LETTER TO THE EDITOR

Discovery of the acetyl cation, CH₃CO⁺, in space and in the laboratory*,**

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ABSTRACT

Using the Yebes 40 m and IRAM 30 m radiotelescopes, we detected two series of harmonically related lines in space that can be fitted to a symmetric rotor. The lines have been seen towards the cold dense cores TMC-1, L483, L1527, and L1544. High level of theory ab initio calculations indicate that the best possible candidate is the acetyl cation, CH₃CO⁺, which is the most stable product resulting from the protonation of ketene. We have produced this species in the laboratory and observed its rotational transitions J = 10 up to J = 27. Hence, we report the discovery of CH₃CO⁺ in space based on our observations, theoretical calculations, and laboratory experiments. The derived rotational and distortion constants allow us to predict the spectrum of CH₃CO⁺ with high accuracy up to 500 GHz. We derive an abundance ratio N(CH₃CO⁺)/N(CH₃CO⁻) ~ 44. The high abundance of the protonated form of H₂CCO is due to the high proton affinity of the neutral species. The other isomer, H₂CCOH⁺, is found to be 178.9 kJ mol⁻¹ above CH₃CO⁺. The observed intensity ratio between the K = 0 and K = 1 lines, ~2.2, strongly suggests that the A and E symmetry states have suffered interconversion processes due to collisions with H and/or H₂, or during their formation through the reaction of H⁺ with H₂CCO.

Key words. astrochemistry – ISM: molecules – ISM: individual objects: TMC-1 – line: identification – molecular data

1. Introduction

The cold dark core TMC-1 presents an interesting chemistry. It produces a significant number of the molecules detected in space, in particular long neutral carbon-chain radicals and their anions (see e.g. Cernicharo et al. 2020a; Marcelino et al. 2020, and references therein) as well as cyanopolyynes (see Cernicharo et al. 2020b and Xue et al. 2020, and references therein). The presence in this object of O-bearing carbon chains, such as C₅O (Ohishi et al. 1991), C₇O (Matthews et al. 1984), HC₅O (McGuire et al. 2017), HC₆O (Cordiner et al. 2017), HCCO, and HC₅O⁺ (Cernicharo et al. 2020c), is a surprising result that has not yet been fully accounted for by chemical models.

The abundance of polyatomic cations in cold interstellar clouds is relatively low because they react fast with electrons.

* Full Table E.2 is only available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsarc.u-strasbg.fr/viz-bin/cat/J/A+A/646/L7
** Based on observations carried out with the Yebes 40 m telescope (projects 19A003, 20A014, and 20D15) and the Institut de Radioastronomie Millimétrique (IRAM) 30 m telescope. The 40 m radiotelescope at Yebes Observatory is operated by the Spanish Geographic Institute (IGN, Ministerio de Transportes, Movilidad y Agenda Urbana). IRAM is supported by INSU/CNRS (France), MPG (Germany), and IGN (Spain).
2. Observations

New receivers, built as part of the Nanocosmos project and installed at the Yebes 40 m radio telescope, were used for the observations of TMC-1. The Q-band receiver consists of two high electron mobility transistor (HEMT) cold amplifiers that cover the 31.0–50.3 GHz band with horizontal and vertical polarizations. Receiver temperatures vary from 22 K at 32 GHz to 31.98–50.42 GHz. This permits the user to check that no spurious ghosts are produced in the down-conversion chain, in which the signal coming from the receiver is down-converted to 1–19.5 GHz and then split into eight bands with a coverage of 2.5 GHz, each of which are analysed by the FFTs. Additional data were taken in October 2020 to improve the line survey at some frequencies and to further check the consistency of all observed spectral features. These observations were also performed in frequency switching but with a throw of 8 MHz. The sensitivity varies along the Q-band between 0.5 and 2.5 mK, which is a considerable improvement compared to previous line surveys in the 31–50 GHz frequency range (Kaufu et al. 2004).

The IRAM 30 m data come from a line survey performed towards TMC-1 and B1, and the observations have been described by Marcelino et al. (2007) and Cernicharo et al. (2012). The observations of L1527 and L1544 were obtained as part of the IRAM 30 m Large Program ASAI and were described by Lefloch et al. (2018). The intensity scale and antenna temperature (\(T_A^*\)) for the two telescopes used in this work were calibrated using two absorbers at different temperatures as well as the atmospheric transmission model ATM (Cernicharo 1985; Pardo et al. 2001). Calibration uncertainties were adopted to be 10%. All data were analysed using the GILDAS package.

3. Results and discussion

The assignment of the observed features in our line surveys was done using the CDMS and JPL catalogues (Muller et al. 2005; Pickett et al. 1998) and the MADEX code (Cernicharo 2012). Most of the weak lines found in our survey of TMC-1 can be assigned to known species and their isotopologues. Nevertheless, many features remain unidentified. Frequencies for the observed lines are given in Table 1. The ordinate is the antenna temperature (in mK). Spectral resolution is 38.1 kHz below 50 GHz and 48.8 kHz above. The blue labels correspond to the series of lines we assign to the A species of CH3CO+, while the red ones correspond to those of the E species.

Fig. 1. Observed lines of CH3CO+ towards TMC-1. The abscissa corresponds to rest frequencies (in MHz) assuming a local standard of rest velocity of 5.83 km s\(^{-1}\) (Cernicharo et al. 2020a,b). Frequencies and intensities for the observed lines are given in Table 1. The ordinate is the antenna temperature (in mK). Spectral resolution is 38.1 kHz below 50 GHz and 48.8 kHz above. The blue labels correspond to the series of lines we assign to the A species of CH3CO+, while the red ones correspond to those of the E species.

(Cernicharo et al. 2020b), the cation HC5O+ (Cernicharo et al. 2020c), the cation HC5S+ (Cernicharo et al. 2021), and the cation HC5NH+ (Marcelino et al. 2020), in addition to several tens of already known molecules and their isotopologues.

Within the unidentified features in our surveys in the 3 mm band and the Q-band, we found two series of four lines with a harmonic relation of 2:4:5:6 (see Fig. 1). Taking into account the line density in TMC-1, the possibility that the observed pattern is fortuitous is very small. The observed lines are shown in Fig. 1, and the derived line parameters are given in Table 1. In fact, the \(J = 5 – 4\) line at 91 342 MHz has intrigued us since 2017 when we detected it in TMC-1, L483, L1527, and L1544. We interpreted the \(K = 0, 1\) lines and the \(U\) line at \(-91 344\) (see Fig. A.1) as the hyperfine structure of a \(J = 1 – 0\) or \(J = 2 – 1\) transition of a molecule containing a nucleus with a spin of 1. Using the older receivers of the Yebes 40 m telescope, and assuming that the three lines around 91 342 MHz could correspond to \(J = 2 – 1\), we searched for lines at 45 671 MHz without success. Only when the new receivers covering the whole Q-band were available at the telescope, and we detected the doublet at 36 537 MHz (see Fig. 1), did we realized that two of the lines around 91 342 MHz correspond to a \(J = 5 – 4\) transition in harmonic relation 2:5 with
The 36.53 kHz doublet. Moreover, the line at 91.344 MHz is produced by another carrier as it is detected in B1, while the other lines are not. Once we relaxed the initial idea that these features were the hyperfine structure of a low-J transition, other features were found in the 3 mm domain (J = 4 – 3 and J = 6 – 5, as well as J = 7 – 6 in L1527).

