First survey of HCNH$^+$ in high-mass star-forming cloud cores

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ABSTRACT

Context. Most stars in the Galaxy, including the Sun, were born in high-mass star-forming regions. It is hence important to study the chemical processes in these regions to better understand the chemical heritage of both the Solar System and most stellar systems in the Galaxy.

Aims. The molecular ion HCNH$^+$ is thought to be a crucial species in ion-neutral astrochemical reactions, but so far it has been detected only in a handful of star-forming regions, and hence its chemistry is poorly known.

Methods. We have observed with the IRAM-30m Telescope 26 high-mass star-forming cores in different evolutionary stages in the J = 3 – 2 rotational transition of HCNH$^+$.

Results. We report the detection of HCNH$^+$ in 16 out of 26 targets. This represents the largest sample of sources detected in this molecular ion so far. The fractional abundances of HCNH$^+$ with respect to H$_2$, [HCNH$^+$], are in the range $0.9 \times 10^{-11}$, and the highest values are found towards cold starless cores, for which [HCNH$^+$] is of the order of $10^{-10}$. The abundance ratios [HCNH$^+$]/[HCN] and [HCNH$^+$]/[HCO$^+$] are both $\leq 0.01$ for all objects except for four starless cores, for which they are well above this threshold. These sources have the lowest gas temperature and average H$_2$ volume density in the sample. Based on this observational difference, we run two chemical models, a “cold” one and a “warm” one, which attempt to match as much as possible the average physical properties of the cold(er) starless cores and of the warm(er) targets. The reactions occurring in the latter case are investigated in this work for the first time. Our predictions indicate that in the warm model HCNH$^+$ is mainly produced by reactions with HCN and HCO$^+$, while in the cold one the main progenitor species of HCNH$^+$ are HCN$^+$ and HNC$^+$.

Conclusions. The observational results indicate, and the model predictions confirm, that the chemistry of HCNH$^+$ is different in cold/early and warm/evolved cores, and the abundance ratios [HCNH$^+$]/[HCN] and [HCNH$^+$]/[HCO$^+$] can be a useful astrochemical tool to discriminate between different evolutionary phases in the process of star formation.

Key words. Stars: formation – ISM: clouds – ISM: molecules – Radio lines: ISM

1. Introduction

It is now clear that the Sun and most stars in the Milky Way are born in rich clusters including, or close to, high-mass stars (e.g. Carpenter 2004; Pudritz 2002; Adams 2010; Rivilla et al. 2014; Lichtenberg et al. 2019). Therefore, the study of the chemical content and evolution of high-mass star-forming regions can give us important information about the chemical heritage of both the Solar System and most stars in the Milky Way. Despite the importance of studying the chemistry of high-mass star-forming cloud cores (i.e. compact structures with mass $\sim 10–100$ M$_\odot$ which have the potential to form single high-mass stars and/or clusters), an evolutionary classification is not yet clear due to both observational and theoretical problems (e.g. Beuther et al. 2007; Tan et al. 2014; Motte et al. 2018; Padoan et al. 2020).

Several attempts to empirically give an evolutionary classification of high-mass star-forming cores have been proposed, which can all be tentatively summarised in three coarse phases: (1) high-mass starless cores (HMSCs), i.e. dense infrared-dark cores characterised by low temperatures ($\sim 10–20$ K) and high densities ($n \geq 10^4$ cm$^{-3}$), and without clear signs of on-going star formation like strong protostellar outflows and masers; (2) high-mass protostellar objects (HMPOs), i.e. collapsing cores with evidence of one (or more) deeply embedded protostar(s), characterised typically by higher densities and temperatures ($n \simeq 10^6$ cm$^{-3}$, $T \geq 20$ K); (3) ultra-compact HII regions (UCHIIIs), i.e. Zero-Age-Main-Sequence stars associated with an expanding HII region, whose surrounding molecular cocoon ($n \simeq 10^5$ cm$^{-3}$, $T \sim 20–100$ K) is affected physically and chemically by its progressive expansion.

