INTERSTELLAR DETECTION OF c-C3D2

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ABSTRACT

We report the first interstellar detection of c-C3D2. Doubly deuterated cyclopropenylidene, a carbene, has been detected toward the starless cores TMC-1C and L1544 using the IRAM 30 m telescope. The 𝐽𝐾𝑎,𝐾𝑐 = 303–212, 313–202, and 221–110 transitions of this species have been observed at 3 mm in both sources. The expected 1:2 intensity ratio has been found in the 303–212 and 313–202 lines, belonging to the para and ortho species, respectively. We also observed lines of the main species, c-C3H2, singly deuterated c-C3HD, and the species with one 13C off of the principal axis of the molecule, c-H13C2H. The lines of c-C3D2 have been observed with high signal-to-noise ratio, better than 7.5σ in TMC-1C and 9σ in L1544. The abundance of doubly deuterated cyclopropenylidene with respect to the normal species is found to be 0.4%–0.8% in TMC-1C and 1.2%–2.1% in L1544. The deuteration of this small hydrocarbon ring is analyzed with a comprehensive gas–grain model, the first including doubly deuterated species. The observed abundances of c-C3D2 can be explained solely by gas-phase processes, supporting the idea that c-C3H2 is a good indicator of gas-phase deuteration.

Key words: ISM: molecules – line: identification – molecular data – molecular processes

Online-only material: color figures

1. INTRODUCTION

Investigating deuterium chemistry is useful to put constraints on the ionization fraction, temperature, density, and thermal history of dense molecular clouds (Guelin et al. 1977; Caselli et al. 2002; Cazaux et al. 2011; Taquet et al. 2012). The observations of multiply deuterated molecules in space (e.g., Ceccarelli et al. 2007 and references therein) have shown the necessity of reexamining some reaction rates in chemical networks (Roberts et al. 2002), elemental D/H ratio in cold dense gas (Roueff et al. 2007), and the density structure in sources such as L1544 and ρ Oph D (Roberts et al. 2004), as well as the effects of accretion on grains (Roberts et al. 2000), possible effects of internal dynamical motion (Aikawa et al. 2005), and the evolution of ice mantles in dense clouds and cores (Cazaux et al. 2011; Taquet et al. 2012).

The first multiply deuterated interstellar molecule detected was D2CO, almost 20 yr ago (Turner 1990). Since then, the study of deuterated molecules in the interstellar medium has rapidly increased as they have been proven to be a unique observational probe of the early stages in low-mass star formation. Multiply deuterated species such as triply deuterated ammonia have been detected with a surprisingly high abundance ratio of 10–4 with respect to their fully hydrogenated forms (Lis et al. 2002). By comparing this ratio with the elemental D/H ratio (1.65 × 10–5; Linsky et al. 1993), it is easily seen that there is a remarkable enrichment in deuterium in this and other molecules. In IRAS

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photodissociation regions, circumstellar envelopes, and planetary nebulae (Thaddeus et al. 1985; Vršnak et al. 1987; Cox et al. 1987; Madden et al. 1989; Lucas & Liszt 2000). Given the high abundance of the normal species, both c-C$_3$HD and the singly substituted $^{13}$C species (off-axis) have been observed with a good signal-to-noise ratio (S/N) in cold dark clouds. Furthermore cyclopropenylidene shows an enhancement in deuterium fractionation in cold dark clouds. For example, Gerin et al. (1987) measured a 1:5 ratio of the $2_1,2$ $-$ $1_0,1$ lines of c-C$_3$HD and c-C$_3$D$_2$ in TMC1. The reactions which lead to such a high deuteration are still poorly understood. Some rates of reactions which may be involved in the formation of deuterated c-C$_3$H$_2$ have been measured by Savic et al. (2005), but to our knowledge they have not been included in models thus far. Last year, the centimeter- and millimeter-wavelength spectra of doubly deuterated c-C$_3$H$_2$ were measured in the laboratory (Spezzano et al. 2012), allowing for the first time a search for c-C$_3$D$_2$ in space.

Like its fully hydrogenated counterpart, c-C$_3$D$_2$ presents the spectrum of an oblate asymmetric top with b-type transitions. Furthermore c-C$_3$D$_2$ shows a deuteron quadrupole splitting resolvable at very low J. Given the presence of two equivalent off-axis bosons, it has ortho and para symmetry species with relative statistical weight of 2:1.

