LETTER TO THE EDITOR

O-bearing complex organic molecules at the cyanopolyne peak of TMC-1: Detection of C₂H₃CHO, C₂H₃OH, HCOOCH₃, and CH₃OCH₃[★]

M. Agúndez¹, N. Marcelino¹, B. Tercero^{2,3}, C. Cabezas¹, P. de Vicente³, and J. Cernicharo¹

¹ Instituto de Física Fundamental, CSIC, Calle Serrano 123, 28006 Madrid, Spain
 e-mail: marcelino.agundez@csic.es

² Observatorio Astronómico Nacional, IGN, Calle Alfonso XII 3, 28014 Madrid, Spain

³ Observatorio de Yebes, IGN, Cerro de la Palera s/n, 19141 Yebes, Guadalajara, Spain

Received 1 April 2021 / Accepted 21 April 2021

ABSTRACT

We report the detection of the oxygen-bearing complex organic molecules propenal (C₂H₃CHO), vinyl alcohol (C₂H₃OH), methyl formate (HCOOCH₃), and dimethyl ether (CH₃OCH₃) toward the cyanopolyne peak of the starless core TMC-1. These molecules were detected through several emission lines in a deep *Q*-band line survey of TMC-1 carried out with the Yebes 40m telescope. These observations reveal that the cyanopolyne peak of TMC-1, which is a prototype of a cold dark cloud rich in carbon chains, also contains O-bearing complex organic molecules such as HCOOCH₃ and CH₃OCH₃, which have previously been seen in a handful of cold interstellar clouds. In addition, this is the first secure detection of C₂H₃OH in space and the first time that C₂H₃CHO and C₂H₃OH have been detected in a cold environment, adding new pieces to the puzzle of complex organic molecules in cold sources. We derive column densities of $(2.2 \pm 0.3) \times 10^{11} \text{ cm}^{-2}$, $(2.5 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$, $(1.1 \pm 0.2) \times 10^{12} \text{ cm}^{-2}$, and $(2.5 \pm 0.7) \times 10^{12} \text{ cm}^{-2}$ for C₂H₃CHO, C₂H₃OH, HCOOCH₃, and CH₃OCH₃, respectively. Interestingly, C₂H₃OH has an abundance similar to that of its well-known isomer acetaldehyde (CH₃CHO), with C₂H₃OH/CH₃CHO ~ 1 at the cyanopolyne peak. We discuss potential formation routes to these molecules and recognize that further experimental, theoretical, and astronomical studies are needed to elucidate the true formation mechanism of these O-bearing complex organic molecules in cold interstellar sources.

Key words. astrochemistry – line: identification – ISM: individual objects: TMC-1 – ISM: molecules – radio lines: ISM

1. Introduction

Complex organic molecules (COMs) such as methyl formate (HCOOCH₃) and dimethyl ether (CH₃OCH₃) have traditionally been observed in the warm gas around protostars, the so-called hot cores and corinos, where they are thought to form upon thermal desorption of ice mantles on grains (Herbst & van Dishoeck 2009). In the last decade, these molecules have also been observed in a few cold sources, such as the dense cores B1-b (Öberg et al. 2010; Cernicharo et al. 2012) and L483 (Agúndez et al. 2019), the dark cloud Barnard 5 (Taquet et al. 2017), the pre-stellar cores L1689B (Bacmann et al. 2012) and L1544 (Jiménez-Serra et al. 2016), and the starless core TMC-1 (Soma et al. 2018). The low temperatures in these environments inhibit thermal desorption, and how these molecules are formed, whether in the gas phase or on grain surfaces followed by some nonthermal desorption process, is still an active subject of debate (Vasyunin & Herbst 2013; Ruaud et al. 2015; Balucani et al. 2015; Chang & Herbst 2016; Vasyunin et al. 2017; Shingledecker et al. 2018; Jin & Garrod 2020).

The cyanopolyne peak of TMC-1, TMC-1(CP), is characterized by a carbon-rich chemistry, with high abundances of carbon chains and a low content of O-bearing COMs

(e.g., Agúndez & Wakelam 2013). Here we report the detection of four O-bearing COMs toward TMC-1(CP). Propenal (C₂H₃CHO) had previously been reported toward massive star-forming regions in the Galactic center (Hollis et al. 2004; Requena-Torres et al. 2008) and in the hot corino IRAS 16293-2422 B (Manigand et al. 2021). Vinyl alcohol (C₂H₃OH) had only been seen toward Sagittarius B2(N), where the high spectral density complicates its identification (Turner & Apponi 2001). Therefore, this is the first clear detection of C₂H₃OH in space and the first time that C₂H₃CHO and C₂H₃OH have been detected in a cold environment. We also report the detection of HCOOCH₃ and CH₃OCH₃, recently detected (the latter tentatively) toward the methanol peak of TMC-1 (Soma et al. 2018) but not toward TMC-1(CP).

