0.16       | 0.37 ± 0.04      | 0.24 ± 0.04      |
| HH211            | 8.5 ± 1.2        | 1.9 ± 0.20       | 0.22 ± 0.03      | 0.30 ± 0.00      |
| L1448IRS2        | 13.9 ± 1.9       | 1.3 ± 0.14       | 0.36 ± 0.05      | <a>          |
| IRAS03282        | 5.1 ± 1.1        | 0.7 ± 0.09       | 0.13 ± 0.03      | <a>          |
| IRAS16293        | 36.4 ± 5.0       | 3.6 ± 0.39       | 0.95 ± 0.13      | 0.43 ± 0.07      |
| L1521F           | 31.5 ± 3.7       | 2.4 ± 0.26       | 0.82 ± 0.10      | 0.20 ± 0.03      |

Notes. The protostars Per 5, HH211, L1448IRS2 and IRAS03282 belong to the Perseus complex, L1521F lies in the Taurus complex, and IRAS16293 is part of the Ophiuchus complex.  
* No data available.

The adopted \(X_{\text{ref}}(\text{C}^{16}\text{O})\) is underestimated by a factor of 2–3. Moreover, one has to keep in mind that the \(\text{C}^{18}\text{O} (1-0)\) emission was observed within 22\(^{\prime}\), while the estimation of \(N(\text{H}_2)\) was done within a 40\(^{\prime}\) beam. This indicates that the derived depletion factor should be considered as a lower limit.

Figure 4 shows no clear trend between the deuteration of \(\text{c-C}_3\text{H}_2\) and the CO depletion among the protostellar cores. This is also confirmed by the Kendall’s rank test that gives \(\tau = 0.32\) with a significance \(p\) of 0.45 as well as by the Spearman’s rank test that results in \(\rho = 0.56\) with \(p = 0.32\) (without considering the protostar L1521F). The source L1521F deviates strongly from the rest of the sources, having a significant depletion factor of 15 and simultaneously showing a low \(\text{c-C}_3\text{H}_2\) deuteration of 8\%. These values are comparable to those found in L1544, where the CO depletion factor is 14 (Crapsi et al. 2005) and the deuteration of \(\text{c-C}_3\text{H}_2\) is 9\%. The peculiarity of L1521F has been proven already in previous works, where the central column density \(N(\text{H}_2)\) is high \((13.5 \times 10^{12} \text{ cm}^{-2})\) despite the low \(N(\text{H}_2)\) deuteration (being a factor of 2 lower than in L1544; Crapsi et al. 2004, 2005).

The large CO depletion factor and low deuteration both in \(\text{N}_2\text{H}^+\) and \(\text{c-C}_3\text{H}_2\) in L1521F could be a signature of episodic accretion of the central protostar. Since L1521F has been classified as a VeLLO (Bourke et al. 2006; Takahashi et al. 2013) it may be in a quiescent phase, following an accretion burst event. During such a burst, CO is expected to return in the gas phase (Visser et al. 2015), thus reducing the deuteration fraction. After the burst, the fast cooling of the dust could quickly lead to CO freeze-out, with short timescales of the order of \(10^5/\text{n}_{\text{H}}\) yr, where \(\text{n}_{\text{H}}\) is the total number density of hydrogen nuclei (e.g., Caselli et al. 1999), while the deuteration of gas-phase molecules is a slower process, especially if during the burst the ortho-to-para-\(\text{H}_2\) ratio (sensitive to the temperature) increases to values larger than 1\% (e.g., Flower et al. 2006; Kong et al. 2015). However, the exact physical and chemical conditions of L1521F are beyond the scope of this work and it is clear that further observations are needed to prove this point.