The two series of lines can be fitted to two linear rotors with rotational constants B = 9134.4738 ± 0.0006 MHz and B = 9134.2860 ± 0.0020 MHz. The distortion constant is exactly the same for both series, D = 4.00 ± 0.02 kHz. The observed spectra is reminiscent of the K = 0 and K = 1 components of the rotational transitions of a symmetric rotor. In fact, the eight observed lines in TMC-1 can be fitted with a single rotational constant and two distortion constants if we assume that the carrier is the same for both series and that it has a Cs symmetry (i.e. that it is a symmetric rotor). Using the standard Hamiltonian for this kind of molecular rotor (Gordy & Cook 1984), we derived the rotational and distortion constants provided in Table 2.

From the derived rotational constant, 9134 MHz, the molecule should contain at least three atoms between C, N, and O. We analysed the possible candidates that could have a rotational constant similar to the observed one. Detailed ab initio calculations for the possible linear and asymmetric carriers are given in Appendix B. Concerning symmetric rotors, it is amazing to realize that all CH₃X, with X = CN, NC, and CCH, have rotational constants close to our rotational and distortion constants. For example, CH₃CN has a rotational constant of 9198.9 MHz (Müller et al. 2009), which is really very close to our result. The other possible candidates, CH₃CN⁺ (B = 8590.5 MHz; Amano et al. 2006) and CH₃CNH⁺ (see, Table B.1), are also too heavy. Hence, the best symmetric rotor candidate seems to be a species similar to CH₃CN. The acetyl radical, CH₃CO, has been observed in the laboratory by Hirota et al. (2006), but it is asymmetric and its lines show a very complex hyperfine structure. However, CH₂CO⁺ is a symmetric rotor (Mosley et al. 2014) and the lowest energy isomer of H₂C₆O⁺. Its possible precursor, if formed through protonation, is ketene, which is one of the most abundant O-bearing species in TMC-1 (see Cernicharo et al. 2020c).

3.1. Quantum chemical calculations and assignment to CH₃CO⁺

Precise geometries and spectroscopic molecular parameters for the species mentioned above were computed using high-level ab initio calculations. The first screening for all plausible candidates (see Appendix B) was done at the CCSD/cc-pVTVZ level of theory (Clézé et al. 1969; Dunning 1989). These results are shown in Table B.1. In a second stage, the most promising candidates, namely CH₂CO⁺, CH₃COH⁺, and CH₃NCH⁺, were calculated at the CCSD(T)-F12b/aug-cc-pVQZ levels of theory (Raghavachari et al. 1989; Adler et al. 2007; Knizia et al. 2009). To obtain more precise values for the rotational parameters of these three species, we calibrated our calculations using experimental to theoretical scaling ratios for analogue molecular species. This method has been proved to be suitable to accurately reproduce the molecular geometry of other identified molecules (Cernicharo et al. 2019, 2020c; Marcellino et al. 2020). In our present case, we used CH₃CN, CH₃CNH, and CH₃NC, which are isoelectronic species of CH₂CO⁺, CH₃COH⁺, and CH₃NCH⁺, respectively, for this purpose. Table B.2 shows the results of these calculations, which are summarized in Table 3. As can be seen, the employed level of theory reproduces the rotational parameters for CH₃CN, CH₃CNH, and CH₃NC very well, with relative discrepancies around 0.08% and 0.04% for B in the cases of CH₃CN and CH₃NC, respectively. After correcting the calculated parameters for CH₂CO⁺, CH₃COH⁺, and CH₃NCH⁺ using the derived scaling ratios for CH₃CN, CH₃CNH, and CH₃NC, respectively, we obtained a B constant of 9129.62 MHz for CH₂CO⁺, which shows the best agreement with that derived from the TMC-1 lines. The centrifugal distortion values, obtained in the same manner but at the MP2/aug-cc-pVQZ level of theory for CH₂CO⁺ and CH₃NCH⁺, are both comparable with those obtained from the fit of the lines. The agreement between the experimental constants and those calculated for CH₂CO⁺ is substantially worse. The calculated dipole moments for CH₂CO⁺ and CH₃NCH⁺ are 3.5 D and 2.0 D, respectively, while the μ₀ and μ₀ values for CH₂CO⁺ are 0.8 and 1.7 D, respectively.

In addition to the geometry optimizations, we calculated the energy associated with the plausible formation of CH₂CO⁺, starting from ketene and three proton donors; H₃⁺, H₂O⁺, and HCO⁺. All these calculations were carried out at the CCSD/cc-pVTZ level of theory. We found a total energy change in the protonation of ketene to form CH₂CO⁺ of −421.8, −130.9, and −244.8 kJ mol⁻¹ when ketene reacts with H₃⁺, H₂O⁺, and HCO⁺, respectively. More details can be found in Appendix C.

Table 1. Observed line parameters for CH₂CO⁺ in TMC-1.

| J, K | ν (MHz) | Δν (kHz) | T (mK) | ΔT (mK s⁻¹) | Jν (mK s⁻¹) |
|------|--------|----------|--------|-------------|------------|
| 2    | 0      | 36537.765 | −3.5   | 39.0 ± 0.6  | 0.63 ± 0.01 | 26.1 ± 0.6 |
| 2    | 1      | 36537.014 | −0.6   | 11.8 ± 0.6  | 0.60 ± 0.03 | 7.5 ± 0.6  |
| 4    | 0      | 73074.769 | 2.7    | 71.0 ± 3.5  | 0.47 ± 0.03 | 35.7 ± 2.0 |
| 4    | 1      | 73073.252 | −6.6   | 25.0 ± 3.5  | 0.65 ± 0.11 | 17.2 ± 2.0 |
| 5    | 0      | 91342.732 | −3.5   | 37.5 ± 3.0  | 0.46 ± 0.04 | 18.2 ± 1.0 |
| 5    | 1      | 91340.865 | 14.2   | 11.9 ± 3.0  | 0.49 ± 0.11 | 6.3 ± 1.0  |
| 6    | 0      | 109601.225 | 2.1    | 12.8 ± 2.8  | 0.45 ± 0.09 | 6.1 ± 1.0  |
| 6    | 1      | 109607.954 | −7.3   | 6.6 ± 2.6   | 0.60 ± 0.10 | 4.2 ± 1.0  |

Notes. (a) Observed frequencies (in MHz) adopting a νLSR of 5.83 km s⁻¹ for TMC-1. The uncertainty is 10 kHz for all the lines. (b) Observed minus calculated frequencies (in kHz) resulting from a fit to the observed frequencies. The J = 7 – 6 K = 0, 1 lines observed in L1527 have been included in the fit (see text). (c) Antenna temperature (in mK).