2. Astronomical observations

The data presented here belong to a *Q*-band line survey of TMC-1(CP), $\alpha_{J2000} = 4^{\text{h}} 41^{\text{m}} 41.9^{\text{s}}$ and $\delta_{J2000} = +25^{\circ} 41' 27.0''$, performed with the Yebes 40m telescope. The cryogenic receiver for the *Q* band, which was built within the Nanocosmos project¹ and covers the 31.0–50.4 GHz frequency range with horizontal and vertical polarizations, was used connected to Fast Fourier Transform spectrometers, which cover a bandwidth of $8 \times 2.5 \text{ GHz}$ in each polarization with a spectral

[★] Based on observations carried out with the Yebes 40m telescope (projects 19A003, 20A014, and 20D023). The 40m radio telescope at Yebes Observatory is operated by the Spanish Geographic Institute (IGN; Ministerio de Transportes, Movilidad y Agenda Urbana).

¹ <https://nanocosmos.iff.csic.es>

Table 1. Observed line parameters of the target O-bearing COMs of this study in TMC-1.

Molecule	Transition	E_{up} (K)	ν_{calc} (MHz)	T_A^* peak (mK)	$\Delta\nu^{(a)}$ (km s ⁻¹)	V_{LSR} (km s ⁻¹)	$\int T_A^* d\nu$ (mK km s ⁻¹)	$S/N^{(b)}$ (σ)	$B_{\text{eff}}/F_{\text{eff}}^{(c)}$
<i>trans</i> -C ₂ H ₃ CHO	4 _{1,4} – 3 _{1,3}	6.2	34 768.987	3.06 ± 0.31	0.62 ± 0.08	5.77 ± 0.03	2.03 ± 0.21	14.5	0.603
	4 _{0,4} – 3 _{0,3}	4.3	35 578.136	3.77 ± 0.33	0.81 ± 0.08	5.79 ± 0.03	3.27 ± 0.27	19.4	0.597
	4 _{1,3} – 3 _{1,2}	6.4	36 435.990	3.17 ± 0.29	0.85 ± 0.09	5.73 ± 0.04	2.87 ± 0.25	19.2	0.590
	5 _{1,5} – 4 _{1,4}	8.3	43 455.469	1.81 ± 0.49	0.72 ± 0.27	5.78 ± 0.08	1.38 ± 0.37	6.5	0.530
	5 _{0,5} – 4 _{0,4}	6.4	44 449.749	3.67 ± 0.54	0.54 ± 0.08	5.80 ± 0.04	2.11 ± 0.31	10.5	0.521
	5 _{1,4} – 4 _{1,3}	8.6	45 538.994	4.72 ± 0.66	0.69 ± 0.09	5.80 ± 0.04	3.45 ± 0.43	12.6	0.511
<i>syn</i> -C ₂ H ₃ OH	4 _{0,4} – 3 _{1,3}	9.3	32 449.221	1.17 ± 0.32	1.07 ± 0.21	5.61 ± 0.11	1.34 ± 0.27	6.8	0.622
	2 _{1,2} – 1 _{1,1}	5.1	37 459.184 ^(d)	–	–	–	–	–	0.581
	2 _{0,2} – 1 _{0,1}	2.8	39 016.387	1.90 ± 0.39	0.89 ± 0.16	5.81 ± 0.07	1.79 ± 0.29	9.0	0.568
	2 _{1,1} – 1 _{1,0}	5.3	40 650.606	1.71 ± 0.41	0.65 ± 0.19	5.88 ± 0.08	1.18 ± 0.28	6.7	0.554
HCOOCH ₃	3 _{1,3} – 2 _{1,2} <i>E</i>	4.0	34 156.889	1.92 ± 0.29	0.62 ± 0.12	5.93 ± 0.06	1.27 ± 0.23	9.6	0.608
	3 _{1,3} – 2 _{1,2} <i>A</i>	3.9	34 158.061	1.86 ± 0.29	0.80 ± 0.16	5.84 ± 0.07	1.59 ± 0.28	10.6	0.608
	3 _{0,3} – 2 _{0,2} <i>E</i>	3.5	36 102.227 ^(e)	–	–	–	–	–	0.593
	3 _{0,3} – 2 _{0,2} <i>A</i>	3.5	36 104.775	2.61 ± 0.29	0.74 ± 0.09	5.80 ± 0.04	2.05 ± 0.22	14.6	0.592
	3 _{1,2} – 2 _{1,1} <i>E</i>	4.4	38 976.085	1.81 ± 0.35	0.66 ± 0.14	5.93 ± 0.07	1.28 ± 0.25	8.3	0.568
	3 _{1,2} – 2 _{1,1} <i>A</i>	4.4	38 980.803	2.45 ± 0.35	0.57 ± 0.09	5.92 ± 0.04	1.49 ± 0.21	10.4	0.568
	4 _{1,4} – 3 _{1,3} <i>E</i>	6.1	45 395.802	2.82 ± 0.57	0.63 ± 0.18	6.00 ± 0.07	1.89 ± 0.40	8.3	0.512
	4 _{1,4} – 3 _{1,3} <i>A</i>	6.1	45 397.360	2.39 ± 0.57	0.42 ± 0.19	5.91 ± 0.10	1.07 ± 0.32	5.8	0.512
	4 _{0,4} – 3 _{0,3} <i>E</i>	5.8	47 534.116	3.19 ± 0.75	0.59 ± 0.12	5.92 ± 0.07	2.01 ± 0.44	7.1	0.493
	4 _{0,4} – 3 _{0,3} <i>A</i>	5.8	47 536.905	2.76 ± 0.75	0.98 ± 0.23	5.99 ± 0.10	2.88 ± 0.60	7.9	0.493
CH ₃ OCH ₃	2 _{1,1} – 2 _{0,2} <i>AE+EA</i>	4.2	31 105.223	1.35 ± 0.39	0.92 ± 0.25	5.72 ± 0.13	1.31 ± 0.36	5.8	0.632
	2 _{1,1} – 2 _{0,2} <i>EE</i>	4.2	31 106.150	1.52 ± 0.39	0.54 ± 0.34	5.94 ± 0.08	0.87 ± 0.29	5.0	0.632
	3 _{1,2} – 3 _{0,3} <i>AE+EA</i>	7.0	32 977.276	1.37 ± 0.25	0.63 ± 0.13	5.84 ± 0.07	0.91 ± 0.19	7.8	0.618
	3 _{1,2} – 3 _{0,3} <i>EE</i>	7.0	32 978.232	1.37 ± 0.25	0.95 ± 0.23	5.84 ± 0.09	1.38 ± 0.27	9.6	0.618
	3 _{1,2} – 3 _{0,3} <i>AA</i>	7.0	32 979.187	1.06 ± 0.25	0.85 ± 0.32	5.99 ± 0.12	0.96 ± 0.29	7.1	0.618
	4 _{1,3} – 4 _{0,4} <i>EE</i>	10.8	35 593.408	1.22 ± 0.27	0.56 ± 0.13	5.82 ± 0.07	0.73 ± 0.16	6.4	0.597
	1 _{1,1} – 0 _{0,0} <i>EE</i>	2.3	47 674.967	3.31 ± 0.62	0.59 ± 0.12	6.02 ± 0.06	2.08 ± 0.38	8.9	0.492