#### 3.3. Correlation between Deuteration and \(\text{H}_2\) Column Density

As already pointed out in Section 3.2, an increase in volume density toward the core center is expected to correlate with an increase in deuteration, because of the consequently larger CO freeze-out rates, as long as the temperature remains below 20K. For this reason we examine how the estimated deuteration of \(\text{c-C}_3\text{H}_2\) in the starless and the pre-stellar cores correlates with the central column density of molecular hydrogen. For the \(N(\text{H}_2)\) calculation we use the Herschel/ SPIRE image of
The deuteration level of N$_2$H$^+$ among the starless cores. However, in L1544, we recognize a substantial increase in the deuteration of N$_2$H$^+$, as was already visible in Figure 1. In Crapsi et al. (2005) there are three additional evolved pre-stellar cores (L183, L429, and L694-2), that show enhanced N$_2$H$^+$ deuteration with increasing N(H$_2$). This indicates that N$_2$H$^+$ is indeed a late-type molecule and stays in the gas phase at high densities, while c-C$_2$H$_2$ is possibly depleted in the central regions, thus it stops tracing the central zone of the core where high levels of deuteration fractions are present. This is in agreement with our current understanding of the chemistry of c-C$_2$H$_2$, and its distribution across the pre-stellar core L1544 (Sipilä et al. 2016, see in Appendix B). Another way of testing this theory is to examine parameters that are related to the kinematics of the gas, such as the width of the detected lines. Figure 6 shows the correlation between the observed linewidth, $\Delta v_{\text{obs}}$, of c-C$_2$H$_2$ (3$_{2,2}$ - 3$_{1,1}$) and of N$_2$H$^+$ (1-0) among the starless and protostellar core sample. Thermal, turbulent, and systematic motions contribute to the total $\Delta v_{\text{obs}}$. Thermal broadening does not play a substantial role, since the thermal linewidth of c-C$_2$H$_2$ is just 0.11 km s$^{-1}$ at 10 K (and 0.13 km s$^{-1}$ for N$_2$H$^+$). As we can clearly see in Figure 6, the observed c-C$_2$H$_2$ line has a larger width in most of the cores (except for L1495 and L1495AN, where the observed linewidths are approximately the same).

This suggests that c-C$_2$H$_2$ traces a different region than N$_2$H$^+$, where turbulent or systematic (i.e., rotation, infall, or outflows in protostellar objects) motion dominates. In both starless and protostellar core samples we see the same trend by studying the linewidth of c-H$^3$C$_2$H (2$_{1,2}$ - 1$_{0,1}$) instead, suggesting that the optical depth broadening of c-C$_2$H$_2$ (3$_{2,2}$ - 3$_{1,1}$) is negligible.

### 3.4. Correlation between Deuteration and Dust Temperature

During the protostellar phase, the core starts to warm up the surrounding material, leading to desorption of CO from dust grains. Moreover, the energetic outflows by protostars can also contribute to the release of CO molecules in the gas phase via...
sputtering or grain–grain collisions (e.g., Caselli et al. 1997; Jiménez-Serra et al. 2008). Back in the gas phase, CO can react and destroy H$_2$D$^+$, reducing the total deuteration in molecules. In addition, Reaction (1) can proceed at high temperatures also in the backward direction, leading to a further reduction of H$_2$D$^+$. Therefore, one expects an anticorrelation between the deuteration and the dust temperature (e.g., Ladd et al. 1991; Myers & Ladd 1993) of a protostar, as has already been confirmed (Emprechtinger et al. 2009; Fontani et al. 2011). In Figure 7 we plot the deuteration fraction of c-C$_3$H$_2$ against $T_{\text{Dust}}$ in the protostellar core sample. The values for $T_{\text{Dust}}$ were taken from Emprechtinger et al. (2009). As in Section 3.2, here we also include the protostar IRAS16293 (Schöier et al. 2002). Figure 7 shows a clear anticorrelation between deuteration and $T_{\text{Dust}}$ when excluding L1521F, that has a Kendall’s $\tau$.

