Abundance of HOCO$^+$ and CO$_2$ in the outer layers of the L1544 prestellar core

C. Vastel$^{1,2}$, C. Ceccarelli$^{3,4}$, B. Lefloch$^{3,4}$, and R. Bachiller$^5$

1 Université de Toulouse. UPS-OMP. IRAP. 31013 Toulouse, France
2 e-mail: charlotte.vastel@irap.omp.eu
3 CNRS, IRAP, 9 Av. Colonel Roche. BP 44346. 31028 Toulouse Cedex 4, France
4 Université de Grenoble Alpes. IPAG. 38000 Grenoble, France
5 Observatorio Astronómico Nacional (OAN, IGN). Calle Alfonso XII, 3. 28014 Madrid. Spain

Received 3 March 2016 / Accepted 18 May 2016

ABSTRACT

The L1544 prestellar core has been observed as part of the ASAI IRAM Large Program at 3 mm. These observations led to the detection of many complex molecules. In this Letter, we report the detection of two lines, at 85.5 GHz ($4_{0,3}-3_{0,2}$) and 106.9 GHz ($5_{0,5}-4_{0,4}$), respectively, of the protonated carbon dioxide ion, HOCO$^+$. We also report the tentative detection of the line at 100.4 GHz ($5_{0,5}-4_{0,4}$) of DOE2. The non-LTE analysis of the detected lines shows that the HOCO$^+$ emission originates in the external layer where non-thermal desorption of other species has previously been observed. Its abundance is $(5 \pm 2) \times 10^{-11}$. Modelling of the chemistry involved in the formation and destruction of HOCO$^+$ provides a gaseous CO$_2$ abundance of $2 \times 10^{-7}$ (with respect to H$_2$), with an upper limit of $2 \times 10^{-6}$.

Key words. astrochemistry – line: identification – molecular data – radiative transfer

1. Introduction

The protonated form of CO$_2$, HOCO$^+$, was first identified in the Galactic centre molecular cloud SgrB2 by Thaddeus et al. (1981). The detection was then confirmed with the laboratory detection by Bogey et al. (1984). Minh et al. (1988) reported a survey towards 18 molecular clouds (dark clouds and active star-forming regions) and concluded that the HOCO$^+$ ion was only detected towards SgrB2, and later towards SgrA (Minh et al. 1991). To date, this ion has been detected towards the Galactic centre, several translucent and dark clouds (Turner et al. 1999), a single low-mass Class 0 protostar (Sakai et al. 2008), and in the prototypical protostellar bow shock L1157-B1 (Podio et al. 2014). HOCO$^+$ was first proposed by Herbst et al. (1977) as an indirect tracer of gas-phase CO$_2$. Through a comparison of the abundances of HOCO$^+$ with that of HCO$^+$, the abundance of gas-phase CO$_2$ relative to that of CO might be constrained. Carbon dioxide (CO$_2$) is an important constituent of interstellar ices and has been widely detected in absorption towards infrared bright sources with the ISO and Spitzer telescopes. However, its formation mechanism is still not completely understood. Unfortunately, CO$_2$ cannot be traced in the millimeter/submillimeter regime because it lacks a permanent dipole moment, therefore it can only be sought towards sources with a bright infrared continuum. In the solid phase, its abundance represents about 15–50% of solid H$_2$O in quiescent molecular clouds, low-mass and high-mass protostars (Whittet et al. 1998, 2007, 2009; Öberg et al. 2011), and the ice abundances seem to be the highest for the coldest sources. The observed abundances of solid CO$_2$ in the interstellar medium are a factor of 100 higher than in the gas phase (van Dishoeck et al. 1996; Boomman et al. 2003a), and the formation of CO$_2$ is therefore assumed to proceed through reactions in the ices of interstellar dust grains. CO$_2$ is readily produced in UV photo-processed CO-H$_2$O laboratory ice, with an efficiency high enough to be driven by the cosmic-ray-induced UV field in dense interstellar regions (Watanabe & Kouchi 2002). Cosmic-ray processing of pure CO laboratory ice has also been shown to be a viable mechanism for CO$_2$ production in the interstellar medium (Jamieson et al. 2006) and is an interesting solution given the large abundances of pure CO ice (Pontoppidan et al. 2003). Recently, Ioppolo et al. (2011) showed a correlation between the formation of CO$_2$ and H$_2$O (under laboratory conditions), which is consistent with the astronomical observation of solid CO$_2$ in water-rich environments. Neill et al. (2014) performed a sensitive line survey of Sgr B2(N), and based on the HOCO$^+$ species, they estimated a CO$_2$/CO ratio in the colder external envelope of between 0.01–0.1, implying a CO$_2$ gas-phase abundance of $10^{-6}$–$10^{-5}$, consistent with the finding of Minh et al. (1988, 1991). Their lower limit to the CO$_2$ gas-phase abundance of $10^{-6}$ relative to H$_2$ indicates that the CO$_2$ abundance in the gas is clearly enhanced, while most of the water is still frozen out in ices in the Sgr B2 envelope.