Notes. The line parameters T_A^* peak, $\Delta\nu$, V_{LSR} , and $\int T_A^* d\nu$ and the associated errors are derived from a Gaussian fit to each line profile. ^(a) $\Delta\nu$ is the full width at half maximum (FWHM). ^(b)The signal-to-noise ratio is computed as $S/N = \int T_A^* d\nu / [\text{rms} \times \sqrt{\Delta\nu \times \delta\nu(c/\nu_{\text{calc}})}]$, where c is the speed of light, $\delta\nu$ is the spectral resolution (0.03815 MHz), the rms is given in the uncertainty of T_A^* peak, and the rest of parameters are given in the table. ^(c) B_{eff} is given by the Ruze formula $B_{\text{eff}} = 0.738 \exp[-(\nu/72.2)^2]$, where ν is the frequency in GHz and $F_{\text{eff}} = 0.97$. ^(d)Line overlaps with a hyperfine component of CH₂CCH (see Agúndez et al. 2021). ^(e)Line detected but not fitted because it overlaps with a negative frequency-switching artifact.

resolution of 38.15 kHz. The system is described in Tercero et al. (2021). The half power beam width (HPBW) of the Yebes 40m telescope ranges from 36.4'' to 54.4'' in the Q band. The intensity scale is antenna temperature, T_A^* , for which we estimate an uncertainty of 10%; the antenna temperature can be converted to main beam brightness temperature, T_{mb} , by dividing by $B_{\text{eff}}/F_{\text{eff}}$ (see Table 1). The line survey was carried out over several observing runs, and various results have already been published. Data taken in November 2019 and in February 2020 resulted in the detection of the negative ions C₃N⁻ and C₅N⁻ (Cernicharo et al. 2020a) and the discovery of HC₄NC (Cernicharo et al. 2020b), HC₃O⁺ (Cernicharo et al. 2020c), and HC₅NH⁺ (Marcelino et al. 2020). A further observing run, carried out in October 2020, resulted in the detection of HDCCN (Cabezas et al. 2021), HC₃S⁺ (Cernicharo et al. 2021a), CH₃CO⁺ (Cernicharo et al. 2021b), and various C₄H₃N isomers (Marcelino et al. 2021). Additional observations were taken in December 2020 and January 2021, which led to the discovery of vinyl acetylene (CH₂CHCCH; Cernicharo et al. 2021c), allenyl acetylene (CH₂CCHCCH; Cernicharo et al. 2021d), and propargyl (CH₂CCH; Agúndez et al. 2021), and a final run was carried out in March 2021. All observations were conducted using the frequency switching technique, with a

frequency throw of 10 MHz during the first two observing runs and 8 MHz in the later ones. All data were reduced with the program CLASS of the GILDAS software (Pety 2005)².

3. Molecular spectroscopy

C₂H₃CHO has two conformers. The most stable, and the only one reported in space (Hollis et al. 2004; Requena-Torres et al. 2008; Manigand et al. 2021), is the *trans* form, which is the one reported here as well. Level energies and transition frequencies were obtained from the rotational constants derived by Daly et al. (2015). The dipole moment along the a axis (all transitions observed here are a -type) is 3.052 D (Blom et al. 1984).