**Table 8**

| Protostellar Core | $N/$c-C$_3$H$_2$/N($c$-C$_3$H$_3$) | $N/$c-C$_3$D$_2$/N($c$-C$_3$H$_3$) | $N$/c-C$_3$D$_2$/N($c$-C$_3$HD) |
|------------------|---------------------------------|---------------------------------|-----------------------------|
| Per 5            | 0.10 ± 0.02                     | 0.017 ± 0.005                  | 0.18 ± 0.05                 |
| HH211            | 0.23 ± 0.06                     | 0.036 ± 0.009                  | 0.16 ± 0.04                 |
| L1448IRS2        | 0.09 ± 0.02                     | *                              | *                           |
| IRAS03282        | 0.14 ± 0.05                     | *                              | *                           |
| IRAS16293        | 0.10 ± 0.02                     | 0.012 ± 0.003                  | 0.12 ± 0.03                 |
| L1521F           | 0.08 ± 0.02                     | 0.006 ± 0.002                  | 0.08 ± 0.02                 |

**Note.**

*a* No data available.

**Figure 3.** Deuterium fraction of c-C$_3$H$_2$ and N$_2$H$^+$ as a function of the CO depletion factor in the starless cores L1495, L1517B, TMC2, and L1544.

**Figure 4.** Deuterium fraction of c-C$_3$H$_2$ and N$_2$H$^+$ as a function of CO depletion factor for the protostellar core sample. The deuteration fraction of N$_2$H$^+$ and the CO depletion factors were taken from Emprechtinger et al. (2009), while the $N$/N$_2$D$^+$/$N$/N$_2$H$^+$ ratio and $f_d$(CO) for L1521F was given in Crapsi et al. (2005).

**Figure 5.** Deuterium fraction of c-C$_3$H$_2$ (blue dots) and N$_2$H$^+$ (red dots) as a function of central column density of H$_2$, measured with Herschel in the starless and pre-stellar core sample. The deuteration of N$_2$H$^+$ was calculated by Crapsi et al. (2005).

**Table 9**

| Starless Core | $N$/H$_2^a$ | $N$/H$_2^b$ |
|---------------|-------------|-------------|
| L1495         | 8.3 ± 1.6   | 31 ± 10     |
| L1495B        | 10.1 ± 2.0  | ...         |
| L1495AN       | 15.1 ± 2.7  | ...         |
| L1495AS       | 22.1 ± 4.1  | ...         |
| TMC2          | 18.9 ± 3.3  | 60 ± 12     |
| L1544         | 27.9 ± 5.1  | 94 ± 16     |
| L1512         | 8.6 ± 1.6   | ...         |
| L1517B        | 11.5 ± 2.3  | 37 ± 10     |
| CB23          | 8.5 ± 1.6   | ...         |

**Notes.**

*a* This work.

*b* Crapsi et al. (2005).
coefficient of $-0.74$ with a significance $p$ of 0.08 and a Spearman’s $\rho$ coefficient of $-0.82$ with a significance $p$ of 0.09. The abundance ratio $N(c$-$c\text{C}_3\text{HD})/N(c$-$c\text{C}_3\text{H}_2)$ peaks in the coldest source, HH211 at 23%, and decreases toward the warmer sources down to 8%.

The young source HH211 could be an example of a protostar where the accretion burst has recently occurred and/or where ices have been recently evaporated. If this is the case, one way to interpret the large deuteration of $c$-$c\text{C}_3\text{H}_2$ is the release of a large amount of deuterated (and non-deuterated) $c$-$c\text{C}_3\text{H}_2$ from the ices into the gas phase. Furthermore, this could imply significant deuteration of $c$-$c\text{C}_3\text{H}_2$ on the surface of dust grains, maybe due to hydrogen–deuterium exchange reactions known to occur for other molecules, such as $\text{CH}_3\text{OH}$ during the preceding cold pre-stellar phase (e.g., Parise et al. 2006).\footnote{Recent experiments of D–H exchanges carried out by Faure et al. (2015) suggest that they are made possible by hydrogen bonds between the hydroxyl functional groups of methanol and water ice. This makes it unlikely that such a process could work for $c$-$c\text{C}_3\text{H}_2$, although experimental and theoretical work is needed to rule out this hypothesis.}

The result for L1521F deviates considerably from the rest of the sources. The dust temperature for L1521F ($T_{\text{Dust}} = 9 \pm 2$ K) was taken from Kirk et al. (2005). As already highlighted in Section 3.2, L1521F hosts a VeLLO which could be a protostar in the very early stages of evolution and/or an example of low activity in protostellar evolution characterized by episodic accretion. This could explain the mismatch between the physical (low $T_{\text{Dust}}$) and chemical conditions (low deuteration).

