1. Introduction

The QUIJOTE\textsuperscript{1} line survey (Cernicharo et al. 2021a) toward TMC-1 performed in recent years with the Yebes 40 m radio telescope has allowed us to detect more than 40 new molecules in space. This underlines the importance of this source for a deep understanding of the different chemical processes in cold dense cores.

Among the latest discoveries, there are several cycles such as cyclopentadiene, indene, ortho-benzene, or fulvenallene (Cernicharo et al. 2021a,b, 2022). Cyano and ethynyl derivatives of cyclopentadiene (McCarthy et al. 2021; Lee et al. 2021; Cernicharo et al. 2021c) and cyano derivatives of benzene, naphthalene, and indene (McGuire et al. 2018, 2021; Sita et al. 2022) have been identified. We have also detected propargyl (Agúndez et al. 2021a), one of the most abundant radicals found. Furthermore, long carbon chains such as vinyl acetylene (Cernicharo et al. 2021d), allenyl acetylene (Cernicharo et al. 2021e), butadiynyllallene (Fuentetaja et al. 2022a), and ethynylbutatrienyldiene (Fuentetaja et al. 2022b) have also been discovered toward TMC-1. Many of these species were not expected because they did not show a high abundance in chemical models. This highlights the importance of further study of the dark cloud TMC-1 in order to understand the chemical processes at work in this kind of environment.

Oxygen-bearing complex organic molecules (COMs) are also an important molecular family present in diverse interstellar environments. The star-forming regions, such as Sgr B2 and Orion KL, are the sources with the highest abundance of COMs. On the contrary, dark clouds like TMC-1 are characterized by carbon-rich chemistry, resulting in long carbon chains with low oxygen content. Agúndez et al. (2021b) reported the detection of O-bearing species, such as CH\textsubscript{2}CHCHO, CH\textsubscript{2}CHOH, HCOOCH\textsubscript{3}, and CH\textsubscript{3}OCH\textsubscript{3} in TMC-1. Long carbon chain O-bearing molecules with formulae HC\textsubscript{n}O and C\textsubscript{n}O (e.g., HC\textsubscript{3}O, HC\textsubscript{5}O, HC\textsubscript{7}O, and C\textsubscript{5}O) have also been detected (McGuire et al. 2017; Cordiner et al. 2017; Cernicharo et al. 2021f). O-bearing cations, such as HC\textsubscript{3}O\textsuperscript{+} and CH\textsubscript{3}CO\textsuperscript{+}, have also been recently detected in this source (Cernicharo et al. 2020, 2021g).

In the family of C\textsubscript{2}H\textsubscript{4}O isomers, the most stable is trans-propenal (trans-CH\textsubscript{2}CHCHO), whose detection was reported by Agúndez et al. (2021b). To date, this is the only isomer in this family detected toward TMC-1. Close in energy, with a difference of 2.8 kJ mol\textsuperscript{-1} compared to trans-propenal, is methyl ketene (CH\textsubscript{2}CHO). Bermúdez et al. (2018) studied this...
species in different environments and made a theoretical study of the stability of all CH₃OH isomers using the coupled cluster (CCSD(T)) ab initio method and the aug-cc-pVTZ basis set. The next member in the series is cis-propanal. It is also close in energy to CH₂CHCHO, with a difference of 5.8 kJ mol⁻¹, and therefore it is a candidate for future detection in TMC-1. The last isomer we refer to is cyclopropanone (c-H₂C₃O). Its energy is considerably higher than that of the previously named molecules, specifically 78.1 kJ mol⁻¹ with respect to cis-propanal (1 kJ mol⁻¹ = 120.3 K), but it is a candidate for detection because the similar and smaller species cyclopropanone (c-CH₂C₂O) has been reported by Loison et al. (2016).

In this Letter we report the first clear detection of CH₃CHCHO (methyl ketene) in TMC-1 using the line survey QUIJOTE (Cernicharo et al. 2021a) performed with the Yebes 40 m telescope. The formation of this species is investigated in detail using state-of-the-art gas-phase chemical models.