C₂H₃OH also has two conformers, named *syn* and *anti*. Turner & Apponi (2001) assigned various emission features to the two conformers in the crowded spectra of Sgr B2(N). Here we report an unambiguous detection of the *syn* form, which is the most stable one, in a colder source that is much less affected by line confusion. Level energies and transition frequencies were computed from the rotational constants given by Melosso et al. (2019). The components of the dipole moment along the a and

² <http://www.iram.fr/IRAMFR/GILDAS>

Fig. 1. Lines of $\text{C}_2\text{H}_3\text{CHO}$ observed in TMC-1 (see the parameters in Table 1). Shown in red are the computed synthetic spectra for $N = 2.2 \times 10^{11} \text{ cm}^{-2}$, $T_{\text{rot}} = 7.5 \text{ K}$, $\text{FWHM} = 0.71 \text{ km s}^{-1}$, and $\theta_s = 80''$.

b axes are 0.616 D and 0.807 D, respectively (Saito 1976). Both a - and b -type transitions are observed here.

HCOOCH_3 is a well-known interstellar molecule in which the internal rotation, or torsion, of the methyl group splits each rotational level into A and E substates, with statistical weights $A:E = 1:1$. We used the spectroscopy from a fit to the lines measured by Ogata et al. (2004) and implemented in MADEX (Cernicharo 2012). Here all observed transitions are a -type, and thus we adopted $\mu_a = 1.63 \text{ D}$ (Curl 1959).

CH_3OCH_3 is an asymmetric rotor in which the large amplitude internal motion of the two equivalent methyl groups leads to level splitting into AA , EE , EA , and AE substates, with nontrivial statistical weights (Endres et al. 2009). We adopted the spectroscopy from the Cologne Database for Molecular Spectroscopy (Müller et al. 2005)³. Due to the geometry of the molecule, it only has nonzero dipole moment along the b axis, with a measured value of 1.302 D (Blukis et al. 1963).

Fig. 2. Lines of $\text{C}_2\text{H}_3\text{OH}$ observed in TMC-1 (see the parameters and note on line $2_{1,1} - 1_{1,0}$ in Table 1). Shown in red are the computed synthetic spectra for $N = 2.5 \times 10^{12} \text{ cm}^{-2}$, $T_{\text{rot}} = 10 \text{ K}$, $\text{FWHM} = 0.87 \text{ km s}^{-1}$, and $\theta_s = 80''$.

4. Results

We detected various lines for each of the O-bearing COMs targeted in this study (see Table 1), with signal-to-noise ratios (S/N) well above 3σ . The position of the lines is consistent with the calculated frequencies based on laboratory data (see Sect. 3) and the systemic velocity of the source, $V_{\text{LSR}} = 5.83 \text{ km s}^{-1}$ (Cernicharo et al. 2020b). Moreover, the relative intensities of the lines are those expected for rotational temperatures in the range 3–10 K, which are typical of TMC-1 (Gratier et al. 2016), and there are no missing lines. We thus consider the detection of the four O-bearing COMs in TMC-1 to be secure. Hereafter we discuss the particularities of each molecule.

The detection of the *trans* form of $\text{C}_2\text{H}_3\text{CHO}$ is very solid since the six observed lines are detected with S/N between 6.5σ and 19.4σ and the V_{LSR} of the lines are fully consistent with the systemic velocity of TMC-1 (see Table 1 and Fig. 1). The rotational temperature (T_{rot}) of $\text{C}_2\text{H}_3\text{CHO}$ is not very precisely determined, $7.5 \pm 3.5 \text{ K}$ from a rotation diagram, but synthetic spectra computed under thermodynamic equilibrium indicate that values in the range 5–10 K are consistent with the relative intensities observed. We thus adopted $T_{\text{rot}} = 7.5 \text{ K}$ to compute the synthetic spectra and derive the column density. The arithmetic mean of the observed $\text{C}_2\text{H}_3\text{CHO}$ line widths, 0.71 km s^{-1} , was adopted when computing the synthetic spectra (see Table 1). We also assumed a circular emission distribution with a diameter $\theta_s = 80''$, as observed for various hydrocarbons in TMC-1 (Fossé et al. 2001). For the other three molecules, we followed the same convention, adopting as the line width the average of the observed values and assuming the same emission distribution. The column density derived for $\text{C}_2\text{H}_3\text{CHO}$ is $(2.2 \pm 0.3) \times 10^{11} \text{ cm}^{-2}$.

In the case of $\text{C}_2\text{H}_3\text{OH}$ (see Table 1 and Fig. 2), three lines are clearly detected, with S/N of 6.7σ and 9.0σ . The frequency of the $2_{1,2} - 1_{1,1}$ transition, 37459.184 MHz, coincides with a hyperfine component of CH_2CCH , which was recently reported in TMC-1 (Agúndez et al. 2021). We predict $T_A^* = 1.1 \text{ mK}$ for the $2_{1,2} - 1_{1,1}$ transition, which indicates that the observed line (see Agúndez et al. 2021) has contributions from both CH_2CCH

