Accurate sub-millimetre rest frequencies for HOCO$^+$ and DOCO$^+$ ions*

L. Bizzocchi, V. Lattanzi, J. Laas, S. Spezzano, B. M. Giuliano, D. Prudenzano, C. Endres, O. Sipilä, and P. Caselli

Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Gießenbachstraße 1, 85748 Garching, Germany
e-mail: bizzocchi@mpa.mpg.de

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ABSTRACT

Context. HOCO$^+$ is a polar molecule that represents a useful proxy for its parent molecule CO$_2$, which is not directly observable in the cold interstellar medium. This cation has been detected towards several lines of sight, including massive star forming regions, protostars, and cold cores. Despite the obvious astrochemical relevance, protonated CO$_2$ and its deuterated variant, DOCO$^+$, still lack an accurate spectroscopic characterisation.

Aims. The aim of this work is to extend the study of the ground-state pure rotational spectra of HOCO$^+$ and DOCO$^+$ well into the sub-millimetre region.

Methods. Ground-state transitions have been recorded in the laboratory using a frequency-modulation absorption spectrometer equipped with a free-space glow-discharge cell. The ions were produced in a low-density, magnetically confined plasma generated in a suitable gas mixture. The ground-state spectra of HOCO$^+$ and DOCO$^+$ have been investigated in the 213–967 GHz frequency range; 94 new rotational transitions have been detected. Additionally, 46 line positions taken from the literature have been accurately remeasured.

Results. The newly measured lines have significantly enlarged the available data sets for HOCO$^+$ and DOCO$^+$, thus enabling the determination of highly accurate rotational and centrifugal distortion parameters. Our analysis shows that all HOCO$^+$ lines with $K_a \geq 3$ are perturbed by a ro-vibrational interaction that couples the ground state with the $v_2 = 1$ vibrationally excited state. This resonance has been explicitly treated in the analysis in order to obtain molecular constants with clear physical meaning.

Conclusions. The improved sets of spectroscopic parameters provide enhanced lists of very accurate sub-millimetre rest frequencies of HOCO$^+$ and DOCO$^+$ for astrophysical applications. These new data challenge a recent tentative identification of DOCO$^+$ towards a pre-stellar core.

Key words. molecular data – methods: laboratory: molecular – techniques: spectroscopic – radio lines: ISM

1. Introduction

Protonated ions were first suggested as proxies for important interstellar molecules by Herbst et al. (1977), shortly after the first detection of charged polyatomic species in space (HCO$^+$, Buhl & Snyder 1970; N$_2$H$^+$, Turner 1974). These first pioneering studies demonstrated that ion–molecule reactions must occur in the interstellar medium (ISM), and are capable of generating ionic forms of non-polar molecules such as N$_2$, C$_2$, CO$_2$, and HCHC. These species are likely to be present to a large extent in the dense gas, but they escape radio-telescope detection owing to the lack of rotational spectra.

Carbon dioxide (CO$_2$) is widespread in space. It is abundant in planetary atmospheres, comets, and especially in interstellar ices, where it has been extensively detected by ISO and Spitzer telescopes towards several lines of sight (e.g. Whittet et al. 1998; Bergin et al. 2005). In the solid phase, the CO$_2$:H$_2$O ratio has been observed to vary in the range of 0.15–0.5 in molecular clouds and protostars (e.g. Boogert et al. 2015; Whittet et al. 2009; Öberg et al. 2011). Because the abundance of CO$_2$ has been observed to be lower in the gas phase by a factor of 100 (van Dishoeck et al. 1996; Boonman et al. 2003), its formation is thought to proceed on dust grains via UV or cosmic-ray induced processing of a variety of icy mixtures (Ioppolo et al. 2009; Mennella et al. 2006; Pontoppidan et al. 2003; Watanabe & Kouchi 2002). Nonetheless, speculation on the possible contribution of a gas-phase formation route remains (e.g. Sakai et al. 2008), and the difficulties involved in the direct observation of CO$_2$ in the infrared make this matter difficult to clarify.