Unlike several of the six known multiply deuterated species observed in the radio band (D$_2$H$^+$, CHD$_2$OH, NH$_2$D, D$_2$CO, D$_2$S, and D$_2$CS), c-C$_3$H$_2$ is believed to form solely by gas-phase reactions (Park et al. 2006). The interplay between the gas phase and grain surface reactions in the deuteration of interstellar molecules is not clear thus far, partially because there are not many probes available for testing the models: c-C$_3$H$_2$ is an ideal molecule for this purpose because of its easily observable transitions and because it has the possibility of double deuteration. Assuming that c-C$_3$D$_2$ is formed in the gas phase like its fully hydrogenated counterpart, cyclopropenylidene will be a unique probe for the deuteration processes happening in the gas phase. Furthermore, since c-C$_3$H$_2$ is, in terms of cloud evolution, an early-type molecule (Herbst & Leung 1989), it is a particularly useful tool to investigate early stages of a molecular cloud. This makes observations of its deuterated forms particularly important to test time-dependent chemical codes which include deuteration processes.

Here we report on the positive detection of three emission lines of c-C$_3$D$_2$ in the 3 mm band, namely, the $K_{upper},K_{lower} = 3_0,3$ $-$ $2_1,2$, $3_1,3$ $-$ $2_0,2$, and $2_1,1$ $-$ $1_0,0$ transitions, toward TMC-1C and L1544: to our knowledge this is the first search for doubly deuterated cyclopropenylidene undertaken.$^{10}$

2. OBSERVATIONS

The observations were carried out from 2012 September 28 until October 2 at the IRAM 30 m telescope, located in Pico Veleta (Spain), toward the starless cores TMC-1C and L1544. The choice of the sources was made on the basis of two simple criteria: the abundance of the normal species (c-C$_3$H$_2$) and a high deuteration fractionation. Both sources are in the Taurus molecular cloud, one of the closest dark cloud systems and low-mass star-forming regions in our Galaxy. L1544 is a perfect test bed to investigate the initial conditions of protostellar collapse: its structure is consistent with a contracting Bonnor–Ebert sphere, with central densities of about $10^7$ cm$^{-3}$ and a peak infall velocity of $\pm 0.1$ km s$^{-1}$ at about 1000 AU from the center (e.g., Keto & Caselli 2010). Its centrally concentrated structure and measured kinematics suggest that this is a prestellar core at a late stage of evolution, toward star formation. TMC-1C is a relatively young core, with evidence of accreting material toward a core and immersed in a cloud with densities higher than those surrounding the L1544 core (Schnee et al. 2007).

The coordinates that were used are $\alpha_{2000} = 04^h41^m16.1^s$, $\delta_{2000} = +25^\circ49'43.8''$ for TMC-1C, and $\alpha_{2000} = 05^h04^m17.21^s$, $\delta_{2000} = 25^\circ10'42.8''$ for L1544. In the case of TMC-1C these are the same coordinates as reported by Bell et al. (1988) and Gerin et al. (1987), while in the case of L1544 they correspond to the coordinates of the peak of the 1.3 mm continuum dust emission from Ward-Thompson et al. (1999). In both cores, we observed two lines of c-C$_3$H$_2$, one line of c-H$^{13}$CC$_2$H (off-axis), two lines of c-C$_3$HD, and three lines of c-C$_3$D$_2$, using three different tuning settings. A summary of the observed lines is reported in Table 1. The EMIR receivers in the E090 configuration were employed, and observations were performed in a frequency switching mode with a throw of $\pm 4.3$ MHz. All four EMIR sub-bands were connected to the Fast Fourier Transform Spectrometers set to high-resolution mode; this delivered a final spectrum with 50 kHz channel spacing (corresponding to 0.15 km s$^{-1}$ at 3 mm) and a total of 7.2 GHz of spectral coverage (nominal bandpass of 1.8 GHz per sub-band). Telescope pointing was checked every 2 hr on Jupiter and was found to be accurate to $3^\prime$–$4^\prime$.