³ <https://cdms.astro.uni-koeln.de/>

Fig. 3. Lines of HCOOCH_3 observed in TMC-1 (see the parameters and note on line $3_{0,3} - 2_{0,2}E$ in Table 1). Shown in red are the computed synthetic spectra for a $N = 1.1 \times 10^{12} \text{ cm}^{-2}$, $T_{\text{rot}} = 5 \text{ K}$, $\text{FWHM} = 0.67 \text{ km s}^{-1}$, and $\theta_s = 80''$.

and $\text{C}_2\text{H}_3\text{OH}$. As a result of the high detection significance of the three lines, the overlap of a fourth line with CH_2CCH , and the fact that there are no missing lines, we consider the detection of $\text{C}_2\text{H}_3\text{OH}$ to be secure. The rotational temperature is not well constrained for $\text{C}_2\text{H}_3\text{OH}$, although the observed relative intensities indicate that it must be in the high range of the values typically observed in TMC-1. We thus adopted $T_{\text{rot}} = 10 \text{ K}$ and a line width of 0.87 km s^{-1} to compute the synthetic spectra. We derive a column density of $(2.5 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$ for $\text{C}_2\text{H}_3\text{OH}$.

We detected five A/E doublets of HCOOCH_3 with S/N in the range $5.8\text{--}14.6\sigma$ (see Table 1 and Fig. 3). The only problematic line was the $3_{0,3} - 2_{0,2}E$ transition of the E substate, which happened to lie close to a negative frequency-switching artifact, making it appear less intense and slightly shifted from the correct position. Therefore, we did not fit this line. The derived rotational temperature is $5.1 \pm 2.5 \text{ K}$, and we thus adopted $T_{\text{rot}} = 5 \text{ K}$ and a line width of 0.67 km s^{-1} to compute the synthetic spectra. The total column density obtained for HCOOCH_3 , including both A and E substates, is $(1.1 \pm 0.2) \times 10^{12} \text{ cm}^{-2}$.

For CH_3OCH_3 , we observed four triplets with the characteristic structure of an intense component corresponding to the EE substate lying between two equally intense components corresponding to the $AE+EA$ and AA substates. The EE component of the four triplets is detected with good confidence levels, between 5.0σ and 9.6σ (see Table 1 and Fig. 4). The weaker components corresponding to the $AE+EA$ and AA substates are sometimes found to lie within the noise, although the computed

Fig. 4. Lines of CH_3OCH_3 observed in TMC-1 (see the parameters in Table 1). Shown in red are the computed synthetic spectra for $N = 2.5 \times 10^{12} \text{ cm}^{-2}$, $T_{\text{rot}} = 3.6 \text{ K}$, $\text{FWHM} = 0.72 \text{ km s}^{-1}$, and $\theta_s = 80''$.

synthetic spectra are consistent with this fact. We consider the detection of CH_3OCH_3 to be secure. From a rotation diagram we derive a low rotational temperature of $3.6 \pm 0.6 \text{ K}$, which is well constrained by the availability of transitions covering upper level energies from 2.3 K to 10.8 K . We thus adopted $T_{\text{rot}} = 3.6 \text{ K}$ and a line width of 0.72 km s^{-1} to compute the synthetic spectra, which implies a total column density, including the four substates, of $(2.5 \pm 0.7) \times 10^{12} \text{ cm}^{-2}$ for CH_3OCH_3 .

The variation in the column densities due to the uncertainty in T_{rot} is small, $\sim 15\%$, for $\text{C}_2\text{H}_3\text{CHO}$ and $\text{C}_2\text{H}_3\text{OH}$, and higher, by a factor of two, for HCOOCH_3 and CH_3OCH_3 .

5. Discussion

The abundances derived for $\text{C}_2\text{H}_3\text{CHO}$, $\text{C}_2\text{H}_3\text{OH}$, HCOOCH_3 , and CH_3OCH_3 are 2.2×10^{-11} , 2.5×10^{-10} , 1.1×10^{-10} , and 2.5×10^{-10} , respectively, relative to H_2 , if we adopt a column density of H_2 of 10^{22} cm^{-2} (Cernicharo & Guélin 1987). Next we wish to discuss how these four O-bearing COMs are formed in TMC-1.

$\text{C}_2\text{H}_3\text{CHO}$ and $\text{C}_2\text{H}_3\text{OH}$ could be formed by gas-phase neutral-neutral reactions between reactive radicals such as OH , CH , or C_2H and abundant closed-shell molecules. However, among the potential sources of $\text{C}_2\text{H}_3\text{OH}$, the reactions $\text{OH} + \text{C}_2\text{H}_4$ and $\text{OH} + \text{CH}_2\text{CHCH}_3$ seem to have activation barriers (Zhu et al. 2005; Zádor et al. 2009) and the reaction $\text{CH} + \text{CH}_3\text{OH}$ seems to yield H_2CO and CH_3 as products (Zhang et al. 2002). In the case of $\text{C}_2\text{H}_3\text{CHO}$, a potential formation reaction is $\text{OH} + \text{allene}$, but the main products are $\text{H}_2\text{CCO} + \text{CH}_3$ (Daranlot et al. 2012). Two more promising routes to $\text{C}_2\text{H}_3\text{CHO}$ are the reactions $\text{CH} + \text{CH}_3\text{CHO}$, which has been found to produce $\text{C}_2\text{H}_3\text{CHO}$ (Goulay et al. 2012), and $\text{C}_2\text{H} + \text{CH}_3\text{OH}$, which to our knowledge has not been studied experimentally or theoretically.