Protonated carbon dioxide (HOCO$^+$) provides a useful, indirect way to trace gaseous CO$_2$ in the ISM. Vastel et al. (2016) constrained the CO$_2$ abundance in the L1544 pre-stellar core using an extensive chemical model that considered the following HOCO$^+$ main formation channels:

\[ \text{CO}_2 + \text{H}_3^+ \rightarrow \text{HOCO}^+ + \text{H}_2, \]

\[ \text{CO} + \text{H}_3^+ \rightarrow \text{HCO}^+ + \text{H}_2, \quad \text{followed by} \]

\[ \text{HCO}^+ + \text{OH} \rightarrow \text{HOCO}^+ + \text{H}. \]  

At the steady state, they derived an indirect estimate of the [CO$_2$]/[CO] ratio from [HOCO$^+$]/[HCO$^+$. The assumptions involved in this approach hold for the external layers of dense cloud cores where CO freeze-out rates are moderate. The same method, in a simplified form (i.e. neglecting reaction (2)), was also adopted by Neill et al. (2014) towards Sgr B2(N), and by Sakai et al. (2008) in the Class 0 protostar IRAS 04368+2557 embedded in L1527.
The first laboratory identification of protonated carbon dioxide was accomplished by Bogey et al. (1984), who observed six rotational lines of HOCO\(^+\) in the 350–380 GHz frequency range. This work substantiated the tentative interstellar detection proposed by Thaddeus et al. (1981), and an additional independent confirmation was provided by the laboratory observation of the \(\nu_1\) ro-vibrational band of HOCO\(^+\) (Amano & Tanaka 1985a,b). Later, Bogey and co-workers published two more papers about laboratory studies in which they enlarged the frequency coverage and extended the study to the isotopic species DOCO\(^+\) and HO\(^13\)CO\(^+\) (Bogey et al. 1986, 1988). More recently, the low-lying \(K_{a,a}=1-0\) line of HOCO\(^+\) was measured by Ohshima & Endo (1996) using a pulsed-jet Fourier-transform microwave (FTMW) spectrometer.

Despite these considerable experimental efforts, the spectroscopic characterisation of this astrophysically relevant ion is still not fully satisfactory. Recordings of the pure rotational spectra are indeed restricted to a rather limited frequency range; only a few lines have been measured in the 3 mm band, and the whole spectral region above 420 GHz is completely unexplored. No \(b\)-type transitions were measured for DOCO\(^+\), thus resulting in a poorly determined \(A\) rotational constant for this isotopic species. Moreover, anomalously large centrifugal distortion effects are present in both HOCO\(^+\) and DOCO\(^+\). As a result, the line positions of many astronomically important features cannot be computed to a desirable accuracy.

For example, the rest frequencies used by Neill et al. (2014) to assign the HOCO\(^+\), \(K_a=1-0\) ladder (\(J = 1-7\) observed towards the Galactic centre are affected by \(1\sigma\) uncertainties of 300–400 kHz, as indicated by the JPL line catalogue (Pickett et al. 1998). Also, the tentative detection of DOCO\(^+\) in L1544 claimed by Vastel et al. (2016) is based on a reference datum that is not fully reliable: the \(J_{K_a,K_c}=5_{0,3}^{-4}_{0,4}\) line position provided by the JPL catalogue is 100 359.55 \(\pm\) 0.035 MHz, but a calculation performed using the "best" literature spectroscopic data (Bogey et al. 1988) gives 100 359.14 MHz. The resulting 410 kHz discrepancy (1.2 km s\(^{-1}\)) therefore hints at possible issues affecting the spectral analysis of DOCO\(^+\).

With the aim of providing highly accurate rest frequencies for astrophysical applications, we have performed a comprehensive laboratory investigation of the pure rotational spectra of HOCO\(^+\) and DOCO\(^+\). About fifty new lines were recorded for each isotopologue; in addition, many laboratory transitions were accurately remeasured in order to refine their frequency positions or to rule out possible incorrect assignments. The measurements presented in this work also extend towards the THz region, thus considerably enlarging the frequency range with respect to previous studies.