Regardless of the evolutionary stage, high-mass star-forming cores are characterised by a complex and rich chemistry (e.g. Fontani et al. 2007; Bisschop et al. 2007; Foster et al. 2011; Belloche et al. 2013; Vasyunina et al. 2014; Coletta et al. 2020). The new generation telescopes have provided a growing amount of observational results including, thanks to their high sensitivity, the detection of “rare” species (i.e. species with fractional abundance with respect to H$_2$ smaller than $\sim 10^{-10}$). These species can have important implications not only for our understanding of the still mysterious process of high-mass star formation, but also for the chemistry that the primordial Solar System might have inherited from its birth environment (e.g. Beltrán et al. 2009; Fontani et al. 2017; Ligerink et al. 2020; Rivilla et al. 2020; Mininni et al. 2020). Among these rare species, protonated hydrogen cyanide, HCNH$^+$ (or iminomethylium), is important in astrochemistry because it is thought to be the main...
Table 1. Line parameters obtained from Gaussian fits (Cols. 2–6), and total column densities (beam averaged) of HCNH+ obtained from the spectra of the $J = 3 \rightarrow 2$ line (Fig. 3 as explained in Sect. 3) The assumed excitation temperatures, in Col. 7, are the kinetic temperatures listed in Fontani et al. (2011), and are the same used in Colzi et al. (2015a) to derive the column densities of the HCN isotopologues. The last column shows the HCNH+ abundances relative to H$_2$ (HCNH+), computed from the H$_2$ column densities given in Fontani et al. (2015a). Because these were averaged values within an area of angular dimension 28", the given [HCNH+] are also average values within 28".

| source | $J_{\text{MBdV}}$ V$_p$ | V$_p$ | FWHM | $T^\text{p}_{\text{MB}}$ | 1$\sigma$ | $T_{\text{ex}}$ | $N_0$(HCNH+) | [HCNH+] |
|--------|---------------------|------|-------|----------------|--------|----------|--------------|---------|
|        | K km s$^{-1}$       | km s$^{-1}$ | km s$^{-1}$ | K                  | K       | cm$^{-2}$ | ×10$^{13}$ | ×10$^{-11}$ |
|        |        |        |        |        |        |        |        |        |
| HMSCs  |        |        |        |        |        |        |        |        |
| I00117-MM2 | 0.08 | - | 2.5(a) | ≤ 0.03 | 0.014 | 14 | ≤ 0.94 | 0.01 |
| AFGLS5142–EC(w) | 0.10(0.03) | -2.8(0.3) | 2.3(0.8) | 0.041 | 0.014 | 25 | 1.0(0.5) | 1.4(1.0) |
| 05358-mm3(w) | 0.11(0.02) | -16.1(0.3) | 3.0(0.7) | 0.035 | 0.015 | 30 | 1.2(0.5) | 1.7(1.0) |
| G034–G2 | 0.21(0.03) | 42.9(0.3) | 4.3(0.6) | 0.05 | 0.016 | 13 | 2.3(0.8) | 8.6(4.9) |
| G034–F2 | 0.12(0.02) | 58.0(0.2) | 2.5(0.7) | 0.045 | 0.013 | 16 | 1.3(0.5) | 12(8) |
| G034–F1 | 0.10(0.02) | 57.0(0.3) | 2.5(0.7) | 0.037 | 0.012 | 16 | 1.1(0.5) | 14(9) |
| G034–C2 | 0.27(0.02) | 79.5(0.7) | 1.7(0.2) | 0.150 | 0.015 | 17 | 2.8(0.8) | 12(6) |
| I20293–WC(b) | 0.05(0.01) | 7.2(0.2) | 1.4(0.4) | 0.03 | 0.011 | 17 | 0.5(0.2) | 10(7) |
| I22134–G(w) | ≤ 0.06 | - | 2.5(a) | ≤ 0.024 | 0.008 | 25 | ≤ 0.61 | ≤ 2.6 |
| I22134–B | ≤ 0.07 | - | 2.5(a) | ≤ 0.03 | 0.017 | 17 | ≤ 0.74 | ≤ 5.7 |
| HMPOs  |        |        |        |        |        |        |        |        |
| 00117-MM1 | 0.07 | - | 1.6(a) | ≤ 0.039 | 0.013 | 20 | ≤ 0.67 | 0.01 |
| AFGLS5142–MM | 0.09(0.02) | -2.3(0.2) | 1.9(0.5) | 0.045 | 0.013 | 34 | 1.0(0.4) | 1.5(1.0) |
| 05358–mm1 | 0.09(0.02) | -16.1(0.2) | 1.4(0.4) | 0.06 | 0.018 | 39 | 1.0(0.5) | 1.9(1.3) |
| 18089–1732 | 0.18(0.07) | 32.5(0.3) | 2.3(0.6) | 0.07 | 0.020 | 38 | 2(1) | 3.2(2.6) |
| 18517+0437 | ≤ 0.06 | - | 1.6(a) | ≤ 0.033 | 0.011 | 40 | ≤ 0.69 | ≤ 1.3 |
| G75–core | ≤ 0.07 | - | 1.6(a) | ≤ 0.042 | 0.014 | 96 | ≤ 1.48 | ≤ 5.2 |
| I20293–MM1 | 0.09(0.02) | 5.6(0.1) | 1.5(0.2) | 0.058 | 0.013 | 36 | 1.0(0.4) | 3.2(2.0) |
| I21307 | ≤ 0.03 | - | 1.6(0.3) | ≤ 0.025 | 0.009 | 21 | ≤ 0.30 | ≤ 1.5 |
| I23385 | ≤ 0.07 | - | 1.6(a) | ≤ 0.039 | 0.013 | 37 | ≤ 0.77 | ≤ 4.9 |
| UCHIs   |        |        |        |        |        |        |        |        |
| G5.89–0.39 | 0.97(0.04) | 8.1(0.6) | 2.5(0.1) | 0.368 | 0.024 | 32 | 10(3) | 2.9(1.5) |
| I19035–VLA1 | ≤ 0.11 | - | 2(a) | ≤ 0.042 | 0.014 | 39 | 1.3(0.3) | 5.4(2.4) |
| 19410+2336 | 0.08(0.01) | 22.5(0.1) | 1.4(0.3) | 0.054 | 0.010 | 21 | 0.8(0.3) | 0.9(0.5) |
| ON1 | 0.22(0.02) | 11.2(0.1) | 3.2(0.3) | 0.065 | 0.010 | 26 | 2.2(0.6) | 3.7(4.4) |
| I22134–VLA1 | 0.08(0.01) | -18.0(0.1) | 1.8(0.3) | 0.042 | 0.009 | 47 | 1.0(0.4) | 3.7(4.4) |
| 23033+5951(1) | 0.10(0.02) | -53.4(0.4) | 3.1(1) | 0.031 | 0.011 | 25 | 1.0(0.5) | 2.0(1.4) |
| NGC7538–IRS9 | ≤ 0.08 | - | 2.4(a) | ≤ 0.033 | 0.011 | 32 | ≤ 0.09 | ≤ 1.1 |