$\text{C}_2\text{H}_3\text{CHO}$ and $\text{C}_2\text{H}_3\text{OH}$ are not specifically considered in the chemical networks UMIST RATE12 (McElroy et al. 2013) or KIDA vva.kida.2014 (Wakelam et al. 2015), but acetaldehyde (CH_3CHO), which is an isomer of $\text{C}_2\text{H}_3\text{OH}$, is included. Since astrochemical databases often do not distinguish between different isomers because information is not available, it is conceivable that some of the reactions that are considered to produce CH_3CHO could also form $\text{C}_2\text{H}_3\text{OH}$. According to a standard pseudo-time-dependent gas-phase chemical model of a cold dark cloud (e.g., Agúndez & Wakelam 2013), there are two main formation reactions for CH_3CHO . The first is $\text{O} + \text{C}_2\text{H}_5$, for which the formation of $\text{C}_2\text{H}_3\text{OH}$ does not seem to be an important channel, according to experiments (Slagle et al. 1988) and theory (Jung et al. 2011; Vazart et al. 2020). The second is the dissociative recombination of CH_3CHOH^+ with electrons, in which case experiments show that the CCO backbone is preserved with a branching ratio of 23% (Hamberg et al. 2010); as such, it is possible that both CH_3CHO and $\text{C}_2\text{H}_3\text{OH}$ are formed. A different route to CH_3CHO starting from abundant ethanol ($\text{C}_2\text{H}_5\text{OH}$) has been proposed (Skouteris et al. 2018; Vazart et al. 2020), but in L483, the only cold environment where $\text{C}_2\text{H}_5\text{OH}$ has been detected, its abundance is half that of CH_3CHO (Agúndez et al. 2019). The column density of CH_3CHO at TMC-1(CP) is $(2.7\text{--}3.5) \times 10^{12} \text{ cm}^{-2}$ (Gratier et al. 2016; Cernicharo et al. 2020c), which implies a $\text{C}_2\text{H}_3\text{OH}/\text{CH}_3\text{CHO}$ ratio of ~ 1 . Therefore, if the two isomers are formed by the same reaction, then the branching ratios should be similar. The reaction $\text{CH}_3^+ + \text{H}_2\text{CO}$ produces $\text{CH}_4 + \text{HCO}^+$ (Smith & Adams 1978), and thus it is unlikely to form $\text{C}_2\text{H}_3\text{OH}$, unlike what was suggested by Turner & Apponi (2001).

Grain-surface processes could also form $\text{C}_2\text{H}_3\text{CHO}$ and $\text{C}_2\text{H}_3\text{OH}$ in TMC-1. Experiments show that $\text{C}_2\text{H}_3\text{OH}$ is formed upon the proton irradiation of $\text{H}_2\text{O}/\text{C}_2\text{H}_2$ ices (Hudson & Moore 2003) as well as the electron irradiation of CO/CH_4 and $\text{H}_2\text{O}/\text{CH}_4$ ices (Abplanalp et al. 2016; Bergantini et al. 2017), while $\text{C}_2\text{H}_3\text{CHO}$ is produced after the electron irradiation of $\text{CO}/\text{C}_2\text{H}_4$ ices (Abplanalp et al. 2015). Non-energetic processing of C_2H_2 ices, in which reactions with H atoms and OH radicals occur on the surface, also produces $\text{C}_2\text{H}_3\text{OH}$ (Chuang et al. 2020). It remains uncertain, however, whether these experimental setups (e.g., in terms of irradiation fluxes and ice composition) resemble those of cold dark clouds. Abplanalp et al. (2016) attempted to resolve this uncertainty by incorporating the results of electron irradiation experiments in a chemical model of a cold dark cloud; they found that cosmic rays could drive the formation of $\text{C}_2\text{H}_3\text{OH}$ on grain surfaces. Recently, Shingledecker et al. (2019) proposed that $\text{C}_2\text{H}_3\text{CHO}$ can be efficiently formed on grain surfaces by successive reactions of addition of an H atom to HC_3O . This process would also produce propynal (HCCCHO), which led these authors to propose a chemical connection, and thus a potential correlation, between HCCCHO and $\text{C}_2\text{H}_3\text{CHO}$. If this mechanism is correct, then $\text{C}_2\text{H}_3\text{CHO}$ would more likely be detected in sources with intense HCCCHO emission (see Loison et al. 2016).