3. RESULTS

Lines of the isotopologues of c-C$_3$H$_2$ listed in Table 1 have been detected in both sources with very high S/N. A selection of spectra of c-C$_3$H$_2$ and isotopologues in TMC-1C and L1544 is shown in Figure 1. Table 1 lists the observed line parameters. Even the weakest line of the doubly deuterated species, $2_1,1$ $-$ $1_0,1$ at 108 GHz, is detected at a 7.5 $\sigma$ level in TMC-1C ($T_{mb, rms} = 2.5$ mK), and at a $\sigma$ level in L1544 ($T_{mb, rms} = 4.6$ mK). The GILDAS$^{11}$ software (Pety 2005) was employed for the data processing: high-order polynomials had to be used for baseline subtraction given the strong baseline produced by the frequency switching observing mode. The column densities and optical depths given in Table 1 were calculated using the expressions given in the Appendix. As was already pointed out by Bell et al. (1988), c-C$_3$H$_2$ shows two velocity components toward TMC-1C, one more intense at 6 km s$^{-1}$ and one less intense at 5.4 km s$^{-1}$; see Figure 1. There is a hint of detection of the component at 5.4 km s$^{-1}$ also in c-H$^{13}$CC$_2$H, but no clear presence in the deuterated species. Assuming that all lines have the same excitation temperature in both components, we expect for the component at 5.4 km s$^{-1}$ a line intensity of 0.06 K for c-C$_3$HD ($3_{03}$ $-$ $2_{12}$) and 0.013 K for c-C$_3$D$_2$ ($3_{13}$ $-$ $2_{02}$). Comparing these estimates with the noise level in our spectra (0.007 K for c-C$_3$HD and 0.002 K for c-C$_3$D$_2$), we can say that the lower velocity component is absent in the deuterated species of cyclopropenylidene: this behavior may suggest that the lower velocity component traces a hotter region, where the deuterated molecules are not present in detectable amounts.

3.1. Excitation

The observed line intensity ratios of c-C$_3$D$_2$ pose the question of whether local thermal equilibrium is a valid assumption for its

$^{10}$ A recent abstract from S. Takano et al. at the Workshop on Interstellar Matter 2012 in Sapporo, Japan, mentions the detection of c-C$_3$D$_2$ toward L1527 in the framework of the Nobeyama 45 m telescope survey at 3 mm.

$^{11}$ http://www.iram.fr/IRAMFR/GILDAS
Figure 1. Spectra of isotopic species of c-C3H2 observed toward TMC-1C and L1544. (A color version of this figure is available in the online journal.)

Table 1
Observed Line Parameters

| Molecule          | Transition (ortho/para) | Frequency (GHz) | Ref. | Em (cm⁻¹) | Tmb (K) | rms (mK) | W (K km s⁻¹) | Brel (%) | bMB (°) | VLSR (km s⁻¹) | δV (K km s⁻¹) | Ntot × 10¹² (cm⁻²) | Nνo × 10¹¹ (cm⁻²) | τν (K km s⁻¹) |
|-------------------|-------------------------|-----------------|------|-----------|---------|----------|-------------|----------|--------|----------------|----------------|---------------------|---------------------|----------------|
| **TMC-1C**        |                         |                 |      |           |         |          |             |          |        |                |                |                     |                     |               |
| c-C3H2            | 212–101 (o)             | 85.338          | 1    | 4.48      | 2.91    | 7        | 1.05(1)    | 81       | 29     | 5.996(2)       | 0.338(4)       | 25(1)               | 22(1)               | 1.887          |
|                   | 212–101 (o)             | 85.338          | 1    | 4.48      | 1.27    | 7        | 0.414(9)   | 81       | 29     | 5.361(4)       | 0.307(8)       |                     |                     |               |
| c-C3D2            | 212–101 (p)             | 84.727          | 1    | 11.21     | 2.91    | 7        | 0.047(2)   | 81       | 29     | 5.984(6)       | 0.27(2)        | 3.5(2)              | 22(1)               | 1.488          |
| **L1544**         |                         |                 |      |           |         |          |             |          |        |                |                |                     |                     |               |
| c-C3H2            | 212–101 (o)             | 85.338          | 1    | 4.48      | 2.44    | 10       | 1.05(1)    | 81       | 29     | 7.180(2)       | 0.520(4)       | 50(2)               | 37(1)               | 3.579          |
| c-C3D2            | 212–101 (p)             | 84.727          | 1    | 11.21     | 0.16    | 10       | 0.047(2)   | 81       | 29     | 7.210(8)       | 0.46(1)        | 4.2(1)              | 37(1)               | 1.720          |
| References.       |                         |                 |      |           |         |          |             |          |        |                |                |                     |                     |               |
|                   |                         |                 |      |           |         |          |             |          |        |                |                |                     |                     |               |

Notes.

a All Nν have been calculated with the optical thin assumption, except for c-C3H2.

b Local thermodynamic equilibrium is assumed.

c Tν has assumed is 5 K in L1544, and 7 K in TMC-1C for the deuterated species, and 6 K in L1544 and 8 K in TMC-1C for the 13C and the main species.