The data analysis shows that the HOCO\(^+\) spectrum is affected by a ro-vibrational interaction, coupling the ground state with the low-lying \(V_5 = 1\) vibrationally excited state. This resonance is characteristic of many quasi-linear molecules, such as HNCO (Niedenhoff et al. 1995b), HNCS (Niedenhoff et al. 1995a), and HN\(_2\) (Krakow et al. 1968). In HOCO\(^+\), this perturbation produces non-negligible effects for rotational levels having a quantum number \(K_a\) greater than 2. A special treatment was adopted to analyse this spectrum in order to retrieve a set of spectroscopic constants with clear physical meaning.

2. Experiments

The spectra described in this work have been recorded with the frequency modulation (FM) sub-millimetre absorption spectrometer recently developed at the Center for Astrochemical Studies (Max-Planck-Institut für extraterrestrische Physik) in Garching.

The instrument is equipped with a negative glow-discharge cell made of a Pyrex tube (3 m long and 5 cm in diameter) containing two stainless steel, cylindrical hollow electrodes separated by 2 m. The plasma region is cooled by liquid nitrogen circulation and is contained inside a 2 m solenoid, which can produce a coaxial magnetic field up to \(\sim 300\) G to enhance the discharge negative column (De Lucia et al. 1983).

The radiation source is an active multiplier chain (Virginia Diodes) that is driven by a synthesizer (Keysight E8257D) operating at centimetre wavelengths. Using a series of frequency multiplication stages, this set-up provides continuous coverage across the 82–1100 GHz frequency range. Accurate frequency and phase stabilisation is achieved by providing the synthesizer with a 10 MHz rubidium frequency standard (Stanford Research Systems). A liquid-He cooled InSb hot electron bolometer (QMC Instr. Ltd.) is used as a detector. Frequency modulation is achieved by modulating the carrier signal with a sine wave at a rate of 15 kHz, and then demodulating the detector output at 2f using a digital lock-in amplifier (SRS SR830). In this way, the second derivative of the actual absorption profile is recorded by the computer controlled acquisition system.

HOCO\(^+\) and DOCO\(^+\) were produced by a DC discharge (5–15 mA, \(\sim 2\) kV) and a 3:1 mixture of CO\(_2\) and H\(_2\) or D\(_2\) diluted in a buffer gas of Ar (total pressure \(\sim 15\) mbar). As it is for other protonated ions, cell cooling is critical in order to enhance the absorption signals. In the present case, the use of a condensable precursor (CO\(_2\)) imposes a practical lower limit of \(\sim 150\) K to the cell wall temperature. Also, magnetic plasma confinement by a \(\sim 200\) G field was found to provide the best conditions for the production of the protonated CO\(_2\) ion.

3. Results and data analysis

Protonated carbon dioxide is a slightly asymmetric protonated rotor (\(k = -0.9996\)); the \(a\) inertial axis is closely aligned to the slightly bent heavy-atom backbone (\(\angle(O-C-O) \approx 174^\circ\)); and the hydrogen atom lies on the \(ab\) plane (\(\angle(H-O-C) = 118^\circ\)) (Fortenberry et al. 2012). Hence, both \(a\)- and \(b\)-type transitions are observable. The electric dipole moment was theoretically computed by Green et al. (1976) yielding \(\mu_a = 2.0\) D, and \(\mu_b = 2.8\) D. Bogey et al. (1988) pointed out that these values might be inaccurate and, indeed, our observations of the intensity ratio between \(a\)- and \(b\)-type lines are not in agreement with these figures. The latest theoretical studies on HOCO\(^+\) (Francisco 1997; Fortenberry et al. 2012) do not report estimates of the dipole moments, thus we have performed an ab initio calculation using the CFOUR software package \(^1\). At the CCSD(T) level of theory (RagHAVACHARI et al. 1989), and using the cc-pCVQZ basis sets (WOON & DUNNING 1994), it yielded \(\mu_a = 2.7\) D and \(\mu_b = 1.8\) D. These values are in fair agreement (\(\sim 30\%\)) with the line intensity ratios observed experimentally.