There is as of yet no consensus on how HCOOCH_3 and CH_3OCH_3 are formed in cold sources. Models in which the synthesis relies on chemical desorption and gas-phase radiative associations usually require a chemical desorption efficiency as high as 10% (Vasyunin & Herbst 2013; Balucani et al. 2015; Chang & Herbst 2016), which can be relaxed if Eley-Rideal processes (Ruaud et al. 2015), radiation chemistry (Shingledecker et al. 2018), or non-diffusive grain-surface processes (Jin & Garrod 2020) are considered. These models can account for abundances relative to H_2 of around

10^{-10} for HCOOCH_3 and/or CH_3OCH_3 under certain assumptions, although they rely on still poorly constrained chemical and physical processes. Astronomical observations have shown that HCOOCH_3 and CH_3OCH_3 could have a chemical connection with CH_3OH , based on the slight abundance enhancement inferred for these O-bearing COMs at the CH_3OH peak with respect to the dust peak in the pre-stellar core L1544 (Jiménez-Serra et al. 2016). The column densities derived here for HCOOCH_3 and CH_3OCH_3 at TMC-1(CP) are similar, within a factor of two, to those reported by Soma et al. (2018) at the CH_3OH peak of TMC-1. A coherent study using the same telescope and a detailed radiative transfer model is needed to see if there is a significant abundance enhancement of HCOOCH_3 and CH_3OCH_3 at the CH_3OH peak of TMC-1.

6. Conclusions

We report the detection of $\text{C}_2\text{H}_3\text{CHO}$, $\text{C}_2\text{H}_3\text{OH}$, HCOOCH_3 , and CH_3OCH_3 toward TMC-1(CP). This region, which is a prototypical cold dark cloud with abundant carbon chains, has now been revealed as a new cold source where the O-bearing COMs HCOOCH_3 and CH_3OCH_3 are present. In addition, we provide the first evidence of two other O-bearing COMs in a cold source, $\text{C}_2\text{H}_3\text{CHO}$ and $\text{C}_2\text{H}_3\text{OH}$, the latter being identified unambiguously for the first time in space here. The derived abundances relative to H_2 are a few 10^{-11} for $\text{C}_2\text{H}_3\text{CHO}$ and a few 10^{-10} for the three other molecules. Interestingly, $\text{C}_2\text{H}_3\text{OH}$ has a similar abundance to its isomer CH_3CHO , with $\text{C}_2\text{H}_3\text{OH}/\text{CH}_3\text{CHO} \sim 1$. We discuss potential formation routes to these molecules and conclude that further experimental, theoretical, and astronomical studies are needed to shed light on the origin of these COMs in cold interstellar sources.

Acknowledgements. We acknowledge funding support from Spanish MICIU through grants AYA2016-75066-C2-1-P, PID2019-106110GB-I00, PID2019-106235GB-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). We thank the anonymous referee for a constructive report that helped to improve this manuscript.

References

- Abplanalp, M. J., Borsuk, A., Jones, B. M., & Kaiser, R. I. 2015, *ApJ*, **814**, 45
- Abplanalp, M. J., Gozem, S., Krylov, A. I., et al. 2016, *PNAS*, **113**, 7727
- Agúndez, M., & Wakelam, V. 2013, *Chem. Rev.*, **113**, 8710
- Agúndez, M., Marcelino, N., Cernicharo, J., et al. 2019, *A&A*, **625**, A147
- Agúndez, M., Cabezas, C., Tercero, B., et al. 2021, *A&A*, **647**, L10
- Bacmann, A., Taquet, V., Faure, A., et al. 2012, *A&A*, **541**, L12
- Balucani, N., Ceccarelli, C., & Taquet, V. 2015, *MNRAS*, **449**, L16
- Bergantini, A., Maksyutenko, P., & Kaiser, R. I. 2017, *ApJ*, **841**, 96
- Blom, C. E., Grassi, G., & Bauder, A. 1984, *J. Am. Chem. Soc.*, **106**, 7427
- Blukis, U., Kasai, P. H., & Myers, R. J. 1963, *J. Chem. Phys.*, **38**, 2753
- Cabezas, C., Endo, Y., Roueff, E., et al. 2021, *A&A*, **646**, L1
- Cernicharo, J. 2012, in *European Conference on Laboratory Astrophysics*, eds. C. Stehlé, C. Joblin, & L. d'Hendecourt, *EAS Pub. Ser.*, **58**, 251
- Cernicharo, J., & Guélin, M. 1987, *A&A*, **176**, 299
- Cernicharo, J., Marcelino, N., Roueff, E., et al. 2012, *ApJ*, **759**, L43
- Cernicharo, J., Marcelino, N., Pardo, J. R., et al. 2020a, *A&A*, **641**, L9
- Cernicharo, J., Marcelino, N., Agúndez, M., et al. 2020b, *A&A*, **642**, L8
- Cernicharo, J., Marcelino, N., Agúndez, M., et al. 2020c, *A&A*, **642**, L17
- Cernicharo, J., Cabezas, C., Endo, Y., et al. 2021a, *A&A*, **646**, L3
- Cernicharo, J., Cabezas, C., Bailleux, S., et al. 2021b, *A&A*, **646**, L7
- Cernicharo, J., Agúndez, M., Cabezas, C., et al. 2021c, *A&A*, **647**, L2
- Cernicharo, J., Cabezas, C., Agúndez, M., et al. 2021d, *A&A*, **647**, L3
- Chang, Q., & Herbst, E. 2016, *ApJ*, **819**, 145
- Chuang, K.-J., Fedoseev, G., Qasim, D., et al. 2020, *A&A*, **635**, A199
- Curl, R. F. 1959, *J. Chem. Phys.*, **30**, 1529