Table 2. Derived spectroscopic parameters (in MHz) for CH₂CO⁺.

| Constant | Space (a) | Laboratory (b) | Merged (c) |
|----------|-----------|----------------|------------|
| B        | 9134.47424(82) | 9134.47083(27) | 9134.47211(20) |
| D_b      | 4.014(12) 10⁻¹ | 3.99198(28) 10⁻¹ | 3.9930(21) 10⁻¹ |
| D_c      | 1.8847(55) 10⁻¹ | 1.87616(41) 10⁻¹ | 1.8773(46) 10⁻¹ |
| H_b      | 8.66(33) 10⁻⁷ | 9.56(37) 10⁻⁷ | 9.7(16) 10⁻⁷ |
| H_c      | 6.58(59) 10⁻⁶ | 7.19(74) 10⁻⁶ | 7.2(40) 10⁻⁶ |

Notes. (a) Fit to the lines of CH₂CO⁺ observed in TMC-1. In this fit, the J = 7 – 6 and K = 0, 1 lines observed in L1527 (with frequencies of 127877.133 ± 0.025 and 127874.494 ± 0.050 MHz, respectively) have been included (see Fig. A.1 and Appendix A). (b) Fit to the lines of CH₂CO⁺ observed in the laboratory. (c) Fit to the lines of CH₂CO⁺ observed in space and in the laboratory. (d) The standard deviation of the fit (in kHz). (e) Number of lines included in the fit.
3.2. Laboratory detection of CH$_3$CO$^+$

We conducted an experiment to detect the CH$_3$CO$^+$ cation in the laboratory using rotational spectroscopy below 500 GHz. The experimental setup was similar to the one used to detect NS$^+$ (Cernicharo et al. 2018). The cation was produced in a liquid-nitrogen-cooled Pyrex absorption cell by glow-discharging a mixture of CH$_3$L, CO (1:1), and Ar. A solenoid coil wound on the cell can generate an axial magnetic field (up to 300 G) to magnetically extend the negative glow, the region known to produce the highest concentrations of cations (compared to the positive column discharge; De Lucia et al. 1983). We also tried acetone and acetaldehyde as precursors (Mosley et al. 2014), but without success.

To optimize the experimental setup, we first observed the $J = 2 \rightarrow 1$ transition of HCO$^+$ at 178 375.056 MHz, which was produced in the same gas mixture. We then searched for the $J = 10 \rightarrow 9$, $K = 0 \rightarrow 2$ series of lines of CH$_3$CO$^+$ between 182.658 and 182.675 GHz based on the rotational constants derived from the lines observed in TMC-1. Weak spectra were observed within 500 kHz. The best experimental conditions were found to be $P$(CH$_3$L) = $P$(CO) = 1.5 mTorr, $P$(Ar) = 5.5 mTorr (gas mixture cooled using liquid nitrogen but pressures measured at room temperature), an electric discharge of 3.5 kV$^{-}$10 mA, and an axial magnetic field of 200 G. These lines disappeared when one of the precursors was suppressed, or when the axial magnetic field was cut off. The latter phenomenon confirmed almost unambiguously that they were due to a cation. Subsequent measurements of higher-$J$ transitions fully support the astrophysical assignment of the observed lines to CH$_3$CO$^+$.

In total, 79 lines were observed in the laboratory with quantum numbers in the ranges $J = 10 \rightarrow 27$ and $K \leq 6$ (see Table E.1). Transitions occurring below 330 GHz were measured by standard frequency modulation absorption spectroscopy, resulting in second-derivative lineshapes. These lines ($K \leq 3$) were found unshifted from the first prediction. Those from 400 to 500 GHz were measured by emission spectroscopy (Zou & Motiyenko 2020), giving Voigt-profile lineshapes. Compared to the prediction, some deviations were observed up to 1 MHz for $K = 6$; these measurements led us to determine the $H_{IK}$ and $H_{JK}$ centrifugal distortion terms. For maximum sensitivity, these lines were measured using the single frequency excitation method with 5–20 million acquisitions (which took 1 to 5 min.). Additionally, a 120 MHz wide chirped excitation spectrum, measured with 67 million acquisitions, is given in Fig. 2 for illustration and comparison purposes. The uncertainty of the laboratory frequency measurements are estimated to be 50 kHz. Given the mass of the cation, and that the negative glow is a nearly electric field-free region, the reported laboratory frequencies are expected to be unshifted by the Doppler effect. The separate and merged least-squares analysis of all (astronomical and laboratory) measured transitions are provided in Table 2. The measured frequencies and the observed minus calculated values are given in Table E.1. Frequency predictions are given in Table E.2.

Table 3. Scaled theoretical values for the spectroscopic parameters of CH$_3$CO$^+$, CH$_2$CO$^+$, and CH$_3$NCH$^+$ together with the experimental values obtained in this work (all in MHz).

| Parameter | Exp. | CH$_3$CO$^+$ | CH$_2$CO$^+$ | CH$_3$NCH$^+$ |
|-----------|------|-------------|--------------|--------------|
| $B$       | $9134.472(8)$ | $9129.6$ | $9309.5$ | $9105.5$ |
| $D_J \times 10^{-3}$ | $4.014(13)$ | $3.9$ | $2.8$ | $4.0$ |
| $D_K \times 10^{-3}$ | $188.47(50)$ | $184.6$ | $378.7$ | $171.7$ |

Notes. (a)This work. (b)$(+C)/2$.

3.3. Chemistry of CH$_3$CO$^+$

From the observed line intensities of CH$_3$CO$^+$, we derived a rotational temperature of $\sim 5$ K and a total column density of $(3.2 \pm 0.3) \times 10^{11}$ cm$^{-2}$ (see Appendix D). The column densities for the $A$ and $E$ species are $(2.2 \pm 0.2) \times 10^{11}$ cm$^{-2}$ and $(9.7 \pm 9.0) \times 10^{10}$ cm$^{-2}$, respectively. Adopting the column density for ketene derived by Cernicharo et al. (2020c), we obtained a H$_2$CCO/CH$_3$CO$^+$ ratio of 44. Assuming the H$_2$ column density derived by Cernicharo & Guélin (1987), the abundance of CH$_3$CO$^+$ is $3.2 \times 10^{-11}$.