2. Observations

The observational data used in this work are part of QUIJOTE, a spectral line survey of TMC-1 in the Q band carried out with the Yebes 40 m telescope at the position α₂₀₀₀ = 4°41'41.9" and δ₂₀₀₀ = +25°41'27.0". The receiver was built within the Nanocosmos project⁡ and consists of two cold high-electron mobility transistor amplifiers covering the 31.0–50.3 GHz band with horizontal and vertical polarizations. Receiver temperatures achieved in the 2019 and 2020 runs vary from 22 K at 32 GHz to 42 K at 50 GHz. Some power adaptation in the down-conversion chains have reduced the receiver temperatures during 2021 to 16 K at 32 GHz and 30 K at 50 GHz. The backends are 2 × 8 × 2.5 GHz fast Fourier transform spectrometers with a spectral resolution of 38.15 kHz, providing the whole coverage of the Q band in both polarizations. A more detailed description of the system is given by Tercero et al. (2021).

The QUIJOTE line survey was carried out in several observing runs between December 2019 and May 2022. All observations are performed using frequency-switching observing mode with a frequency throw of 8 and 10 MHz. The total observing time on source for data taken with frequency throws of 8 MHz and 10 MHz is 293 and 253 h, respectively. Hence, the total observing time on source by May 2022 is 546 h. The observed lines in TMC-1 with K_a = 0 or 1, the predictions lie within the experimental error. Some transitions of higher K_a show slightly higher uncertainty than expected; however, this can be explained by the difficulties of the model to account for the lower energy transitions, already observed in the previous work. These issues are related to the strong coupling of the internal motion and the overall rotation of the molecule, and hence to the high complexity of the model. The dipole moments used in this work, μ_o = 1.65 D and μ_b = 0.33 D, were reported by Bermúdez et al. (2018).

The line identification was achieved using the MADEX catalogue (Cernicharo 2012). We detected a total of 11 lines (divided into A and E components, due to an internal rotation of the methyl group) within the Q band, together with eight lines having an intensity lower than 3σ. The intensities range from 0.26 to 0.9 mK. The quantum numbers involved range from J = 3 to J = 5 and K_a ≤ 2. The derived line parameters are given in Table A.1. To obtain the column density, we used a model line fitting procedure, with the LTE approach for the thin optical lines (see e.g., Cernicharo et al. 2021d). We obtained N(CH₃CHCHO) = 1.5 × 10¹¹ cm⁻² with a rotational temperature of 9 K. The models predict the line intensities in antenna temperature taking into account the assumed size of the source to correct for beam dilution, and the beam efficiency of the telescope at the different frequencies of the observations. We assume a source of uniform brightness with a diameter of 80" (Fossé et al. 2001). The H₂ column density for TMC-1 is 10²² cm⁻² (Cernicharo & Güélin 1987), so the abundance of CH₃CHO is 1.5 × 10⁻¹¹. The predicted synthetic lines for these data are shown in Fig. 1 for K_a = 0,1 and in Fig. 2 for K_a = 2.

There are several molecules related to CH₃CHO, so it is interesting to compare their abundances. The most obvious is trans-propanal, which is its more stable isomer. The abundance ratio CH₃CHO/CH₃CHO is 1.5. This means that the abundance ratio between the two most stable isomers of the CH₃OH family is similar to that of the two most stable isomers of the C₂H₅O family, in which case C₂H₅OH/CH₃CHO ~1 (Agúndez et al. 2021b). We can also compare CH₃CHO with ketene, one of the most abundant O-bearing molecules in

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2 https://nanocosmos.iff.csic.es/
3 http://www.iram.fr/IRAMFR/GILDAS