References. (1) Thaddeus et al. 1985; (2) Bogey et al. 1987; (3) Spezzano et al. 2012.

excitation. Only for para-C3D2 is more than one optically thin line was detected. The ratios of the integrated 301–210/221–110 lines should be 4.3 and 3.3 for TMC-1C (Tν = 7 K) and L1544 (Tν = 5 K), respectively, assuming thermalization of both lines to their assumed excitation temperature, while they are 1.5 and 1.35. To gain insight into the excitation of the lines, we performed radiative transfer calculations with RADEX (van der Tak et al. 2007). Collision rates of C3H2 with H2 calculated by Chandra & Kegel (2000) and supplied by the LAMDA database (Schöier et al. 2005) were used together with molecular
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Table 2
Abundance Ratios of Deuterated Molecules in TMC-1C and L1544

|                  | TMC-1C                  | L1544                  |
|------------------|-------------------------|------------------------|
| [c-C3D2]/[c-C3H2]| 0.4%–0.8%               | 1.2%–2.1%              |
| [c-C3D2]/[c-C3HD]| 3%–15%                  | 7%–17%                 |
| [c-C3HD]/[c-C3H2]| 5%–13%                  | 12%–17%                |
| [D2CO]/[H2CO]    | ...                     | 4%                     |
| [DCO+]/[HCO+]    | 2%b                     | 4%c                    |
| [N2D+]/[N2H+]    | 8%b                     | 20%c                   |
| [NH2D]/[NH3]     | 1%b                     | 13%d                   |

Notes.

a Bacmann et al. (2003).
b Tiné et al. (2000).
c Caselli et al. (2002).
d Shah & Wootten (2001).

4. DISCUSSION

In addition to the observation of two lines of c-C3H2, one line of c-H13CC3H with the 13C off of the molecular axis and two lines of c-C3HD, we also claim the detection of three lines of c-C3D2 in both TMC-1C and L1544. This first interstellar detection of c-C3D2 is validated for the following reasons.

1. We detected all favorable transitions of c-C3D2 available in the covered frequency range.
2. The rest frequencies employed have laboratory accuracy (Spezzano et al. 2012), and in both sources the line shapes and velocities are in agreement with each other and with those observed for more abundant isotopologues (see Figure 1).
3. The intensities of the c-C3D2 lines are consistent with what is expected from the deuteration of the ring in these sources, i.e., c-C3H2/c-C3HD is consistent with c-C3HD/c-C3D2, as will be discussed below.

In Table 2 we present the relative abundances of the deuterated species with respect to the hydrogenated ones for cyclopropenylidene over the 27′′ beam for TMC-1C and L1544 obtained from this work, and also for H2CO, HCO+, N2H+, and NH3 obtained from previous work. The abundance of doubly deuterated cyclopropenylidene with respect to the normal species is 0.4%–0.8% in TMC-1C and 1.2%–2.1% in L1544. This interval has been determined considering the differences in Ntot obtained from different lines. The deuteration of c-C3H2 follows the same trend observed for other molecules in both sources. It is interesting to note that the ratios [c-C3D2]/[c-C3H2] and [c-C3HD]/[c-C3H2] are quite similar in both sources. We calculated the D/H ratio of c-C3H2 in prestellar cores using the network model of Aikawa et al. (2012).

For the physical structure of the core, we adopt the collapsing core model of Aikawa et al. (2005; the α = 1.1 model) and also a static model of L1544 from Keto & Caselli (2010). For CO depletion factors consistent with those of the two objects, i.e., fD = 3.8 for TMC-1C (Schnee et al. 2007) and fD = 14 for L1544 (Crapsi et al. 2005), the calculated column density ratio of c-C3D2/c-C3H2 is ∼10⁻², consistent with the observed value of 0.6% for TMC-1C and 1.5% for L1544. There is no need for any deuterium fractionation reactions of c-C3H2 on grain surfaces to account for the observed D/H ratio: the deuteration of cyclopropenylidene can be explained solely by gas-phase reactions. The main route of formation of deuterated cyclopropenylidene is the successive deuteration of the main species via reaction with H2D⁺, D2H⁺, and D³. An example of the reaction scheme is sketched in Figure 3, considering only H2D⁺ as reaction partner.