The chemistry of protonated molecules in cold dense clouds has been discussed by Agúndez et al. (2015). Chemical model calculations similar to those that they presented predict that the abundance of protonated ketene is controlled by the typical routes operating for protonated molecules. That is, CH$_3$CO$^+$ is mostly formed by proton transfer to H$_2$CCO from HCO$^+$, H$_3^+$, and H$_2$O$^+$, while it is destroyed through dissociative recombination with electrons. The radiative association between CH$_3^+$ and CO is also an important route to CH$_3$CO$^+$. The abundance ratio H$_2$CCO/CH$_3$CO$^+$ predicted by the model is in the range 250–450 and depends on whether the UMIST RATE12 (McElroy et al. 2013) or KIDA kida uva.2014 (Wakelam et al. 2015) chemical networks are used. As occurs for most protonated molecules observed in cold dense clouds, the abundance of the protonated form with respect to the neutral is underestimated by the chemical model. In this case, there is a factor of 5–10 difference between the model and observations. Incorrect estimates for the rate constants of the dominant reactions of the formation and destruction of CH$_3$CO$^+$ may be behind this disagreement. Alternatively, the chemical network may miss some important formation route to CH$_3$CO$^+$, although it is difficult to identify reactions producing this ion from abundant reagents. For example, plausible reactions of CH$_3^+$ ions with CO, H$_2$CO, or CH$_3$OH tend to form products other than CH$_3$CO$^+$ (Adams & Smith 1978). In this context, it is worth noting that not all species resulting from the protonation of abundant molecules in TMC-1 are detected. For example, CH$_3$NCH$^+$ is not detected in TMC-1 despite the CH$_3$CN proton affinity of 787.4 ± 5.9 kJ mol$^{-1}$ (Williams et al. 2001). The 3σ upper limit to the column density of CH$_3$NCH$^+$ is $2.5 \times 10^{11}$ cm$^{-2}$. The column density of CH$_3$CN is $(3.2 \pm 0.2) \times 10^{12}$ cm$^{-2}$ (see Appendix A); hence, the abundance ratio between the neutral and its protonated form is $\geq 13$. The low dipole moment of CH$_3$NCH$^+$ compared to that of CH$_3$CN (1.01 D versus 3.93 D) limits the chances of detecting this species.
3.4. A-CH_3CO^+/-E-CH_3CO^+ abundance ratio

The column densities derived for the A and E species of CH_3CO^+ are not identical, as would be expected for a symmetric top. The A/E abundance ratio for this molecule is 2.27. However, all symmetric molecules of CH_3X detected in TMC-1 have an abundance ratio between their A and E species that is close to unity (see Appendix D and Fig. D.2). In a symmetric top, the ever all symmetric molecules of CH_3 are a cation, and its reactive collisions with H_2 or H could produce a proton interchange if there is no barrier to the reaction. The lowest energy level of the E symmetry state is the J = 1, K = 1, which is 7.8 K above the ground J = 0, K = 0 level of the A state. Hence, the reaction of interchange of a proton

E-CH_3CO^+ + H_2/3 → A-CH_3CO^+ + H_2/3 + 7.8 K

is exothermic, although it is unknown if there is a barrier; this is something that has to be established via detailed theoretical calculations. At thermal equilibrium, and for a kinetic temperature of 10 K, the A/E abundance ratio could be e^{1570} ≈ 2.18, which is very close to the observed value of 2.27. For neutral molecules with two or more symmetric hydrogens, the proton interchange could be mainly produced through collisions with H^+, H^+, HCO^+, and H_2O^+, which are much less abundant than H_2 and H. In Appendix D, we discuss the A/E abundance ratio of all neutral symmetric rotors that have been detected so far in TMC-1, including CH_3NC, which has previously only been observed in two cold dense clouds: L1544 (Jiménez-Serra et al. 2016) and L483 (Agúndez et al. 2019). For all these species, the A/E abundance ratio is close to unity.

Alternatively, we could also consider the possibility that the collisional rates of the acetyl cation with H_2 or He are higher for the A species than for the E species. As the acetyl cation is isoelectronic to CH_3CN, we could use the collisional rates of the latter species (Khalifa et al. 2020) to estimate possible differences in the excitation temperature of the K = 0 and K = 1 lines. We explored a density range of (4−10) x 10^4 cm^-3 and a kinetic temperature range of 5–10 K. No significant differences were found in the predicted brightness temperature between these lines. Of course, if the effect is due to inelastic collisions, then methyl cyanide (CH_3CN) would also show a similar behaviour. Nevertheless, although both species are isoelectronic, the fact that CH_3CO^+ is positively charged could result in very different collisional rates with H_2 compared to CH_3CN.

We could also consider that the A/E abundance ratio is affected by the formation process of the molecule. As shown in Sect. 3.1, the reaction of ketene with H_2 is the most favourable for protonation from the thermodynamical point of view. Both species, ketene and H_2, could also have their ortho/para ratio affected by the low temperature of dense dark clouds, which will introduce a non-trivial spin statistic into the formation process of CH_3CO^+. Additional calculations are needed to evaluate the role of collisional excitation and of spin interchange in order to understand the anomalous behaviour exhibited by the A and E symmetry species of CH_3CO^+.

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Appendix A: CH$_3$CO$^+$ in other sources

The acetyl cation, CH$_3$CO$^+$, has also been detected towards L483, L1544, and L1527 (see Fig. A.1). However, it is not observed towards Sgr B2 (PRIMOS$^3$ line survey; Neill et al. 2012), towards Orion-KL (Tercero et al. 2010, 2011), or in our line survey of B1 (Marcelino et al. 2007, 2009, 2010; Cernicharo 2012). In the PRIMOS data on SgrB2, a very tentative detection of the $J = 1 - 0$ $K = 0$ line could be claimed at a velocity of 80 km s$^{-1}$. However, only an upper limit can be obtained for the $J = 2 - 1$ transition as this line is heavily blended with a strong line of acetone. It seems, hence, that CH$_3$CO$^+$ is typical of cold interstellar clouds.