(a) fixed FWHM assumed to compute the upper limit on $N_0$(HCNH+), obtained as the average value of the detected lines in the corresponding evolutionary group; (b) tentative detections; (c) column density of H$_2$ not available; (d) warm HMSCs. The other HMSCs are classified as cold (or quiescent. See Fontani et al. 2011).
temperature range 10–100 K, the critical density of the transition is \( \sim 4 \times 10^4 \) cm\(^{-3}\). The lines were fitted with the CLASS package of the GILDAS\(^{[1]}\) software using standard procedures.

3. Results

3.1. Detection rate and line shapes

We detected HCNH\(^+\) \( J = 3 – 2 \) with signal to noise ratio, S/N, higher than \( \sim 3 \) towards 14 out of the 26 targets. In two cases, I20293–WC and 23033+5951, the peak main beam temperature is slightly below the 3\( \sigma \) rms, but the line profile suggests a real line at the limit of the detection level. Hence, we have considered them as tentative detections, which provides a total of 16 detected sources including the tentative ones (detection rate \( \sim 62\% \)). The transition has hyperfine structure that, however, cannot be resolved in our spectra because the separation in velocity of the components is smaller than the velocity resolution. Therefore, we fitted the lines with single Gaussian profiles. This method gives good results with residuals lower than, or comparable to, the noise in the spectra.

Table 1 reports the results of the Gaussian fits to the lines: integrated line intensity (\( \int T_{\text{MB}}dv \)), velocity at line peak (\( V_p \)), line full width at half maximum (FWHM), peak main beam temperature (\( T_{\text{MB}} \)), and 1\( \sigma \) rms on the fit and on FWHM are given by the fit procedure. The uncertainties on \( \int T_{\text{MB}}dv \) are the sum in quadrature of the error given by the fit and the calibration error on \( T_{\text{MB}} \) (assumed to be 10\%). The latter is dominant in the sum in quadrature.