The absorption profiles of the observed transitions were modelled with the proFFit line profile analysis code (Dore 2003) in order to extract their central frequency with high accuracy. We adopted a modulated Voigt profile, and the complex component of the Fourier-transform of the dipole correlation function (i.e. the dispersion term) was also taken into account to model the line asymmetry produced by the parasitic etalon effect of the absorption cell (i.e. background standing-waves between

\(^1\) See www.cfour.de
The search for new rotational transitions of HOCO\(^+\) was guided by the spectrosopic parameters previously reported by Bogey et al. (1988), thus their assignment was accomplished in a straightforward way. However, at frequencies above 500 GHz, increasingly larger discrepancies (~500 kHz) were found between observed and predicted line positions. Forty-three new rotational lines were recorded, reaching a maximum quantum number \(J\) values of 29 and a frequency as high as 967 GHz. These data included 12 \(b\)-type transitions belonging to the \(bF_{\pm 1,1}, bQ_{\pm 1,1},\) and \(bR_{\pm 1,\pm 1}\) branches. In addition, 18 lines previously reported by Bogey et al. (1986, 1988) were remeasured to check and/or improve their frequency positions. Figure 1 (left panel) shows the recording of the \(J_{K_a,K_c} = 30_{0,30} - 29_{0,29}\) line of HOCO\(^+\) located at approximately 640 GHz, which is the highest frequency reached for \(a\)-type transitions.

The combined data set of literature and newly measured lines was fitted employing a \(S\)-reduced, asymmetric rotor Hamiltonian in its \(I'\) representation (Watson 1977) using Pickett’s CALPGM programme suite (Pickett 1991). Statistical weights \((w_i = 1/\sigma_i^2)\) were adopted for each \(i\)th datum to account for the different measurement precisions. In our measurements, an estimated uncertainty \((\sigma_i)\) of 20 kHz is assigned to the \(a\)-type lines; instead, 50 kHz is assigned to the weaker \(b\)-type transitions, which derive from comparatively noisier spectra. For the data taken from the literature, we adopted the assumed uncertainties given in the corresponding papers. The complete list of the analysed rotational transitions is provided as electronic supplementary material at the CDS. An excerpt is reported in Table 1 for guidance.

The analysis clearly shows that the ground-state spectrum of HOCO\(^+\) is perturbed. An anomalous slow convergence of the rotational Hamiltonian had already been noted by Bogey et al. (1986), such that high-order terms were used to achieve a satisfactory fit of the measured frequencies. Similar perturbations have been observed in many quasi-linear molecules, for which HNCO (isoelectronic with HOCO\(^+\)) serves as a case study (Niedenhoff et al. 1995b). These anomalies reflect the breakdown of the Watson-type asymmetric rotor Hamiltonian because of the accidental \(\Delta K_a = \pm 1\) degeneracy occurring between ground-state rotational levels and those of a low-lying, totally symmetric excited state.

We carried out the analysis of the HOCO\(^+\) spectrum following two different approaches. The first, simpler analysis was performed by applying a cut-off at \(K_a = 2\). This excluded from the least-squares fit all the lines affected by the resonance, and allowed us to consider the HOCO\(^+\) ground state as isolated. The \(K_a = 0–2\) lines were fitted using a single-state Hamiltonian, and these results are listed in the first numerical column of Table 2 (fit 1). This analysis provides a compact set of rotational parameters, including four quartic and two sextic centrifugal distortion constants. Because we observed only one subset of \(b\)-type transitions (\(K_a = 0–1\)), the \(D_K\) constant could not be determined reliably, and it was thus constrained to the value derived from previous infrared \(v_1\) measurements (Amano & Tanaka 1985b). The \(H_I\) and \(H_K\) sextic constants were also held fixed at their corresponding theoretically computed values (Fortenberry et al. 2012).