Appendix B: Potential carriers of the series of lines

All known diatomic species in cold dark clouds have overly large rotational constants compared with those derived from the lines in TMC-1. For example, a molecule containing one S (CS, NS, SO) will have a rotational constant that is too high by more than 12 GHz. Adding one or two H atoms to these combinations of sulphur produces radicals (with overly high rotational constants, such as HCS) or asymmetric rotors such as H$_2$CS, which is too heavy (Müller et al. 2019). A molecule with two S atoms is, of course, too heavy (for example, $B$(S$_2$) = 8831 MHz; Pickett & Boyd 1979), and we do not expect to have Si- or P-bearing polyatomic species in this cloud. The first step in finding candidates is to exclude the possibility of having a slightly asymmetric species. In that case, we could expect to have lines corresponding to $K = \pm 1$ at roughly $(B-C)$ from the $K = 0$ lines. We searched in the $Q$-band survey ($J = 2 - 1$) for such a pattern. No lines up to one-fourth of the intensity of the $K = 0$ line are observed. Moreover, taking into account that there is no evidence for a radical as a possible carrier, the species resulting from the addition of one hydrogen to the closed-shell asymmetric species HNCO, HCOOH, and H$_2$CCC have to be excluded. However, their protonated species are also, at least in principle, closed-shell species. Hence, possible candidates are H$_2$CCCH$^+$, CH$_3$CCH$^+$, HCN$^+$, HNCO$^+$, HCOOH$^+$, and CH$_3$OO$^+$, all of which, with the exception of the last one, are protonated forms of known neutral and abundant species in TMC-1. Nevertheless, the resulting molecular structures will be highly asymmetric for most of them, or they are too light or too heavy, as are the cases for H$_2$CCCH$^+$ and CH$_3$CCH$^+$, respectively. HNCOH$^+$ is a linear species characterized in the laboratory with a rotational constant of 9955 MHz (Latanzi et al. 2012) and is not detected in our data. Other exotic species, such as NH$_2$CHOH$^+$, CH$_3$ONH$^+$, and CH$_3$NOH$^+$, which could result from the protonation of interesting molecules (NH$_2$CHO for example), are discarded for their molecular asymmetry and because the neutral species have not been observed in TMC-1. Ab initio calculations have been performed for the most promising candidates (see Table B.1), and their isomers and the results are discussed in Sect. 3.1.

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$^3$ Access to the entire PRIMOS data set, specifics on the observing strategy, and overall frequency coverage information is available at http://www.cv.nrao.edu/~aremijan/PRIMOS/.

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Fig. A.1. Observations of the $J = 5 - 4$ transition of CH$_3$CO$^+$ towards L483, L1544, L1527, and B1 (top panels); bottom panel: $J = 7 - 6$ line towards L1527. The abscissa corresponds to the rest frequency (in MHz) and the ordinate is the antenna temperature (in mK). The spectral resolution is 48.8 kHz for all sources except L1527, for which it is 198 kHz. The vertical dashed blue lines indicate the position of the $K = 0$ and $K = 1$ lines (detected in all sources except B1), and the cyan line corresponds to the U feature at 91 344 MHz (detected in all sources except L1527). The rest velocities of L1527 and L1544 were taken as $v_{LSR} = 5.9$ km s$^{-1}$ and 7.2 km s$^{-1}$, respectively, based on Sakai et al. (2009) and Vastel et al. (2015), respectively.
Table B.1. Rotational constants and electric dipole moments of potential candidates.

| Species \(^{(a)}\) | ∆E/kJ/mol \(^{(b)}\) | A, B, C/MHz | D\(_J\), D\(_K\)/kHz | \(\mu_a, \mu_b, \mu_c/D\) |
|------------------|-----------------|----------|----------------|----------------|
| \(\text{H}_3\text{CCO}^+\) | 0.0 | 154355.3 | 9107.2 | 178.7 | 0.0 | 2.5 |
| \(\text{H}_2\text{COH}^+\) | 178.0 | 201325.3 | 9411.2 | 341.6 | 0.1 | 0.0 |
| \(\text{H}_3\text{CCNCH}^+\) | 0.0 | 155571.2 | 9090.7 | 160.6 | 0.0 | 1.9 |
| \(\text{H}_2\text{CCCH}^+\) | 0.0 | 285625.5 | 9673.5 | 457.3 | 0.0 | 0.0 |
| \(\text{H}_2\text{CCN}^+\) | 0.0 | 280905.8 | 10338.2 | 492.0 | 0.0 | 5.0 |
| \(\text{H}_2\text{CNC}^+\) | 5.9 | 277331.4 | 11582.1 | 685.4 | 0.0 | 3.7 |
| \(\text{H}_2\text{NCC}^+\) | 176.4 | 328396.0 | 10180.7 | 593.3 | 0.0 | 4.6 |
| \(\text{HCNCH}^+\) | 196.2 | 11120.9 | 2.9 | 0.0 |
| \(\text{H}_2\text{NCO}^+\) | 0.0 | 324210.9 | 10295.5 | 380.4 | 0.0 | 3.8 |
| \(\text{HNCOH}^+\) | 70.4 | 723374.4 | 10034.0 | 1255.3 | 1.7 | 1.3 |
| \(\text{HCNOH}^+\) | 285.4 | 625942.1 | 10400.0 | 1859.1 | 1.6 | 2.4 |
| \(\text{H}_2\text{CON}^+\) | 333.8 | 268002.3 | 11140.1 | 461.1 | 0.0 | 2.9 |
| \(\text{H}_2\text{CON}^+\) | 613.2 | 259994.7 | 11321.2 | 484.7 | 0.0 | 2.3 |

**Notes.** \(^{(a)}\)Calculations at the CCSD/cc-pVTZ level of theory. \(^{(b)}\)The energy taken as reference is the lowest energy species within the same isomer family.
Table B.2. Scaled theoretical values for the spectroscopic parameters of CH$_3$CO$^+$, CH$_3$COH$^+$, and CH$_3$NCH$^+$ (all in MHz).

| Parameter | CH$_3$CN | CH$_3$CO$^+$ | CH$_3$COH$^+$ | CH$_3$NCH$^+$ |
|-----------|----------|--------------|--------------|--------------|
|           | Calc. ($a$) | Exp. ($b$) | Calc. ($a$) | Exp. ($b$) | Calc. ($a$) | Exp. ($b$) | Calc. ($a$) | Exp. ($b$) |
| $(A$-$B)\times 10^{-3}$ | 150.4 | 148.900074(65) | 145.0 | 143.5 | – |
| $B$       | 9191.5 | 9198.899134(11) | 9122.3 | 9129.6 | 9134.4742(8) |
| $D_1 \times 10^3$ | 3.6 | 3.807528(9) | 3.7 | 3.9 | 4.014(13) |
| $D_J \times 10^3$ | 174.0 | 177.40796(28) | 181.0 | 184.6 | 188.47(50) |
| $A$       | 198393.1 | 201443.685(75) | 198278.8 | 201327.7 | – |
| $B$       | 9666.3 | 9663.168(2) | 9411.8 | 9408.7 | – |
| $C$       | 9488.0 | 9470.127(2) | 9227.6 | 9210.2 | 9134.4742(8) |
| $D_1 \times 10^3$ | 2.9 | 2.980(2) | 2.7 | 2.8 | 4.014(13) |
| $D_J \times 10^3$ | 244.4 | 232.8(3) | 397.7 | 378.7 | 188.47(50) |
| $A$       | 198393.1 | 201443.685(75) | 198278.8 | 201327.7 | – |
| $B$       | 9666.3 | 9663.168(2) | 9411.8 | 9408.7 | – |
| $C$       | 9488.0 | 9470.127(2) | 9227.6 | 9210.2 | 9134.4742(8) |
| $D_1 \times 10^3$ | 2.9 | 2.980(2) | 2.7 | 2.8 | 4.014(13) |
| $D_J \times 10^3$ | 244.4 | 232.8(3) | 397.7 | 378.7 | 188.47(50) |

Notes. ($a$)Rotational constants calculated at the CCSD(T)-F12b/aug-cc-pVQZ level of theory, and centrifugal distortion constants calculated at the MP2/aug-cc-pVQZ level of theory. ($b$)Müller et al. (2009). ($c$)Scaled by the ratio Exp/Calc. of the corresponding parameter for CH$_3$CN species. ($d$)This work. ($e$)Rodler et al. (1984). ($f$)Scaled by the ratio Exp/Calc. of the corresponding parameter for CH$_3$CNH species. ($g$)Pliva et al. (1995). ($h$)Scaled by the ratio Exp/Calc. of the corresponding parameter for CH$_3$NC species.