As part of the IRAM-30 m Large Program ASAI$^1$ (Lefloch et al., in prep.), we carried out a highly sensitive, unbiased spectral survey of the molecular emission of the L1544 prestellar core with high spectral resolution. This source is a prototypical starless core in the Taurus molecular cloud complex ($d \sim 140$ pc) on the verge of the gravitational collapse (Caselli et al., 2002, and references within). It is characterised by a central high density ($2 \times 10^6$ cm$^{-3}$) and a low temperature ($\sim 7$ K). We reported the detection of many oxygen bearing complex organic molecules produced through the release in the gas phase of methanol and

---

$^1$ Astrochemical Surveys At Iram: http://www.oan.es/asai/
ethene through non-thermal desorption processes (Vastel et al. 2014, hereafter Paper I). The sensitivity of these IRAM observations also led to the detection of the hyperfine structure of CH$_3$CN (Vastel et al. 2015a). In the present study we report on the detection of the HOCO$^+$ ion in the L1544 prestellar core, as well as a tentative detection of its deuterated form, DOCO$^+$.  

2. Observations and results

The observations were performed at the IRAM-30 m towards L1544 ($\alpha_{2000} = 05^h04^m17.21^s$, $\delta_{2000} = 25^\circ 42.8''$) using the broad-band receiver EMIR at 3 mm, connected to an FTS spectrometer in its 50 kHz resolution mode. The beam of the observations is 29$''$ and 23$''$ at 85 and 106 GHz, respectively. Line intensities are expressed in units of main-beam brightness temperature (see Paper I for more details).

The frequencies and other spectroscopic parameters of the HOCO$^+$ transitions have been retrieved from the JPL database\footnote{http://spec.jpl.nasa.gov/} from laboratory measurements by Bogey et al. (1988). Two lines of HOCO$^+$ (the 4$_{0,4}$–3$_{0,3}$ and 5$_{0,5}$–4$_{0,4}$ at 85.531 and 106.913 GHz, respectively) lie in the frequency range covered by the ASAI survey for upper level energies lower than 30 K and were detected. Their spectra are shown in Fig. 1. Table 1 reports the spectroscopic parameters as well as the properties of the two detected lines, obtained by Gaussian fitting.

For the deuterated form of HOCO$^+$, DOCO$^+$, we used the JPL database with the spectroscopic parameters from Bogey et al. (1986, 1988). Three transitions lie in the frequency range for upper level energies lower than 30 K. In Fig. 2 and Table 1 we present the first tentative detection of this ion using the 5$_{0,5}$–4$_{0,4}$ transition, as well as the upper limits on the other transitions. The observed frequency (re-shifted by the 7.2 km s$^{-1}$ $V_{LSR}$ of L1544) is 100.359.81 MHz, compared to the computed 100.359.55 $\pm$ 0.035 MHz frequency provided by the JPL database. This is a 0.26 MHz difference and larger than the 0.035 MHz uncertainty quoted for this transition. However, the JPL and CDMS databases do not contain any other transition that could contaminate this frequency, so that we tentatively assign it to DOCO$^+$. New spectroscopic measurements and observations with a lower root-mean square (rms 2 mK for a 10$\sigma$ detection) are necessary to confirm the detection of the DOCO$^+$ ion.

3. Discussion

3.1. Origin and abundance of HOCO$^+$ and DOCO$^+$

Using the CASSIS\footnote{http://cassis.irap.omp.eu} software (Vastel et al. 2015b), we first performed a local thermodynamic equilibrium (LTE) analysis of the detected HOCO$^+$ lines of Table 1, where we varied the excitation temperature and HOCO$^+$ column density. The best fit of the two lines is obtained with a column density of $1.9 \times 10^{11}$ cm$^{-2}$ and an excitation temperature of 8.5 K (see Fig. 1). As a second step, we performed a non-LTE modelling using the LVG code by Cecarelli et al. (2003) and the collision rates between HOCO$^+$ and