The spectra and their fits are shown in Fig. 1. In two sources, the line profile cannot be fitted with a single Gaussian, i.e. in 18089–1732 and G5.89–0.39. Both spectra show an excess emission in the red tail of the line (see Fig. 1). Towards G5.89–0.39, this excess has the form of a high-velocity wing. Hence, it likely arises from the red-shifted lobe of the outflow associated with the embedded UC HII region (Zapata et al. 2020). Towards 18089–1732, the excess emission has the shape of a Gaussian peak with intensity almost half of the main peak. Hence, in this case it is more likely due to a secondary velocity feature, or to another line blended with the HCNH\(^+\)(3–2). One high excitation lines (\( E_a \sim 200K \)) of CH\(_3\)OCH\(_3\), detected in this source (Coletta et al. 2020), are predicted at \( \sim 222326 \) MHz, which could hence contribute to the secondary peak centred approximately at \( \sim 222327 \) MHz. Moreover, the profile of the H\(^{13}\)CO\(^+\) \( J = 1 – 0 \) does not show this secondary peak (Fig. 1). Therefore, hence a second velocity feature is very unlikely. A contribution from the red lobe of the outflow associated with the embedded Hyper-compact HII region is also possible (Beuther et al. 2010), but because, again, it is not seen in H\(^{13}\)CO\(^+\) \( J = 1 – 0 \), its contribution to this secondary peak should be negligible. In general the lack of high-velocity wings, except maybe in the two cases discussed above, indicates that the emission of the line does not arise from shocks and/or outflows, but likely from more quiescent material.

Because HCNH\(^+\) was detected in a handful of star-forming regions before this study, it is not yet clear which kind of material (i.e. with which physical and kinematical properties) is responsible for the emission of this molecule. To investigate this, in Fig. 2 we compare the profiles of HCNH\(^+\) \( J = 3 – 2 \) with those of H\(^{13}\)CO\(^+\) \( J = 1 – 0 \) analysed in Fontani et al. (2018), thought to be a good tracer of the envelope of star-forming cores. Inspection of the plot suggests that in some sources (e.g. G028–C1, AFGL5142–EC, 05358–mm1, I20293–MM1, 19410+2336), the two lines have similar peak velocity, suggesting a common origin in the envelope of the cores. On the other hand, in some targets, e.g. G034–F1, I20293–WC, I22134–VLA1, and G5.89–0.39, the HCNH\(^+\) emission does not coincide with the central velocity of H\(^{13}\)CO\(^+\), even though towards G034–F1 and I20293–WC, the H\(^{13}\)CO\(^+\) \( J = 1 – 0 \) shows multiple velocity features, and the HCNH\(^+\) \( J = 3 – 2 \) emission is centred on one of these. These second velocity features, in principle, could also be originated by self-absorption or polluting lines from other species. These scenarios, however, are both unlikely in G034–F1 and I20293–WC. In fact, self-absorption signatures were never observed in other lines towards these sources, and polluting lines are very unlikely in cold HMSCs (like these two targets). Furthermore, a second velocity feature towards G034–F1 was already found in the HCN isotopologues by Colzi et al. (2018a).

About the line widths, the stronger H\(^{13}\)CO\(^+\) lines are generally broader than the HCNH\(^+\) ones, except than in a few targets (G034–G2, 18089–1732, I22134–VLA1). Also, we see no hints of high velocity wings in HCNH\(^+\) \( J = 3 – 2 \), except than in the already discussed spectrum of G5.89–0.39. However, high velocity wings could not be detected due to the limited signal-to-noise ratio in the spectra. All this indicates that: (1) the gas emitting HCNH\(^+\) is mostly quiescent, or not clearly associated with shocks, and (2) there is not a general agreement with the profiles of the H\(^{13}\)CO\(^+\) \( J = 1 – 0 \) lines. We propose that in the targets

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1 https://www.iram.fr/IRAMFR/GILDAS/
in which both lines have the same velocity peak, the HCNH$^+$ $J = 3 \rightarrow 2$ line arises from the envelope of the cores, but likely from a more compact portion of that traced by $^{13}$CO$^+ J = 1 \rightarrow 0$. In fact, the HCNH$^+$ $J = 3 \rightarrow 2$ line has a higher energy of the upper level than $^{13}$CO$^+ J = 1 \rightarrow 0$ (21.3 K against 4 K), and the spectra were observed with different beam sizes ($\sim 11''$ against $\sim 28''$).