- Daly, A. M., Bermúdez, C., Kolesníková, L., & Alonso, J. L. 2015, *ApJS*, **218**, 30
- Daranlot, J., Hickson, K. M., Loison, J.-C., et al. 2012, *J. Phys. Chem. A*, **116**, 10871
- Endres, C. P., Drouin, B. J., Pearson, J. C., et al. 2009, *A&A*, **504**, 635
- Fossé, D., Cernicharo, J., Gerin, M., & Cox, P. 2001, *ApJ*, **552**, 168
- Goulay, F., Trevitt, A. J., Savee, J. D., et al. 2012, *J. Phys. Chem. A*, **116**, 6091
- Gratier, P., Majumdar, L., Ohishi, M., et al. 2016, *ApJS*, **225**, 25
- Hamberg, M., Zhaunerchyk, V., Vigren, E., et al. 2010, *A&A*, **522**, A90
- Herbst, E., & van Dishoeck, E. F. 2009, *ARA&A*, **47**, 427
- Hollis, J. M., Jewell, P. R., Lovas, F. J., et al. 2004, *ApJ*, **610**, L21
- Hudson, R. L., & Moore, M. H. 2003, *ApJ*, **586**, L107
- Jiménez-Serra, I., Vasyunin, A. I., Caselli, P., et al. 2016, *ApJ*, **830**, L6
- Jin, M., & Garrod, R. T. 2020, *ApJS*, **249**, 26
- Jung, S.-H., Park, Y.-P., Kang, K.-W., et al. 2011, *Theor. Chem. Acc.*, **129**, 105
- Loison, J.-C., Agúndez, M., Marcelino, N., et al. 2016, *MNRAS*, **456**, 4101
- Manigand, S., Coutens, A., Loison, J.-C., et al. 2021, *A&A*, **645**, A53
- Marcelino, N., Agúndez, M., Tercero, B., et al. 2020, *A&A*, **643**, L6
- Marcelino, N., Tercero, B., Agúndez, M., & Cernicharo, J. 2021, *A&A*, **646**, L9
- McElroy, D., Walsh, C., Markwick, A. J., et al. 2013, *A&A*, **550**, A36
- Melosso, M., McGuire, B. A., Tamassia, F., et al. 2019, *ACS Earth Space Chem.*, **3**, 1189
- Müller, H. S. P., Schlöder, F., Stutzki, J., & Winnewisser, G. 2005, *J. Mol. Struct.*, **742**, 215
- Öberg, K. I., Bottinelli, S., Jørgensen, J. K., & van Dishoeck, E. F. 2010, *ApJ*, **716**, 825
- Ogata, K., Odashima, H., Takagi, K., & Tsunekawa, S. 2004, *J. Mol. Spectr.*, **225**, 14
- Pety, J., 2005, in *SF2A-2005: Semaine de l’Astrophysique Française*, eds. F. Casoli, et al. (Les Ulis: EDP), 721
- Requena-Torres, M. A., Martín-Pintado, J., Martín, S., & Morris, M. R. 2008, *ApJ*, **672**, 352
- Ruad, M., Loison, J.-C., Hickson, K. M., et al. 2015, *MNRAS*, **447**, 4004
- Saito, S. 1976, *Chem. Phys. Lett.*, **42**, 399
- Shingledecker, C. N., Tennis, J., Le Gal, R., & Herbst, E. 2018, *ApJ*, **861**, 20
- Shingledecker, C. N., Álvarez-Barcia, S., Korn, V. H., & Kästner, J. 2019, *ApJ*, **878**, 80
- Skouteris, D., Balucani, N., Ceccarelli, C., et al. 2018, *ApJ*, **854**, 135
- Slagle, I. R., Sarzynski, D., Gutman, D., et al. 1988, *J. Chem. Soc. Faraday Trans.*, **84**, 491
- Smith, D., & Adams, N. G. 1978, *Chem. Phys. Lett.*, **54**, 535
- Soma, T., Sakai, N., Watanabe, Y., & Yamamoto, S. 2018, *ApJ*, **854**, 116
- Taquet, V., Wirstrom, E. S., Charnley, S. B., et al. 2017, *A&A*, **607**, A20
- Tercero, F., López-Pérez, J. A., Gallego, J. D., et al. 2021, *A&A*, **645**, A37
- Turner, B. E., & Apponi, A. J. 2001, *ApJ*, **561**, L207
- Vasyunin, A. I., & Herbst, E. 2013, *ApJ*, **769**, 34
- Vasyunin, A. I., Caselli, P., Dulieu, F., & Jiménez-Serra, I. 2017, *ApJ*, **842**, 33
- Vazart, F., Ceccarelli, C., Balucani, N., et al. 2020, *MNRAS*, **499**, 5547
- Wakelam, V., Loison, J.-C., Herbst, E., et al. 2015, *ApJS*, **217**, 20
- Zádor, J., Jasper, A. W., & Miller, J. A. 2009, *Phys. Chem. Chem. Phys.*, **11**, 11040
- Zhang, X.-B., Liu, J.-J., Li, Z.-S., et al. 2002, *J. Phys. Chem. A*, **106**, 3814
- Zhu, R. S., Park, J., & Lin, M. C. 2005, *Chem. Phys. Lett.*, **408**, 25