| Transitions | Frequency (MHz) | $A_{ij}$ | $E_{up}$ (K) | $V_{\text{peak}}$ (km s$^{-1}$) | FWHM (km s$^{-1}$) | $\int T_{mb}dV$ (K km s$^{-1}$) | rms (mK) |
|-------------|----------------|---------|-------------|-----------------|----------------|-----------------------|--------|
| 4$_{0,4}$–3$_{0,3}$ | 85.531.51 | 1.29 $\times$ 10$^{-5}$ | 10.26 | 7.25 $\pm$ 0.01 | 0.43 $\pm$ 0.03 | 0.022 $\pm$ 0.004 | 3.2 |
| 5$_{0,5}$–4$_{0,4}$ | 106.913.56 | 2.59 $\times$ 10$^{-5}$ | 15.39 | 7.19 $\pm$ 0.02 | 0.34 $\pm$ 0.04 | 0.013 $\pm$ 0.003 | 4.6 |

| Transitions | Frequency (MHz) | $A_{ij}$ | $E_{up}$ (K) | $V_{\text{peak}}$ (km s$^{-1}$) | FWHM (km s$^{-1}$) | $\int T_{mb}dV$ (K km s$^{-1}$) | rms (mK) |
|-------------|----------------|---------|-------------|-----------------|----------------|-----------------------|--------|
| 4$_{0,1}$–3$_{0,3}$ | 59.42 | 1.14 $\times$ 10$^{-5}$ | 59.42 | 7.2 $\pm$ 0.02 | 0.02 $\pm$ 0.02 | 5.2 |
| 5$_{0,5}$–4$_{0,4}$ | 100.359.55 | 2.28 $\times$ 10$^{-5}$ | 14.45 | 6.40 $\pm$ 0.03 | 0.28 $\pm$ 0.06 | 0.004 $\pm$ 0.001 | 3.5 |
| 4$_{1,4}$–3$_{1,3}$ | 79.776.48 | 1.05 $\times$ 10$^{-5}$ | 30.07 | 10.26 $\pm$ 0.03 | 0.001 $\pm$ 0.002 | 4.5 |

**Table 1.** Properties of the observed HOCO$^+$ and DOCO$^+$ lines ($E_{\text{up}} \leq 30$ K).
which we described in Paper I. For both methanol and HOCO+
this, we used the same method as in Paper I: we plotted the
BASECOL database
core center, in angular diameter.

layer is
in its dense inner core. The H
79.8 GHz DOCO
×
+ to

HOCO+
+ H_2O \rightarrow H_3O^+ + CO_2.

At steady state, we can therefore express the [HOCO+]/[HCO+] ratio as the following:

\[
[HOCO^+] = \frac{k_1[H_2][CO_2] + k_6[HOCO^+][OH]}{k_2[CO][H] + k_3[H_2O][CO]} + k_4[OH] + k_5[OH] \]

\[
\text{(3)}
\]

HOCO+ was first proposed by Herbst et al. (1977) as an indirect
trace of gas-phase CO2 and was more recently used for this
purpose by Sakai et al. (2008) and Neill et al. (2014). However,
they neglected reaction 2 between HOCO+ and OH and obtained
a simple relation between [HOCO+]/[HCO+] and [CO2]/[CO] at
steady state. The reaction rates (at 10 K) relevant to the for-
mation and destruction of HOCO+ and HCO+ using the KIDA
network5 are the following (in cm^3 s^-1): \(k_1 = 1.90 \times 10^{-9}\),
\(k_2 = 2.47 \times 10^{-9}\), \(k_3 = 5.56 \times 10^{-9}\), \(k_4 = 1.03 \times 10^{-9}\),
\(k_5 = 2.93 \times 10^{-6}\), \(k_6 = 1.23 \times 10^{-8}\), \(k_7 = 7.14 \times 10^{-8}\), and
\(k_8 = 1.14 \times 10^{-8}\). Both reactions 1 and 2 must be taken into
account, and the latter cannot be neglected, leading to an indi-
rect estimate of the [CO2]/[CO] ratio from [HOCO+]/[HCO+].