### 3.2. Total column densities and abundances of HCNH$^+$

Assuming that the lines are optically thin and in Local Thermodynamic Equilibrium (LTE), from $\int T_{MB} dV$ we have computed the beam-averaged total column densities of HCNH$^+$, $N_{\text{tot}}(\text{HCNH}^+)\), using Eq. (1) of Fontani et al. (2018). For undetected sources, we have estimated upper limits on $N_{\text{tot}}(\text{HCNH}^+)$ from the upper limit on the integrated intensity. This was computed from the relation $\int T_{MB} dV = 3.1 \frac{\Delta \nu}{\sqrt{\tau_{25}}} \text{FWHM}$, which expresses the integral of velocity of a Gaussian line with peak intensity given by the $3\sigma$ rms in the spectrum. We assumed as FWHM the average value obtained from the detected lines in each evolutionary group which the undetected source belongs to: 2.5 km s$^{-1}$ for HMSCs, 1.6 km s$^{-1}$ for HMPOs, 2.4 km s$^{-1}$ for UCHIIs (see Table 1). The assumption of optically thin emission is consistent with the low abundance of the molecule and with the fact that the observed line shapes have generally no hints of high optical depths such as, e.g., asymmetric or flat topped profiles. Only towards G034–G2, the almost flat-top line shape could indicate non-negligible optical depths. Hence, in this source, the HCNH$^+$ total column density should be regarded as a lower limit. The assumption of LTE is also reasonable because the critical density of the line ($\sim 4 \times 10^6$ cm$^{-3}$, see Sect. 2) is smaller than, or comparable to, the average H$_2$ volume densities of the sources. These, calculated within a beam of $28''$, are in between $10^4$ and $10^6$ cm$^{-3}$ (see e.g. Fontani et al. 2018 and Sect. 3). A few sources have H$_2$ volume density of $\sim 1 \times 2 \times 10^4$ cm$^{-3}$, i.e. the HMSCs G034–F2, G034–F1, and G028–C1, and the UCHII I22134–VLA1 (see Sect. 4). For these targets, the approximation could not be valid.

We have estimated by how much $N_{\text{tot}}(\text{HCNH}^+)$ would change in the conservative case in which the excitation temperature is lower than the kinetic temperature by 10 K: $N_{\text{tot}}(\text{HCNH}^+)$ would increase by a factor $\sim 4$. Therefore, in the following the column densities of these targets should be considered lower limits.

The total column densities, averaged within the telescope beam of $11''$, are in the range $0.5 \sim 10 \times 10^{13}$ cm$^{-2}$. If we analyse separately the three evolutionary groups, we find hints of possible differences. In fact, the average values are: $\sim 1.5 \times 10^{13}$ cm$^{-2}$ for the HMSCs, $\sim 1.25 \times 10^{13}$ cm$^{-2}$ for the HMPOs, $\sim 2.7 \times 10^{13}$ cm$^{-2}$ for the UCHIIs. However, the average value in the UCHIIs is strongly biased by G5.89–0.39, which is by far the most luminous object in the sample. Without G5.89–0.39, the average value in the UCHIIs is $\sim 1.3 \times 10^{13}$ cm$^{-2}$, consistent with those of the other two evolutionary groups.

We have computed abundances of HCNH$^+$ relative to H$_2$ by using the H$_2$ column densities published in Fontani et al. (2018). These were average values derived in an angular diameter of $28''$, hence the HCNH$^+$ column densities have been smoothed to this larger angular diameter. The corresponding abundances, [HCNH$^+$], are listed in Table 1 and range from $\sim 0.9$ to $\sim 14 \times 10^{-11}$. Interestingly, HMPOs and UCHIIs have average [HCNH$^+$] of the order of $10^{-11}$, and consistent among them (specifically, $\sim 2.5$ and $\sim 3.7 \times 10^{-11}$, respectively), while HMSCs have an average [HCNH$^+$] of $\sim 7.3 \times 10^{-11}$, i.e. a factor 2–3 higher. In particular, the HMSCs with the highest abundances are all classified as "cold", or "quiescent", by Fontani et al. (2011), and have [HCNH$^+$] of the order of $10^{-10}$.