4. Conclusion

In this work we presented single-pointing observations of $c$-$c\text{C}_3\text{H}_2$, the singly and doubly deuterated species, $c$-$c\text{C}_3\text{HD}$ and $c$-$c\text{C}_3\text{D}_2$, as well as the isotopologue $c$-$c\text{H}^3\text{C}_2\text{H}$ toward 10 starless cores and five protostellar cores in the Taurus and Perseus complexes. The pre-stellar core L1544 and the protostellar core IRAS16293 were also included in our study. We calculated the deuterium fractionation $N(c$-$c\text{C}_3\text{HD})/N(c$-$c\text{C}_3\text{H}_2)$ and studied its correlation with the CO depletion factor, the dust temperature, and the $\text{H}_2$ column density toward the core center. We also examined the differences between the deuteration of $c$- and $N$-bearing molecules. Here is a summary of our main conclusions.

1. The ratio $N(c$-$c\text{C}_3\text{HD})/N(c$-$c\text{C}_3\text{H}_2)$ is, within the error bars, equal to 10% in all starless and pre-stellar cores where $c$-$c\text{C}_3\text{HD}$ has been detected. This also accounts for the protostars except for the source HH211 where we measure a high deuteration level of $(23 \pm 6)\%$. The $N(c$-$c\text{D}_2)/N(c$-$c\text{H}_2)$ ratio ranges from 0.4 to 1.5% in starless and pre-stellar cores, and from 0.6 to 3.6% among the protostellar cores. The deuteration of $c$-$c\text{C}_3\text{H}_2$ and $N_2\text{H}^+$ follows the same trend in both samples. However, in case of the evolved pre-stellar core L1544, the deuteration of $N_2\text{H}^+$ is significantly higher (factor of 2.6) compared to the $N(c$-$c\text{C}_3\text{HD})/N(c$-$c\text{C}_3\text{H}_2)$ ratio. This can be understood by the well-known fact that $N_2\text{H}^+$ remains in the gas phase even at densities of about $10^6$ cm$^{-3}$, where the $c$-bearing molecules (including $c$-$c\text{C}_3\text{H}_2$ and its deuterated forms) are highly frozen and where deuterium fractionation proceeds rapidly, thanks to the large abundances of the deuterated $H_2^+$ isotopologues.

2. Among the starless cores, we find no correlation between the deuteration of $c$-$c\text{C}_3\text{H}_2$ and the CO depletion factor or the central $\text{H}_2$ column density (measured with Herschel). However, the $N_2\text{H}^+$ deuteration substantially increases toward L1544, which is the most evolved source within the starless core sample. This indicates that $N_2\text{H}^+$ traces the central dense core, unlike $c$-$c\text{C}_3\text{H}_2$, which is more likely tracing an outer shell surrounding the dense region of the pre-stellar core. This theory is also favored by the fact that the observed linewidth of the $c$-$c\text{C}_3\text{H}_2$ emission is larger than that of the $N_2\text{H}^+$ emission among the starless and the protostellar cores. As a consequence, the information resulting from observing $c$-$c\text{C}_3\text{H}_2$ and $N_2\text{H}^+$ is complementary because it brings insights on different regions of the core.

3. Among the protostellar cores, there is a tight anticorrelation between the deuteration of $c$-$c\text{C}_3\text{H}_2$ and the dust temperature ($\tau = -0.74$ and $p = -0.82$), with the exception of L1521F. The $N(c$-$c\text{C}_3\text{HD})/N(c$-$c\text{C}_3\text{H}_2)$ ratio drops with increasing $T_{\text{Dust}}$, reaching the maximum value of 0.23 in the coolest source, HH211 ($T_{\text{Dust}} < 21$ K), and...
decreasing toward the warmest sources, down to a deuteration level of 0.08. The \( c\)-C\(_3\)H\(_2\) deuteration does not correlate with the CO depletion factor within the protostellar core sample. L1521F differs substantially from the rest of the sources showing, in both species, \( c\)-C\(_3\)H\(_2\) and N\(_2\)H\(^+\), a low deuteration and at the same time a high depletion factor of 15 (see the comment below for explanation).