In the second stage of the analysis, the interaction coupling the ground and the \(v_5 = 1\) states was explicitly treated, and all the available transitions (\(K_a = 1–5\)) were included in the least-squares fit. Assumptions for the rotational parameters of the \(v_5 = 1\) state (actually unobserved) were derived from the ground-state constants (\(A_0, B_0, C_0\)) and the theoretically computed vibration-rotation \(\alpha\) constants from Fortenberry et al. (2012). An optimal fit was achieved by adjusting the same ground-state constants of the previous simplified analysis, plus the resonance parameters \(\eta^{ab}\) and \(\eta^{bb}\). The quartic centrifugal distortion constant \(D_K\) of the perturbing state was held fixed in the fit, but its value was updated iteratively until a minimum of the root mean square (RMS) deviation was reached.

### Table 1

| Frequency / MHz | J\(_{K_a,K_c}\) | Detection signal / a.u. |
|----------------|---------------|------------------------|
| 323119         | J\(_{16,15}=15_{1,14}\) | DOCO\(^+\),          |
| 323121         | J\(_{16,15}=15_{1,14}\) | detection signal / a.u. |
| 323123         | J\(_{16,15}=15_{1,14}\) | HOCO\(^+\), J\(_{30,30}=29_{0,29}\) |
| 323125         | J\(_{30,30}=29_{0,29}\) |                        |
resulting spectroscopic constants of this analysis are gathered in the second numerical column of Table 2 (fit II). Full details of this analysis are given in Appendix A.

### 3.2. DOCO+

A limited portion of the millimetre spectrum of DOCO+ was recorded by Bogey et al. (1986), but the quality of the resulting spectral analysis was not completely adequate. Indeed, in a second study, Bogey et al. (1988) encountered serious difficulties in fitting new low-Ka transitions together with the bulk of the previously measured data. They thus excluded all the Ka = 0 lines from the final, published analysis. This represents a severe shortcoming for the astronomical utility of this data, as the lines that are detected most often in the ISM arise from these low-energy levels. We have thus carefully reinvestigated the rotational spectrum of DOCO+, focusing on low-Ka lines that show predictions errors up to about 1 MHz.

To identify b-type transitions, extensive spectral searches had to be performed owing to the large error associated with the previous determination of the A rotational constant. Lines belonging to the Qa−1,−1 and Ra+1,−1 branches were finally assigned at a distance of about 500 MHz from the position computed from the literature data. Ten b-type transitions were recorded in total. The final DOCO+ data set comprises 85 lines, covering the frequency range from 120 to 672 GHz, with quantum number J spanning values 5–30. The frequency list is provided as electronic supplementary material at the CDS. Figure 1 (right panel) shows the recording of the Ka,Kc = 161,15–151,14 line of DOCO+, obtained in about 3.5 min of integration time.

Contrary to the parent isotopologue, the ground-state spectrum of DOCO+ does not show evidence of perturbation. For the deuterated variant, the A rotational constant is smaller (14.4 cm−1 compared to 26.2 cm−1 for HOCO+), thus the ΔKu = ±1 quasi-degeneracy between the ground and vu = 1 excited state occurs at a higher value of Ku. As a result, the transitions involving low energy levels are essentially unperturbed. The analysis was therefore carried out by considering the ground vibrational state of DOCO+ as isolated, and including in the fitting transitions with Ku up to 4. A few possibly perturbed lines involving Ku = 5,6 showed large deviations and were then excluded from the final data set. We adopted the same weighting scheme described in the previous section, where the assumed uncertainties (σJ) were set to 20 kHz and 50 kHz for a- and b-type lines, respectively. For the 3 mm lines previously recorded by Bogey et al. (1988), we retained the error reported by these authors. These fit results are reported in Table 3.

### 4. Discussion

The spectral analyses presented here have been performed on an enlarged and improved data set, and have yielded a more precise set of rotational and centrifugal distortion constants for HOCO+ and DOCO+. In comparison to the latest literature data (Bogey et al. 1988), the new spectroscopic constants presented in Tables 2 and 3 exhibit a significant reduction of their standard uncertainties. The improvement is particularly relevant for DOCO+ thanks to the identification of the weaker b-type spectrum, such that the precision of its A rotational constant has been enhanced by a factor of 104. As a consequence, predictive capabilities at millimetre and sub-millimetre wavelengths have been improved.