3. Results

Methyl ketene is a nearly prolate molecule having a planar molecular skeleton (C₃ frame) with only the two hydrogen atoms of the methyl group out of the plane (C₃h), and therefore the internal rotation of the methyl top, it belongs to the G₆ symmetry group. As was shown in the previous rotational analysis of methyl ketene (Bermúdez et al. 2018), its ρ parameter, which accounts for the coupling of the methyl torsion with the overall rotation of the molecule, is relatively high (ρ = 0.196). For this reason, it was necessary to employ a Hamiltonian aligned to the ρ vector (ρ-axis-method, RAM) that accounts for the coupling of the two movements. This employed method is incorporated in the RAM36 software (Rho-axis method for 3- and 6-fold barriers; Ilyushin et al. 2010). The previous model for CH₃CHCHO reported by Bermúdez et al. (2018) was slightly adapted to account for the laboratory observed transitions from Bak et al. (1966) and Bermúdez et al. (2018). The model presented in this work also contains the observed transitions in TMC-1 between 32.0 and 50.4 GHz since no lines at those frequencies were accounted for in the previous model. A comparison of the parameters obtained in the previous model (Bermúdez et al. 2018) with the current parameters is presented in Table 1. The parameters of the model have barely changed, showing that the transitions were perfectly incorporated in the fit. Furthermore, for all the observed lines in TMC-1 with K_a = 0 or 1, the predictions lie within the experimental error. Some transitions of higher K_a show slightly higher uncertainty than expected; however, this can be explained by the difficulties of the model to account for the lower energy transitions, already observed in the previous work. These issues are related to the strong coupling of the internal motion and the overall rotation of the molecule, and hence to the high complexity of the model. The dipole moments used in this work, μ_o = 1.65 D and μ_b = 0.33 D, were reported by Bermúdez et al. (2018).

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TMC-1, with an abundance of $1.4 \times 10^{-9}$ relative to H$_2$, reported by Cernicharo et al. (2020). This gives an abundance ratio of CH$_2$CO/CH$_3$CHO $\sim 93$, which means that the methylated form of ketene is about two orders of magnitude less abundant than ketene itself. Finally, we compared the abundance of methyl ketene with acetaldehyde (CH$_3$CHO), which has an abundance of $3.5 \times 10^{-10}$ reported by Cernicharo et al. (2020). This gives an abundance ratio of CH$_3$CHO/CH$_3$CHO $\sim 23$.

4. Chemical model

To investigate the formation of methyl ketene in TMC-1 we carried out gas-phase chemical modelling calculations. The model parameters and chemical network are the same used in Cernicharo et al. (2021) to model the chemistry of O-bearing molecules following the discovery of H$_2$CO and C$_2$O. We added CH$_3$CHO as a new species, with a simple chemical scheme of formation and destruction. Although some
chemical models (e.g., Garrod et al. 2022) indicate that grain surface processes can help to explain the presence of some complex organic molecules (e.g., methyl formate and dimethyl ether; Agúndez et al. 2021b) in cold sources such as TMC-1, here we aim to evaluate whether purely gas phase processes can account for the formation of CH$_3$CHCO in TMC-1.

Methyl ketene is not included in the UMIST\textsuperscript{4} (McElroy et al. 2013) or KIDA\textsuperscript{5} (Wakelam et al. 2015) databases, although some information is available in the NIST Chemical Kinetics database\textsuperscript{6}. There are several plausible reactions of formation. The reaction between OH and CH$_3$CCH is a potential source of methyl ketene because it is relatively rapid at low temperatures, with a measured rate coefficient of $5.08 \times 10^{-12}$ cm$^3$ s$^{-1}$ at 69 K (Taylor et al. 2008). However, no information is available on the product distribution, and thus here we assume that CH$_3$CHCO and H are the main products. The reaction between OH and the non-polar isomer allene (CH$_2$CCH$_2$) has also been found to

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\textsuperscript{4} http://udfa.ajmarkwick.net/  
\textsuperscript{5} https://kida.astrochem-tools.org/  
\textsuperscript{6} https://kinetics.nist.gov/
be rapid at low temperatures, although the main products seem to be H$_2$CCO and CH$_3$ (Daranlot et al. 2012), and we thus do not include it as a source of methyl ketene. Another reaction that can provide an efficient formation route to methyl ketene is CH + CH$_3$CHO. This reaction was studied by Goulay et al. (2012), who found that CH$_3$CHO is formed with a branching ratio of 0.39. However, the rate coefficient has not been measured, although Wang et al. (2017) studied the reaction theoretically and found that the formation of CH$_3$CHO is barrierless. We thus adopted a rate coefficient of 2.41 × 10$^{-10}$ cm$^3$ s$^{-1}$, as measured for CH and H$_2$CO (Hancock & Heal 1992), and the branching ratio measured by Goulay et al. (2012).