In the centre of the prestellar core region, CO is highly deple-
ted (Caselli et al. 1999) from the gas phase and is unlikely to produce
HCO+ and therefore HOCO+. As a consequence, the HOCO+
ion might be visible in an external layer, where CO is released
from the grain surfaces in the gas phase. HOCO+ depends on
the cosmic ray ionisation rate \(\zeta_{CR}\), which governs the H2+
and HCO+ abundances, and on the CO2 gaseous abundance when
reaction (1) is more efficient than reaction (2). We considered
the observations by Vastel et al. (2006), who measured a HCO+
column density of \(4 \times 10^{13} \text{cm}^{-2}\) in the external layer of L1544.
If the bulk of the HCO+ emission arises from the outer layer,
where \(H_2\) column density is \(5 \times 10^{21} \text{cm}^{-2}\) (see Sect. 3.1), this yields a
HCO+ abundance equal to \(-8 \times 10^{-9}\). Using the measured abund-
ance of both HCO+ and HOCO+, we can now constrain the
gaseous CO2 abundance. To this end, we ran the Nahoon gas-
phase chemical model (Wakelam et al. 2015) and compared the
predicted and measured abundance of HOCO+ and HCO+.

Nahoon computes the chemical evolution of a species as a func-
tion of time for a fixed temperature and density. The chemi-
cal network kida.uva.2014 contains 6992 unique chemical reac-
tions and in total 7506 rate coefficients, and these reactions in-
volve 489 different species. We built upon the model described in
Paper I, that is, we considered a two-step model where in the first
step we let the chemical composition reach steady state, and in
the second step we injected a variable amount of CO2 in the
gas phase and injected methanol (6 \times 10^-9 with respect to H atoms)
and ethene (5 \times 10^-9), as in Paper I, to reproduce the detected
COMs described there. The underlying hypothesis is that the
gaseous CO2 is injected by the non-thermal desorption of iced
CO2, as in the case of methanol (Paper I).

For the first step model, we adopted an elemental gaseous
carbon abundance of 5 \times 10^{-3} and a C/O ratio equal to 0.5, co-
munic ionisation rate \(\zeta_{CO}\) of 3 \times 10^{-11} \text{s}^{-1}, \text{H} density of 2 \times 10^{5} \text{cm}^{-3},
temperature of 10 K and \(A_e = 10 \text{ mag},\) as used in Paper I.

The steady abundances of HOCO+ and HCO+ are 4 \times 10^{-11}
and 10^{-8}; respectively; this is fully consistent with the observed
ones. We note that a higher C/O ratio of unity will decrease to
about 5 \times 10^{-12} for HOCO+ and show no substantial change for
HCO+. We used this two-step model to derive an upper limit to
the quantity of injected CO2, taking the error bars on the ob-
erved HOCO+ into account. To stay below the upper value of
the HOCO+ abundance (7 \times 10^{-11}), the quantity of injected CO2
in the gas-phase (through the second step) must be \(\leq 2 \times 10^{-6}\)

4 http://basecol.obspm.fr/

5 http://kida.obs.u-bordeaux1.fr
(with respect to H$_2$), namely ~4% of gaseous CO. We note that no CO$_2$ injection in the gas phase is compatible with our HOCO$^+$ observed abundance of $5 \times 10^{-11}$, with a abundance (w.r.t. H$_2$) from the gas-phase chemical modelling of $2 \times 10^{-7}$. This value is consistent with the tentative gas-phase abundance average over the line of sight of four deeply embedded massive young stars, (van Dishoeck et al. 1996), the value found in the direction of Orion-IRC2/BN (Boonman et al. 2003a) as well as the average value found towards 8 massive protostars (Boonman et al. 2003b). The inferred abundance is also lower than the solid-state age value found towards 8 massive protostars (Boonman et al. 2016), and that the FUV photons impinging on a methanol $\leq$ methanol has a very low yield, $\leq$ methanol. Three mechanisms are invoked in the literature: FUV absorption. Three mechanisms are invoked in the literature: FUV take into account the relevant e $\leq$ mechanism of non-thermal desorption. It turns out that the density and abundance, which was compared to a chemical modelling, constraining the properties and formation of HOCO+ at the early stages towards collapse. The result shows that our detection is compatible with an emission in an external layer, with a CO$_2$/H$_2$ abundance of $2 \times 10^{-7}$ and an upper limit of $2 \times 10^{-6}$.

4. Conclusions

We detected two transitions of the HOCO$^+$ ion at 85.5 and 106.9 GHz and obtained a tentative detection of a low energy level transition of its deuterated form at 100.3 GHz. Based on the HOCO$^+$ detections, we were able to estimate the column density and abundance, which was compared to a chemical modelling, constraining the properties and formation of HOCO+ at the early stages towards collapse. The result shows that our detection is compatible with an emission in an external layer, with a CO$_2$/H$_2$ abundance of $2 \times 10^{-7}$ and an upper limit of $2 \times 10^{-6}$.