Regarding HOCO+, we have presented two different analyses. Fit I includes only lines originating from levels with Ku ≤ 2. Within the precision of our measurements, these transitions are essentially unaffected by the centrifugal distortion resonance that perturbs the ground-state spectrum (see Appendix A), and they can be treated with a standard asymmetric rotor Hamiltonian. This simple solution provides reliable spectral predictions for all the transitions with upper-state energies Eu/k < 220 K, hence it is perfectly suited to serve as a guide for astronomical searches of HOCO+ in the cold ISM.

In fit II, all the experimental data are considered, and the interaction that couples the ground state with the vu = 1 vibrationally excited state has been treated explicitly. Here, extensive use of the latest high-level theoretical calculations (Fortenberry et al. 2012) has been made to derive reliable assumptions for those spectroscopic parameters which could not be directly determined from the measurements. Though more complex, fit II implements a more realistic representation of the rotational dynamics of this molecule, and yields a set of spectroscopic constants with clearer physical meaning. Indeed, the anomalously large centrifugal distortion effects noted in the previous investigations (Bogey et al. 1986, 1988) have been effectively accounted for. No octic (LJK) or decic (PJK) constants were required for the analysis, and the agreement between experimental and ab initio quartic centrifugal distortion constants is reasonably good. On the other hand, the values determined for

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**Table 1.** Assignments, measured line positions, and least-squares residuals (MHz) for the analysed transitions of HOCO+.

| J′ | K′a | K′c | J | K | K | observed | o – c. (fit I) | o – c. (fit II) | ass. unc. |
|----|----|----|---|---|---|---------|-------------|-------------|----------|
|    |    |    |   |   |   |         | (8)         | (9)         | (10)     | (11)     |
| 19 | 1  | 19 | 18 | 18 | 404 581.85 | 0.30 | 0.024 | 0.060 | B86     |
| 19 | 0  | 19 | 18 | 0  | 406 154.381 | 0.064 | 0.062 | 0.050 | B86     |
| 10 | 2  | 9  | 2  | 8  | 213 743.316 | 0.021 | 0.040 | 0.020 | TW      |
| 10 | 2  | 8  | 9  | 2  | 213 747.465 | −0.011 | 0.006 | 0.020 | TW      |
| 10 | 1  | 9  | 9  | 1  | 214 619.241 | 0.004 | −0.006 | 0.020 | TW      |
| 11 | 1  | 11 | 10 | 1  | 234 270.871 | 0.013 | 0.004 | 0.020 | TW      |
| 11 | 3  | *  | 10 | 3  | 235 016.895 | −0.013 | 0.020 | TW      |

**Notes.** The full table is available in electronic form at the CDS. Column content: (1–3) upper state rotational quantum numbers J′Ka,K′c; (4–6) lower state rotational quantum numbers JKa,Kc; (7) measured line position; (8) least-squares residual in fit I (see text); (9) least-squares residual in fit II (see text); (10) assumed uncertainty; (11) references: TW (this work), B86 (Bogey et al. 1986). Asterisks inCols. (3) and (6) mark unresolved asymmetry doublets. An empty field in Col. (8) indicates that the line is not considered in fit I.
the $H_{IK}$ and $H_{KJ}$ sextic constants should be considered only as effective approximations, since they include spurious resonance contributions not explicitly treated by this analysis. Finally, it is to be noted that fit I and fit II, when limited to $K_a \leq 2$ lines, yield spectral predictions that are coincident within the 1σ computed uncertainties.