4. The high \( c\)-C\(_3\)H\(_2\) deuteration of the youngest source, HH211, might be the result of a recent evaporation of \( c\)-C\(_3\)H\(_2\) and \( c\)-C\(_3\)HD coming from a recent accretion burst. The timescale must be short enough to avoid the enhanced abundance of CO in the gas phase to significantly alter the \( c\)-C\(_3\)H\(_2\) abundance and deuterium fraction. As similarly large values are not seen in the prestellar phase, deuteration processes taking place also on dust grains would be a possible scenario for the observed high deuteration of \( c\)-C\(_3\)H\(_2\) in this young protostar.

5. The source L1521F shows a peculiar behavior, having a low deuteration of 0.08 in spite of a significant CO depletion factor \( (f_d(\text{CO}) = 15 \pm 3.6)\) and a low dust temperature \( (T_{\text{Dust}} = 9 \pm 2\, \text{K})\). The peculiarity of this source has been highlighted in other studies as well (Crapsi et al. 2005, 2004). L1521F could be an episodically accreting low-mass protostar in a quiescent phase (Bourke et al. 2006; Takahashi et al. 2013). The fact that it shows a low deuteration and dust temperature, while having a high CO depletion, might imply that after a recent burst, which heated dust and gas, the ortho-to-para-H\(_2\) ratio possibly increased, thus slowing down the deuteration process in the now cold envelope.

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Appendix A

Observed Spectra of \( c\)-C\(_3\)H\(_2\) and Its Isotopologues toward the Starless and Protostellar Core Samples

In Figures 8–23 we show the observed spectra toward all sources.

Figure 8. Spectra of several isotopologues of \( c\)-C\(_3\)H\(_2\) toward the protostellar core HH211. The red line plots the CLASS Gaussian fit.
Figure 9. Spectra of the isotopologues of $c$-$c_3H_2$ observed toward the protostellar core IRAS03282. The red line plots the CLASS Gaussian fit.

Figure 10. Spectra of the isotopologues of $c$-$c_3H_2$ observed toward the protostellar core L1448IRS2. The red line plots the CLASS Gaussian fit.
Figure 11. Spectra of the isotopologues of $c$-$C_3H_2$ observed toward the protostellar core L1521F. The red line plots the CLASS Gaussian fit.
Figure 12. Spectra of the isotopologues of c-C$_3$H$_2$ observed toward the protostellar core IRAS16293. The red line plots the CLASS Gaussian fit.
Figure 13. Spectra of the isotopologues of $\text{c-C}_3\text{H}_2$ observed toward the protostellar core Per5. The red line plots the CLASS Gaussian fit.

Figure 14. Spectra of the isotopologues of $\text{c-C}_3\text{H}_2$ observed toward the starless core CB23. The red line plots the CLASS Gaussian fit.
Figure 15. Spectra of the isotopologues of \( c\text{-C}_3\text{H}_2 \) observed toward the starless core L1400A. The red line plots the CLASS Gaussian fit.

Figure 16. Spectrum of the main species \( c\text{-C}_3\text{H}_2 \) observed toward the starless core L1400K. The red line plots the CLASS Gaussian fit.
Figure 17. Spectra of the isotopologues of $c$-$C_3H_2$ observed toward the starless core L1495. The red line plots the CLASS Gaussian fit.

Figure 18. Spectra of the isotopologues of $c$-$C_3H_2$ observed toward the starless core L1495AN. The red line plots the CLASS Gaussian fit.
Figure 19. Spectra of the isotopologues of \( c\text{-}C_3\text{H}_2 \) observed toward the starless core L1495AS. The red line plots the CLASS Gaussian fit.

Figure 20. Spectra of the isotopologues of \( c\text{-}C_3\text{H}_2 \) observed toward the starless core L1495B. The red line plots the CLASS Gaussian fit.
Figure 21. Spectra of the isotopologues of $c$-C$_3$H$_2$ observed toward the starless core L1512. The red line plots the CLASS Gaussian fit.