Figure 2. RADEX radiative transfer calculations on the excitation of para-C3D2. The color scale gives the 30 values as described in the Appendix. From Figure 2, by knowing the density of molecular hydrogen, para constants of Figure 2. RADEX radiative transfer calculations on the excitation of para-C3D2. The color scale gives the 30 values as described in the Appendix. From Figure 2, by knowing the density of molecular hydrogen, the calculated χ² values are drawn in as a red contour. The observed integrated line intensities of the para-C3D2, c - C3HD, or c-H 13CC2H, it is in principle possible to read the column density of c-C3D2 obtain from different lines. The predicted excitation temperatures tend to be rather uncertain in the column density determinations. Since the deuterium fractionation reactions of c-C3H2, it is difficult to derive conclusive results. Despite these uncertainties, we have assumed local thermodynamic equilibrium with Tex values as described in the Appendix.
The depicted cycle of reactions starts with c-C$_3$H$_2$ and H$_2$D$^+$, producing in the first step c-C$_3$HD and subsequently c-C$_3$D$_2$. The same reactions happen with D$_2$H$^+$ and D$_2$$^+$. The overall process is a series of two reactions: the proton–deuteron transfer (slow step, red arrows) and the subsequent dissociative recombination with electrons (fast step, blue arrows). The presence of this deuteration cycle results in a time-dependent deuteration fractionation. Assuming low levels of deuteration at the start, it is expected that this level increases as a function of time, reaching a stationary level after some time. Other deuteration processes, e.g., the formation of c-C$_3$HD from the reaction of C$_3$H$^+$ with HD, were found to be negligible. The D/H ratio of cyclopropenylidene is, therefore, directly related to that of H$_2$$^+$, the main deuterium donor in dark interstellar clouds. Recently, Huang & Lee (2011) have calculated highly accurate spectroscopic constants for $^{13}$C and D isotopologues of c-C$_3$H$_2$, in order to guide the laboratory and astronomical search. Since these species are intermediates in the formation of isotopic species of c-C$_3$H$_2$, their detection would be useful to put more constraints on the models.

Doubly deuterated cyclopropenylidene appears to be a very interesting probe for the earliest stages of star formation. Its formation mechanism puts important constraints on gas-phase deuteration models, and suggests the possibility of using c-C$_3$D$_2$ as a chemical clock. Furthermore, the brightness of c-C$_3$D$_2$ at the same time. By mapping the core it will be possible to locate the deuteration peak, and put more constraints on current gas–grains models.

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![Figure 3. Mechanism of formation of c-C$_3$D$_2$: a cycle of proton/deuteron transfer and dissociative recombination with electrons.](Image)

(A color version of this figure is available in the online journal.)

**APPENDIX**

The column densities and optical depths given in Table 1 were calculated using the following expressions. The line center opacity $\tau_0$ is

$$\tau_0 = \ln \left( \frac{J(T_{\text{ex}}) - J(T_{\text{bg}})}{J(T_{\text{ex}}) - J(T_{\text{bg}}) - T_{\text{mb}}} \right),$$

where $J(T) = (h\nu/k)(e^{\frac{\nu}{kT}} - 1)^{-1}$ is the source function in Kelvin. The upper state column density in case of optically thin emission and the total column density are defined as

$$N_{\text{up}}^{\text{thin}} = \frac{8\pi \nu^3 \sqrt{\pi \Delta \nu} \tau_0}{e^3 A_{\text{ul}} 2 \ln(2) (e^{\frac{\nu}{kT_0}} - 1)},$$

$$N_{\text{tot}} = \frac{N_\nu Q_{\text{rot}}(T_{\text{ex}})}{g_u e^{\frac{\nu}{kT_0}}},$$

where $k$ is the Boltzmann constant, $\nu$ is the frequency of the line, $h$ is the Planck constant, $c$ is the speed of light, $A_{\text{ul}}$ is the Einstein coefficient of the transition, $\Delta \nu$ is the FWHM, $g_u$ is the degeneracy of the upper state, $E_u$ is the energy of the upper state, $Q_{\text{rot}}$ is the partition function of the molecule at the given temperature $T_{\text{ex}}$, $T_{\text{bg}}$, and $T_{\text{mb}}$ are the excitation, the background (2.7 K), and the main beam temperatures, respectively, in kelvin. To calculate $N_{\text{tot}}$ and $\tau$, we assumed a $T_{\text{ex}}$ of 7 K for TMC-1C and 5 K for L1544 for all deuterated isotopologues, following Gerin et al (1987), and 8 K for TMC-1C and 6 K for L1544 for the main species and the $^{13}$C isotopologues as they trace also warmer regions of the cloud.

The effect of the excitation temperature on the derived column density ratios in Table 2 was found to be small, with a change of few percent upon a variation of $\pm 1$ K. By using these expressions, we assumed that the source fills the beam, and optically thin emission obeying LTE. Since lines of c-C$_3$H$_2$ are optically thick, we derived its total column density from the total column density of c-H$^{13}$CC$_2$H assuming a $^{12}$C/$^{13}$C ratio of 77, determined by Wilson & Rood (1994) from H$_2$CO and CO as a function of distance from the Galactic center, $N_u$ and $\tau$ were calculated backward.

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