New HOCO$^+$ and DOCO$^+$ line catalogues, based on the spectroscopic constants of Table 2 (fit I only) and Table 3, have been computed and are provided as supplementary data available at the CDS. These data listings include the 1σ uncertainties (calculated taking into account the correlations between spectroscopic constants), the upper-state energies, the line strength factors $S_{ij}\mu_r^2 (g = a,b)$, and the Einstein $A$ coefficients for spontaneous emission,

$$A_{ij} = \frac{16\pi^3\gamma^3}{3} \frac{1}{\gamma^3 2J + 1} S_{ij}\mu_r^2 \quad \text{(3)}$$

where all the quantities are expressed in SI units and the line strengths $S_{ij}$ are obtained by projecting the squared rotation matrix onto the basis set that diagonalises the rotational Hamiltonian (Gordy & Cook 1984). The computation was performed using $\mu_a = 2.7$ D and $\mu_b = 1.8$ D. The compilation contains 57 lines for HOCO$^+$ and 72 lines for DOCO$^+$. They are selected in the frequency range 60 GHz $\leq \nu \leq$ 1 THz and applying the cut-offs $E_p/k < 100$ K. The precision of these rest frequencies is at least $4 \times 10^{-8}$, which corresponds to 0.011 km s$^{-1}$ (or better) in units of radial velocity.

Our analysis suggests that the line observed in L1544 by Vastel et al. (2016) and tentatively assigned to DOCO$^+$, $J_{Ka,Kc}$ = 5$_{0,5}^{-}q_{0,4}$, cannot actually be attributed to this ion. The observed frequency, once red-shifted by the 7.2 km s$^{-1}$ $V_{LSR}$ of L1544, has a rest frequency of 100 359.81 MHz, whereas our predicted line position is 100 359.515 $\pm$ 0.002 MHz. This 295 kHz discrepancy corresponds to 0.88 km s$^{-1}$, which is over twice the average FHWM of the HOCO$^+$ lines detected in the same source. It is thus likely that the line tentatively detected by Vastel et al. (2016) does not belong to DOCO$^+$ and, indeed, these authors stated that this needed confirmation from laboratory measurements.

### 5. Chemical model

Predictions for the HOCO$^+$ and DOCO$^+$ abundances in L1544 can be derived from the chemical model developed by Sipilä et al. (2015), which considers a static physical structure.
and an evolving gas-grain chemistry (as described in Sipilä et al. 2016). Table 4 shows the model computed column densities of HOCO+ and DOCO+ for different cloud evolutionary ages averaged over a 30″ beam. Vastel et al. (2016) found a HOCO+ column density of about 2 × 10^{13} cm⁻². Comparison with the predicted column densities, shown in Table 4, suggests that the best agreement is found at late evolutionary times. However, since above 3 × 10⁵ yr, the model predicts too much CO freeze-out compared to the observations of Caselli et al. (1999), we consider 3 × 10⁵ yr as the best agreement time. At this stage, the DOCO+/HOCO+ ratio is about 10% and the predicted DOCO+, \( J = 5_0,5 - 4_0,4 \) main beam brightness temperature is 6 mK (assuming an excitation temperature of 8.5 K, as deduced by Vastel et al. 2016 for their observed HOCO+ line).

### 6. Conclusions

This laboratory study substantially improves the spectroscopic characterisation of the protonated CO₂ ion. The spectral region sampled by the measurements has been considerably extended into the sub-millimetre regime, reaching maximum frequencies of 967 GHz for HOCO⁺, and 672 GHz for DOCO⁺. In addition, new recordings were obtained for most of the previously reported lines in order to enhance their measurement precision using a sophisticated line profile analysis. Our analysis shows that the line tentatively detected towards the pre-stellar core L1544 cannot be attributed to DOCO⁺.

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Appendix A: Analysis of the ground-state \( \nu_5 = 1 \) interaction

The perturbation that affects the ground-state spectrum of HOCO\(^+\) is a common feature of quasi-linear molecules, and reflects a breakdown of the Watson-type asymmetric rotor Hamiltonian caused by accidental rotational level degeneracies. It was first described by Yamada (1980), and the theory has been treated in particular detail by Urban & Yamada (1993).