Appendix C: Additional quantum chemical calculations for CH$_3$CO$_2$H

The potential energy surface (PES) for the protonation of ketene has been explored at the CCSD/cc-pVTZ level of theory. In the calculations, we considered three possible proton donors: H$_3^+$, H$_3$O$^+$, and HCO$^+$, as well as the formation of the two isomers of protonated ketene, CH$_3$CO$^+$ and CH$_3$COH$^+$. Figure C.1 depicts the PES along the reaction coordinate for the protonation of ketene and the relative energies for all the stationary points when ketene reacts with H$_3^+$, H$_3$O$^+$, or HCO$^+$. For each reaction, the two reactants, ketene and the proton donor, that separated from each other were assumed to be the energy zero. The protonation of ketene in the CH$_3$ in the three cases is exothermic, and it proceeds without any transition state (TS) to form CH$_3$CO$^+$. This formation is more favourable in the case of H$_3^+$ on the other hand, the formation of CH$_3$COH$^+$ is exothermic in the case of H$_3$O$^+$ and HCO$^+$, but endothermic in the case of H$_3^+$. The less stable isomer, CH$_3$COH$^+$, can interconvert through a hydrogen migration to CH$_3$CO$^+$, which has a TS barrier height of 210.1 kJ mol$^{-1}$. As shown in Fig. C.1, the TS for this interconversion lies over the energy of the reactants in the protonation of ketene with H$_3$O$^+$ and HCO$^+$. In contrast, this TS lies below the energy of the reactants when ketene reacts with H$_3^+$.

Fig. C.1. Energy diagram for the protonation of ketene. Total energies relative to those of the separated reactants, ketene and the proton donor X, are given in the enclosed table in kJ mol$^{-1}$. C* is the TS energy for the interconversion between CH$_3$COH$^+$ and CH$_3$CO$^+$ isomers. Y** is the energy difference between the reactants and the interconversion TS; a negative value indicates that the TS is submerged below the reactant energy, and a positive value implies that the TS lies above the reactant energy.

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Appendix D: CH$_3$X species in TMC-1

As noted above, the intensity of the $J = 2 - 1$ $K = 1$ line in TMC-1 is well below the expected value if the rotational temperature for the $A$ and $E$ species is the same. In order to check this point, we show in Fig. D.1 the rotational diagrams for the $A$ and $E$ species of CH$_3$CO$^+$ using the observed line parameters given in Table 1. The observed intensities have been corrected for beam dilution and the beam efficiencies of the Yebes 40 m and IRAM 30 m telescopes. We assumed a uniform source of radius 40" (Fossé et al. 2001). The derived rotational temperatures, $T_{\text{rot}}(A) = 4.4 \pm 0.4$ K and $T_{\text{rot}}(E) = 5.0 \pm 0.5$ K, are consistent with a common excitation through collisions with H$_2$. The derived column densities are $N(A-\text{CH}_3\text{CO}^+) = (2.2 \pm 0.2) \times 10^{11}$ cm$^{-2}$ and $N(E-\text{CH}_3\text{CO}^+) = (9.7 \pm 0.9) \times 10^{10}$ cm$^{-2}$. Hence, as discussed in Sect. 3.4, the $A/E$ abundance ratio for CH$_3$CO$^+$ has been modified through collisions with H$^+$, H$_3^+$, HCO$^+$, and H$_3$O$^+$. This is a similar effect to that found in cold molecular clouds for molecules having ortho and para symmetry species.

In order to check this peculiar result, we analysed all symmetric rotors having transitions within our line survey: CH$_3$CCH, CH$_3$C$_2$H$_2$, CH$_3$CN, and CH$_2$NC. The cation CH$_3$CNH$^+$ has not been detected in TMC-1 (see Sect. 3.3). The symmetric top CH$_3$C$_3$N is discussed in Marcelino et al. (2021). Figure D.2 shows the $J = 2 - 1$ transition for CH$_3$CN, CH$_3$CCH, CH$_3$NC, and CH$_2$CO$^+$ (for this species, see also Fig. 1). The $K = 0$ and $K = 1$ lines of CH$_3$CN exhibit the typical hyperfine structure introduced by the quadrupole moment of the N nucleus. For all these additional molecules, we assumed a rotational temperature of 10 K and a source radius of 40" (Fossé et al. 2001), and we produced a synthetic spectrum that is compared to the observations. We found that the $A/E$ abundance ratio is $\approx 1$ for all species but CH$_3$CO$^+$. Adopting a lower rotational temperature has little effect on the derived $A/E$ abundance ratio for these symmetric rotors.

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**Fig. D.1.** Rotational diagrams for the $A$ (black line) and $E$ (red line) symmetry species of CH$_3$CO$^+$ in TMC-1.

**Fig. D.2.** Observed lines in the transition $J = 2 - 1$ $K = 0,1$ of different symmetric rotors in TMC-1. The colour lines represent the expected line profiles for the $A$ species (red) and $E$ species (blue). The abundance ratio between them in the model is indicated in each panel.
Appendix E: Observed and calculated frequencies of CH$_3$CO$^+$

The frequencies observed in space and in the laboratory were merged to obtain the recommended rotational and distortion constants. A total of 89 rotational transitions, ten in space (see Table 1) and 79 in the laboratory (see Table E.1), were fitted to the standard Hamiltonian of a symmetric rotor (Gordy & Cook 1984). For the lines observed in TMC-1 and other dark clouds, only $B$, $D_J$, and $D_{JK}$ can be obtained as only rotational transitions with $K = 0$ and 1 have been observed. The results are given in Table 2. For the 79 lines observed in the laboratory, the constants $H_{JK}$ and $H_{KJ}$ were included in the fit, and the results are given in Table 2. Finally, the merged fit to the astronomical and laboratory lines produces the recommended set of rotational constants given in the last column of Table 2. The observed and calculated frequencies, together with the observed minus calculated values for the merged fit, are given in Table E.1.

We used the rotational and distortion constants that resulted from the merged fit to the astronomical and laboratory lines (see Table 2) to produce frequency predictions, frequency uncertainties, line strengths, upper energy levels, and Einstein coefficients for all transitions involving levels with energies below 2000 K. They are given in Table E.2. The whole table is electronically available at the CDS. It should be noted that this table contains the transitions for the A and E species, and that the E lowest energy level, $J_K = 1$, is 7.8 K above the 0_0 level of the A species.