References

Bertin, M., Romanzin, C., Doronin, M., et al. 2016, ApJ, 817, L12
Bogey, M., Demuy Nack, C., & Destombes, J. L. 1984, A&A, 138, L11
Bogey, M., Demuy Nack, C., & Destombes, J. L. 1986, J. Chem. Phys., 84, 10
Bogey, M., Demuy Nack, C., Destombes, J. L., & Krupn. A. 1988, J. Mol. Struct., 190, 465
Boonman, A. M. S., van Dishoeck, E. F., Lahuis, F., et al. 2003a, A&A, 399, 1047
Boonman, A. M. S., van Dishoeck, E. F., Lahuis, F., Doty, S. 2003b, A&A, 399, 1063
Caselli, P., Walmsley, C. M., Tafalla, M., et al. 1999, ApJ, 523, L165
Caselli P., Walmsley C. M., Zucconi A. et al. 2002, ApJ, 565, 331
Caselli, P., van der Tak, F. F. S., Ceccarelli, C., & Bachmann, A. 2003, A&A, 403, L37
Caselli, P., Keto, E., Bergin, E. A., et al. 2012, ApJ, 759, L37
Ceccarelli, C., Maret, S., Tielens, A. G. G. M., et al. 2003, A&A, 410, 587
Gerakines, P. A., Whittet, D. C. B., Ehrenfreund, P., et al. 1999, ApJ, 522, 357
Hamann, K., Lique, F., Jaidane, N., et al. 2007, A&A, 469, 1089
Herbst, E., Green, S., Thaddeus, P., & Klemperer, W. 1977, ApJ, 215, 503
Ioppolo, S., van Boheemen, Y., Cuppen, H. M., et al. 2011, MNRAS, 413, 2281
Jamieson, C. S., Mebel, A. M., & Kaiser, R. I. 2006, ApJS, 163, 184
Leger, A., Jura, M., & Montmerle, A. 1985, A&A, 144, 147
Martin-Domenech, R., Manzano-Santamaría, J., Muñoz Caro, G. M., et al. 2015, A&A, 584, A14
Minh, Y. C., Irvine, W. M., & Ziurys, L. M. 1988, ApJ, 334, 175
Minh, Y. C., Brewer, M. K., Irvine, W. M. et al. 1991, A&A, 244, 470
Minissale, M., Moudens, A., Bausche, S. et al. 2016, MNRAS, accepted
Neill, J. L., Bergin, E. A., Lis, D. C., et al. 2014, ApJ, 789, 8
Oberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, ApJ, 740, 109
Podio, L., Lefloch, B., Ceccarelli, C., et al. 2014, A&A, 565, A64
Pontoppidan, K. M., Fraser, H. J., Dartois, E., et al. 2003, A&A, 408, 981
Quénard, D., Taquet, V., Vastel, C., et al. 2016, A&A, 585, A36
Sakai, N., Sakai, T., Aikawa, Y., & Yamamoto, S. 2008, ApJ, 675, L89
Shen, C. J., Greenberg, J. M., Schutte, W. A., van Dishoeck, E. F. 2004, A&A, 415, 203
Thaddeus, P., Guelin, M., & Linke, R. A. 1981, ApJ, 246, L41
Turner, B. E., Terzieva, R., & Herbst, E. 1999, ApJ, 518, 699
van Dishoeck, E. F., Helmich, P. F., de Graauw, T., et al. 1996, A&A, 315, L37
Vastel, C., Caselli, P., Ceccarelli, C., et al. 2003, ApJ, 585, A14
Vastel, C., Ceccarelli, C., Lefloch, B., & Bachiller, R. 2014, ApJ, 795, L2
Vastel, C., Yamamoto, S., Lefloch, B., Bachiller, R. 2015a, A&A, 582, L3
Vastel, C., Bottinelli, S., Caux, E., et al. 2015b, SP2A-2015: Proc. Annual meeting of the French society of Astronomy and Astrophysics, 313
Wakelam, V., Loison, J.-C., Herbst, E., et al. 2015, ApJS, 217, 20
Watanabe, N., & Kouchi, A. 2002, ApJ, 567, 651
Whittet, D. C. B., Gerakines, P. A., Tielens, A. G. G. M., et al. 1998, ApJ, 498, L159
Whittet, D. C. B., Shenefy, S. S., Bergin, E. A., et al. 2007, ApJ, 655, 332
Whittet, D. C. B., Cook, A. M., Chiar, J. E., et al. 2009, ApJ, 695, 94

L2, page 4 of 4