Owing to the small \( a \) component of the moment of inertia, \( K_a + 1 \) levels of the ground state can become close in energy with the \( K_a \) levels of a low-lying, totally symmetric, vibrationally excited state. These levels can be coupled by the \( \hat{H}_{12} \) term (i.e. the centrifugal distortion term) of the molecular Hamiltonian defined as

\[
\hat{H}_{12} = -\sum_s \omega_s q_s C_{s}^{ab} [J_a, J_b],
\]

(A.1)

where the \([ \cdot, \cdot ]\) notation represents the anti-commutator, the sum runs over the totally symmetric \( s \) vibrational states, and \( ab \) refers to the principal axis plane where the molecule lies.

In HOCO\(^+\), the closest totally symmetric (\( A' \)) state is the \( \nu_5 = 1 \), which is located approximately 536 cm\(^{-1}\) above the ground state (Fortenberry et al. 2012). Therefore, given the magnitude of the \( A \) rotational constant at \( \approx 26 \) cm\(^{-1}\), its \( K_a \) rotational levels are crossed by the \( K_a + 1 \) ground-state levels at \( K_a \approx 10 \). While the transitions are expected to show the largest deviations around this value of \( K_a \), significant contributions are already present at \( K_a \geq 3 \) as sizeable centrifugal distortion effects.

Substitution of \( s = 5 \) to represent the \( \nu_5 \) normal mode thus reduces Eq. (A.1) to

\[
\hat{H}_{12} = -\omega_{5q} q_5 C_{5}^{ab} [J_a, J_b],
\]

(A.2)

where \( \omega_{5q} \) is the harmonic frequency, and \( C_{5}^{ab} \) is the adimensional rotational derivative relative to the principal axes \( a, b \) (Papoušek & Aliev 1982). In practice, the treatment of this resonance is accomplished by fitting the empirical parameter that multiply the rotational operator \( J_a J_b + J_b J_a \). This parameter has the form

\[
\eta_{5}^{ab} = \frac{1}{\sqrt{2}} \omega_{5} C_{5}^{ab}.
\]

(A.3)

A full analysis of this kind of ro-vibrational interaction requires, in principle, measurements of perturbed lines belonging to both interacting states. For our study of HOCO\(^+\), this approach is not feasible due to the lack of experimental data for the perturbing \( \nu_5 = 1 \) state. Nonetheless, the results of the theoretical study of Fortenberry et al. (2012) can be used to derive reasonable assumptions for the missing data. For this case, the rotational constants were computed from the ground-state values of \( A_0, B_0, C_0 \), and the relevant ab initio vibration-rotation interaction constants \( (\alpha_{5}^{a}, \alpha_{5}^{b}, \alpha_{5}^{c}) \). For the pure vibrational energy difference between the ground and \( \nu_5 = 1 \) state, we used the estimate of \( \nu_5 \) that includes quartic anharmonicity. Finally, all five quartic and four sextic centrifugal distortion constants were assumed equal to the theoretically computed equilibrium values. All these parameters were held fixed in the least-squares analysis, where we adjusted the same set of ground-state parameters from fit I with the addition of the resonance parameter \( \eta_{5}^{ab} \) and its centrifugal correction \( \eta_{5}^{abJ} \). By adopting this scheme, it was possible to reproduce the measured transitions for \( K_a \leq 5 \) without the need of additional high-order centrifugal distortion terms. The fit was finally optimised by adjusting the \( D_K \) constants of the \( \nu_5 = 1 \) states through a step-by-step procedure until the RMS deviation was minimised.

Determining the value of \( \eta_{5}^{ab} \) (see Table 2, fit II) also provides an estimation of the magnitude of the adimensional resonance parameter, \( C_{5}^{ab} \). Using the theoretical \( \omega_{5} \) value (535.6 cm\(^{-1}\), Fortenberry et al. 2012), we find \( \approx 4 \times 10^{-4} \). This value is in fair agreement with those of the isoelectronic molecules H\(_2\)CCO, H\(_2\)CNN (\( \approx 2 \times 10^{-3} \), Urban & Yamada 1993), and HNCO (\( \approx 8 \times 10^{-3} \), Niedenhoff et al. 1995b).