### Table E.1. Observed and calculated frequencies (in MHz) for CH$_3$CO$^+$.

| $J_u$ | $K$ | Freq. Obser. (Unc) | Freq. Calc. (Unc) | Obs-Calc |
|------|-----|-------------------|------------------|---------|
| 2    | 0   | 36537.765 0.010   | 36537.761 0.001  | 0.004   |
| 2    | 1   | 36537.014 0.010   | 36537.010 0.001  | 0.004   |
| 4    | 0   | 73074.769 0.010   | 73074.755 0.002  | 0.014   |
| 4    | 1   | 73073.252 0.010   | 73073.253 0.002  | -0.001  |
| 5    | 0   | 91342.732 0.010   | 91342.725 0.003  | 0.007   |
| 5    | 1   | 91340.865 0.010   | 91340.848 0.003  | 0.017   |
| 6    | 0   | 109607.225 0.010  | 109607.215 0.003 | 0.010   |
| 6    | 1   | 109607.954 0.010  | 109607.963 0.003 | -0.009  |
| 7    | 0   | 127877.133 0.025  | 127877.131 0.004 | 0.002   |
| 7    | 1   | 127874.494 0.050  | 127874.504 0.006 | -0.001  |
| 10   | 3   | 182639.714 0.050  | 182639.724 0.011 | -0.010  |
| 10   | 2   | 182658.451 0.050  | 182658.469 0.006 | -0.018  |
| 10   | 1   | 182669.687 0.050  | 182669.719 0.005 | -0.032  |
| 10   | 0   | 182673.442 0.050  | 182673.470 0.005 | -0.028  |
| 11   | 3   | 200900.043 0.050  | 200900.014 0.012 | 0.029   |
| 11   | 2   | 200920.617 0.050  | 200920.630 0.007 | -0.013  |
| 11   | 1   | 200933.010 0.050  | 200933.002 0.006 | 0.008   |
| 11   | 0   | 200937.148 0.050  | 200937.127 0.006 | 0.021   |
| 12   | 3   | 219159.236 0.050  | 219159.253 0.013 | -0.017  |
| 12   | 2   | 219181.745 0.050  | 219181.737 0.008 | 0.010   |
| 12   | 1   | 219195.209 0.050  | 219195.232 0.006 | -0.023  |
| 12   | 0   | 219199.712 0.050  | 219199.731 0.006 | -0.019  |
| 13   | 3   | 237417.332 0.050  | 237417.345 0.014 | -0.013  |
| 13   | 2   | 237441.706 0.050  | 237441.696 0.008 | 0.010   |
| 13   | 1   | 237456.320 0.050  | 237456.311 0.007 | 0.009   |
| 13   | 0   | 237461.178 0.050  | 237461.184 0.007 | -0.006  |
| 14   | 3   | 255674.171 0.050  | 255674.193 0.015 | -0.022  |
| 14   | 2   | 255700.388 0.050  | 255700.410 0.009 | -0.022  |
| 14   | 1   | 255716.107 0.050  | 255716.145 0.007 | -0.038  |
| 14   | 0   | 255721.370 0.050  | 255721.391 0.007 | -0.021  |
| 16   | 3   | 292183.778 0.050  | 292183.777 0.017 | 0.001   |
| 16   | 2   | 292213.646 0.050  | 292213.722 0.010 | -0.075  |
| 16   | 1   | 292231.636 0.050  | 292231.694 0.008 | -0.058  |
| 16   | 0   | 292237.659 0.050  | 292237.685 0.008 | -0.026  |
| 17   | 3   | 310436.291 0.050  | 310436.322 0.019 | -0.031  |
| 17   | 2   | 310468.201 0.100  | 310468.127 0.011 | 0.074   |
| 17   | 1   | 310487.210 0.050  | 310487.216 0.009 | -0.006  |
| 17   | 0   | 310493.523 0.050  | 310493.580 0.009 | -0.057  |
| 18   | 3   | 328687.226 0.050  | 328687.241 0.020 | -0.015  |
| 18   | 2   | 328720.866 0.050  | 328720.905 0.012 | -0.039  |
| 18   | 1   | 328741.056 0.050  | 328741.110 0.010 | -0.054  |
| 18   | 0   | 328747.827 0.050  | 328747.846 0.010 | -0.019  |
| 21   | 6   | 383217.758 0.050  | 383217.721 0.096 | 0.037   |
Table E.1. continued.

| $J_\nu$ | K | Freq. Obser. (Unc) | Freq. Calc. (Unc) | Obs-Calc |
|--------|---|-------------------|-------------------|----------|
| 21     | 5 | 383303.931       | 383303.862       | 0.069    |
| 21     | 4 | 383374.395       | 383374.396       | 0.001    |
| 21     | 3 | 383429.306       | 383429.289       | 0.017    |
| 21     | 2 | 383468.517       | 383468.517       | 0.000    |
| 21     | 1 | 383492.044       | 383492.060       | -0.016   |
| 21     | 0 | 383499.892       | 383499.910       | -0.018   |
| 22     | 6 | 401451.192       | 401451.205       | -0.013   |
| 22     | 5 | 401541.411       | 401541.408       | 0.003    |
| 22     | 4 | 401615.264       | 401615.268       | -0.004   |
| 22     | 3 | 401672.742       | 401672.750       | -0.008   |
| 22     | 2 | 401713.849       | 401713.827       | 0.022    |
| 22     | 1 | 401738.482       | 401738.481       | 0.001    |
| 22     | 0 | 401746.707       | 401746.700       | 0.007    |
| 23     | 6 | 419682.601       | 419682.598       | 0.003    |
| 23     | 5 | 419776.829       | 419776.858       | -0.029   |
| 23     | 4 | 419854.065       | 419854.039       | 0.026    |
| 23     | 3 | 419914.100       | 419914.106       | -0.006   |
| 23     | 2 | 419957.037       | 419957.031       | 0.006    |
| 23     | 1 | 419982.794       | 419982.794       | 0.000    |
| 23     | 0 | 419991.387       | 419991.383       | 0.004    |
| 24     | 6 | 437911.779       | 437911.807       | -0.026   |
| 24     | 5 | 438010.092       | 438010.117       | -0.025   |
| 24     | 4 | 438090.613       | 438090.615       | -0.002   |
| 24     | 3 | 438153.261       | 438153.263       | -0.002   |
| 24     | 2 | 438198.039       | 438198.033       | 0.006    |
| 24     | 1 | 438224.913       | 438224.903       | 0.010    |
| 24     | 0 | 438233.877       | 438233.861       | 0.016    |
| 25     | 6 | 456138.764       | 456138.735       | 0.029    |
| 25     | 5 | 456240.963       | 456241.090       | -0.127   |
| 25     | 4 | 456324.889       | 456324.900       | -0.011   |
| 25     | 3 | 456390.167       | 456390.126       | 0.041    |
| 25     | 2 | 456436.758       | 456436.737       | 0.021    |
| 25     | 1 | 456464.703       | 456464.712       | -0.009   |
| 25     | 0 | 456474.048       | 456474.039       | 0.009    |
| 26     | 5 | 474469.660       | 474469.681       | -0.021   |
| 26     | 4 | 474556.835       | 474556.798       | 0.037    |
| 26     | 3 | 474624.604       | 474624.597       | 0.007    |
| 26     | 2 | 474673.034       | 474673.048       | -0.014   |
| 26     | 1 | 474702.158       | 474702.127       | 0.031    |
| 26     | 0 | 474711.811       | 474711.821       | -0.010   |
| 27     | 5 | 492695.931       | 492695.796       | 0.135    |
| 27     | 4 | 492786.129       | 492786.214       | -0.085   |
| 27     | 3 | 492856.584       | 492856.582       | 0.002    |
| 27     | 2 | 492906.862       | 492906.869       | -0.007   |
| 27     | 1 | 492937.060       | 492937.050       | 0.010    |
| 27     | 0 | 492947.117       | 492947.112       | 0.005    |
Table E.2. Frequency predictions for CH₃CO⁺.