There are other reactions that could potentially form CH$_3$CHCO, although they are unlikely to be efficient in TMC-1. For example, the reaction between HCO and C$_2$H$_3$ has a barrier (Lescaux et al. 1986; Xie et al. 2005a), and the same happens for the reaction between C$_2$H$_3$ and H$_2$CO (Xie et al. 2005b). The reaction between CH$_3$ and H$_2$CCO could provide a simple pathway to CH$_3$CHCO by simply substituting one H atom of ketene by a methyl group, although ketene does not show a high reactivity with radicals. Semenikhin et al. (2018) studied theoretically the reaction between CH$_3$ and H$_2$CCO; however, they did not consider the formation of CH$_3$CHCO and H, they found that all the explored channels have barriers. Therefore, we did not include this reaction. Finally, we considered that in TMC-1 methyl ketene is mostly destroyed through reactions with the most abundant cations, such as C$^+$, HCO$^+$, and H$_2$O$^+$.

The fractional abundance calculated for CH$_3$CHCO is shown in Fig. 3 as a function of time. It is seen that the peak abundance, reached at a time of some 10$^5$ yr, agrees very well with the abundance derived from the observations. The two formation reactions considered here (i.e., OH + CH$_2$CCH and CH + CH$_2$CHO) contribute to the formation of methyl ketene. The abundances calculated for CH$_3$CCH and CH$_3$CHO are in good agreement with those obtained in Cabezas et al. (2021) and Cernicharo et al. (2020). Further research on the low temperature kinetics and the product distribution of these two reactions will be of great interest to shed light on the origin of methyl ketene in TMC-1.

### 5. Conclusions

We have presented the first detection of CH$_3$CHCO towards TMC-1. We used the QUIJOTE line survey taken with the Yebes 40 m radiotelescope, with which we observed a total of 11 lines with an intensity higher than 3σ and another 8 lines with an intensity lower than 3σ, involving J = 3 to J = 5 and $K_a \leq 2$. The rotational temperature is 9 K and the derived column density N(CH$_3$CHCO) = 1.5 × 10$^{12}$ cm$^{-2}$. These results imply that methyl ketene is 1.46 less abundant than its most stable isomer (trans-CH$_3$CHCHO), a value quite similar to the abundance ratio of the isomers vinyl alcohol to acetaldehyde of 1. The observed abundance of methyl ketene is well explained using our gas-phase chemical model, considering the formation reactions from propyne and acetaldehyde, and the destruction reactions with the most abundant cations of TMC-1.

### Acknowledgements.

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### References

Cernicharo, J. 1985, Internal IRAM report (Granada: IRAM)
Hancock, G., & Heal, M. R. 1992, J. Mol. Spectrosc., 154, 1
Appendix A: Observed line parameters

The line parameters derived for this work were obtained by fitting a Gaussian line profile to the observed data, using the software Class (GILDAS package). We use a window of ±15 km s⁻¹ around the V_{LSR} (5.83 km s⁻¹) of the source for each transition. The results are given in Table A.1. The observed lines of methyl ketene are shown in Fig. 1 for K_a = 0.1 and in Fig. 2 for K_a = 2.

### Table A.1. Observed line parameters for CH₃CHCO

<table>
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<tr>
<th>Transition¹</th>
<th>ν_{obs}² (MHz)</th>
<th>ν_{obs}-ν_{cal}³ (MHz)</th>
<th>∫ T^{a}_A dν (mK km s⁻¹)</th>
<th>Δν (km s⁻¹)</th>
<th>T^{a}_A (mK)</th>
<th>Notes</th>
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<td>33830.302±0.010</td>
<td>-0.013</td>
<td>0.51±0.13</td>
<td>0.98±0.31</td>
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<td>0.38±0.15</td>
<td>0.76±0.35</td>
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**Notes.** ¹Quantum numbers are J′_{K_a,K′} - J_{K_a,K}. ²Observed frequency of the transition assuming a LSR velocity of 5.83 km s⁻¹. ³Line intensity in mK km s⁻¹. ⁴Integrated line intensity at half intensity derived by fitting a Gaussian function to the observed line profile (in km s⁻¹). ⁵Antenna temperature in millikelvin. ⁶Frequency switching data with a throw of 10 MHz only. Negative feature present in the data with a 8 MHz throw. ⁷Frequency switching data with a throw of 8 MHz only. Negative feature present in the data with a 10 MHz throw. ⁸The line is blended and corresponds to two transitions.