Figure 22. Spectra of the isotopologues of $c$-C$_3$H$_2$ observed toward the starless core L1517B. The red line plots the CLASS Gaussian fit.
Appendix B

The $c$-$C_3H_2$ and $c$-$C_3HD$ Distribution across the Pre-stellar Core L1544

We use the chemical/physical model for L1544 described in Sipilä et al. (2016) to simulate the abundances of gaseous and solid $c$-$C_3H_2$, $c$-$C_3HD$ and the ratio $c$-$C_3HD$/$c$-$C_3H_2$ as functions of distance from the core center, defined by the position of the millimeter dust continuum peak. Figure 24 shows the abundances of the gaseous and solid species as well as the deuteration level $c$-$C_3HD$/$c$-$C_3H_2$ at three different times: $10^4$, $10^5$, and $10^6$ yr. The depletion of $c$-$C_3H_2$ and $c$-$C_3HD$ toward the center increases with the evolution of the core, as expected. At $t = 10^6$ yr the depletion zone of both species reaches a few 1000 au. Here we confirm the fact that $c$-$C_3H_2$ and its deuterated counterpart stop tracing the zone where high levels of deuterium

Figure 23. Spectra of the isotopologues of $c$-$C_3H_2$ observed toward the pre-stellar core TMC2. The red line plots the CLASS Gaussian fit.
fraction are present, as already suggested in Section 3.2. The right panel of Figure 24 shows that the total deuteration level of gaseous and solid c-C₃H₂ is less than 20% at \( t = 10^6 \) yr. This means that one of the most advanced gas--grain chemical codes including deuterium fractionation is not able to reproduce the large deuterium fraction of 23% observed in c-C₃H₂ toward the young protostar HH211 (which represents the next evolutionary state after the evolved pre-stellar core L1544), suggesting either that some important surface processes are missing in the current chemical scheme, or that the relative rates of the currently included processes need to be modified.

Figure 24. Abundance profiles of gaseous and solid c-C₃H₂ (red), c-C₃HD (blue), and the ratio c-C₃HD/c-C₃H₂ toward L1544, as functions of distance, from the core center to a radius of 10⁵ au. The solid species are marked with an asterisk. The abundances and abundance ratios are plotted at three different times: 10⁴, 10⁵, and 10⁶ yr.

**Appendix C**

**Error Estimation of the H₂ Column Density**

One source of uncertainty in the estimation of \( N(\text{H}_2) \), which is derived from the SPIRE images at (250, 350, 500) \( \mu \text{m} \), is the flux uncertainty. The flux calibration of the SPIRE photometer is based on Neptune. Being a bright source, Neptune produces high-S/N spectra and has a well understood submillimeter spectrum. The calibration flux densities for Neptune at (250, 350, 500) \( \mu \text{m} \) are (160, 100, 60) Jy and the absolute flux uncertainty is estimated to be 4%, which corresponds to the absolute calibration uncertainty. Considering also the relative calibration and the extended source calibration uncertainty, the total flux uncertainty for the SPIRE bands amounts to 7% according to the SPIRE handbook.

The column density of H₂ and its total error are estimated by applying a Monte Carlo fitting procedure with 1000 iterations. After every iteration, the noise level \( \epsilon_{\text{noise}} \) is added to every map, pixel by pixel, following the equation

\[
\epsilon_{\text{noise}} = \epsilon_1 \cdot 0.07 \cdot I_\nu + \delta I_\nu \cdot \epsilon_2,
\]

where \( I_\nu \) is the detected intensity at a frequency \( \nu \), \( \epsilon_{1,2} \) describes a random number taken from a standard normal distribution, and \( \delta I_\nu \) is the statistical error on the flux density value in each pixel produced by the pipeline. The fitting method gives a cube of \( N = 1000 \) maps. The first map with \( \epsilon_{\text{noise}} = 0 \) gives the resulting \( N(\text{H}_2) \), while its uncertainty is given by the standard deviation of the remaining maps.

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