| Jₜ (a) | Kₜ (a) | Jₗ (a) | Kₗ (a) | ν(MHz) (b) | Unc(MHz) (c) | E_up(K) (d) | A_ij(s⁻¹) (e) | S_ij (f) | g_u (g) |
|--------|--------|--------|--------|------------|--------------|------------|---------------|-----------|--------|
| 1      | 0      | 0      | 0      | 18268.92826 | 0.00039      | 0.9        | 2.898×10⁻⁰⁷  | 1.0000    | 3      |
| 2      | 1      | 1      | 1      | 36537.00979 | 0.00072      | 9.5        | 2.086×10⁻⁰⁶  | 1.5000    | 5      |
| 2      | 0      | 1      | 0      | 36537.76068 | 0.00079      | 2.6        | 2.782×10⁻⁰⁶  | 2.0000    | 5      |
| 3      | 2      | 2      | 2      | 54801.89688 | 0.00115      | 32.8       | 5.587×10⁻⁰⁶  | 1.6667    | 7      |
| 3      | 1      | 2      | 1      | 54805.27517 | 0.00107      | 12.1       | 8.941×10⁻⁰⁶  | 2.6667    | 7      |
| 3      | 0      | 2      | 0      | 54806.41043 | 0.00117      | 5.3        | 1.006×10⁻⁰⁵  | 3.0000    | 7      |
| 4      | 3      | 3      | 3      | 73061.24457 | 0.00265      | 32.8       | 5.587×10⁻⁰⁶  | 1.6667    | 7      |
| 4      | 2      | 3      | 2      | 73068.74904 | 0.00151      | 36.3       | 1.854×10⁻⁰⁵  | 3.0000    | 9      |
| 4      | 1      | 3      | 1      | 73073.25310 | 0.00141      | 15.7       | 2.318×10⁻⁰⁵  | 3.7500    | 9      |
| 4      | 0      | 3      | 0      | 73074.75469 | 0.00154      | 8.8        | 2.473×10⁻⁰⁵  | 4.0000    | 9      |
| 5      | 4      | 4      | 4      | 91312.71293 | 0.00563      | 123.3      | 1.776×10⁻⁰⁵  | 1.8000    | 11     |
| 5      | 3      | 4      | 3      | 91325.83851 | 0.00326      | 75.1       | 3.159×10⁻⁰⁵  | 6.4000    | 22     |
| 5      | 2      | 4      | 2      | 91335.21824 | 0.00186      | 40.7       | 4.148×10⁻⁰⁵  | 4.2000    | 11     |
| 5      | 1      | 4      | 1      | 91340.84780 | 0.00173      | 20.0       | 4.741×10⁻⁰⁵  | 4.8000    | 11     |
| 5      | 0      | 4      | 0      | 91342.72461 | 0.00189      | 13.2       | 4.939×10⁻⁰⁵  | 5.0000    | 11     |
| 6      | 5      | 5      | 5      | 109553.96919 | 0.01021     | 190.5      | 2.644×10⁻⁰⁵  | 1.8333    | 13     |
| 6      | 4      | 5      | 4      | 109574.20539 | 0.00662     | 128.6      | 4.810×10⁻⁰⁵  | 3.3333    | 13     |
| 6      | 3      | 5      | 3      | 109589.95432 | 0.00384     | 80.4       | 6.496×10⁻⁰⁵  | 9.0000    | 26     |
| 6      | 2      | 5      | 2      | 109601.20873 | 0.00219     | 46.0       | 7.701×10⁻⁰⁵  | 5.3333    | 13     |
| 6      | 1      | 5      | 1      | 109607.96344 | 0.00203     | 25.3       | 8.425×10⁻⁰⁵  | 5.8333    | 13     |
| 6      | 0      | 5      | 0      | 109610.21536 | 0.00223     | 18.4       | 8.666×10⁻⁰⁵  | 6.0000    | 13     |
| 7      | 6      | 6      | 6      | 127782.68995 | 0.01698     | 272.3      | 3.683×10⁻⁰⁵  | 3.7143    | 30     |
| 7      | 5      | 6      | 5      | 127811.51930 | 0.01162     | 196.6      | 6.805×10⁻⁰⁵  | 3.4286    | 15     |
| 7      | 4      | 6      | 4      | 127835.12506 | 0.00755     | 134.7      | 9.361×10⁻⁰⁵  | 4.7143    | 15     |
| 7      | 3      | 6      | 3      | 127853.49637 | 0.00439     | 86.5       | 1.135×10⁻⁰⁴  | 11.4286   | 30     |
| 7      | 2      | 6      | 2      | 127866.62477 | 0.00249     | 52.1       | 1.278×10⁻⁰⁴  | 6.4286    | 15     |
| 7      | 1      | 6      | 1      | 127874.50422 | 0.00232     | 31.4       | 1.363×10⁻⁰⁴  | 6.8571    | 15     |
| 7      | 0      | 6      | 0      | 127877.13111 | 0.00254     | 24.5       | 1.391×10⁻⁰⁴  | 7.0000    | 15     |

Notes. The entire table is available at the CDS. (a) Upper and lower Jₑ quantum numbers. (b) Predicted frequency (in MHz). (c) Uncertainty in the predicted frequency (in MHz). (d) Energy (in K) of the upper energy level of the transition. (e) Einstein coefficient of the transition (in s⁻¹). (f) Line strength. (g) Degeneracy of the upper level. It is 2J+1 for all levels except for those with K = 3 × n (n = 1, 2, . . . ), for which g_u is 2 × (2J+1).