### 4. Discussion of the observational results

One of the most important and direct findings from the parameters in Table 1 is that the HMSCs classified as quiescent have
HCNH$^-$ abundances larger by about an order of magnitude with respect to warmer objects. This suggests that in cold and quiescent cores some formation pathways of HCN$^-$ are more efficient than in warmer cores, and/or that some destruction pathways are less efficient. The chemistry of HCN$^-$ is thought to be related to that of HCN, HCO$^+$, and CN, as discussed in Quénard et al. (2017). However, Quénard et al. (2017) focussed on the pre-stellar core L1544, i.e. a cold core with a known physical structure. Which are the dominant formation pathways in warmer environments (and under different physical conditions in general), are not yet clear.

To investigate the chemical origin of HCN$^+$, we have searched for correlations between some physical parameters of HCN$^+$ and those of HCN, HCO$^+$, and CN. In Fig. 3 we compare column densities, abundances, and FWHM of HCN$^+$ and HCN. Fig. 4 shows the same comparison between HCN$^+$ and HCO$^+$. The latter has been computed from the H$^3$CN $J = 1 − 0$ line (Colzi et al., 2018b), by correcting it for the $^{12}$C/$^{13}$C ratio obtained at the Galactocentric distance of the sources from the trend of Yan et al. (2019). $N_{\text{tot}}$(HCN$^+$) has been rescaled to the (larger) beam of the H$^2$CO observations, i.e. $\sim 28"$. Red stars are HMSCs; blue stars are UCHII; black symbols are HMPOs; among which the filled circles represent the "quiescent" ones while the stars indicate the "warm" ones (see Table 1). Triangles indicate upper limits on $N_{\text{tot}}$(HCN$^+$). The dashed line is the locus where $N_{\text{tot}}$(HCN$^+$) $= 0.01 N_{\text{tot}}$(HCN). MIDDLE PANEL: same as left panel, but for the fractional abundances with respect to H$_2$ calculated on a beam of $\sim 28"$. The purple rectangle indicates the range of abundances that reproduces the observed [HCN], and [HCN$^+$] in the predictions of the Warm Model (WM, see Sect. 5 and right panel of Fig. 7). Similarly, the cyan square indicates the prediction of the Cold Model (CM, see Sect. 5 and left panel of Fig. 7).

RIGHT PANEL: comparison between the line FWHM of HCNH$^+$, derived in this work from the $J = 3 − 2$ line, and H$^3$CN, derived by Colzi et al. (2018a) from the $J = 1 − 0$ line at $\sim 87$ GHz. The symbols have the same meaning as those in the left and middle panels.
of \( \sim 28'' \), and the abundances [HCN] and [HCO\(^+\)] were computed dividing \( N_{\text{tot}}(\text{HCN}) \) and \( N_{\text{tot}}(\text{HCO}^+) \) by the same \( N_{\text{tot}}(\text{H}_2) \) used for HCNH\(^+\).

Two relevant results emerge clearly from the plots in Figs. 3 and 4:

(i) the abundance ratios \([\text{HCN}^+] / [\text{HCN}]\) and \([\text{HCNH}^+] / [\text{HCO}^+]\) are both \( \leq 0.01 \) for all objects except for the four quiescent HMSCs G034–G2, G034–F2, G034–F1, and G028–C1, for which they are one order of magnitude above this threshold. This difference could be even more pronounced because, as discussed in Sect. 5.1, for three of these four sources [HCNH\(^+\)] could be underestimated because the transition could be sub-thermally excited.

(ii) the FWHM of the lines of different species do not appear clearly correlated. However, if one excludes the four quiescent HMSCs mentioned in item (i), a tentative correlation is apparent in both Fig. 3 and Fig. 4 with Spearman \( \rho \) correlation coefficients \( \sim 0.55 \) and \( \sim 0.63 \), respectively.

These findings suggest that the dominant formation pathways of HCNH\(^+\) in cold and warm regions are likely different. Only one quiescent HMSC, I20293–WC, does not follow a tentative correlation and the possible chemical relationship between HCNH\(^+\) and CN seems unlikely.

Finally, in Fig. 6 we plot the column density ratio \( N_{\text{tot}}(\text{HCN}^+) / N_{\text{tot}}(\text{HCN}) \) as a function of the following core physical parameters: \( N_{\text{tot}}(\text{H}_2) \), volume density of \( \text{H}_2 \), \( n(\text{H}_2) \); gas kinetic temperature, \( T_k \) (Fontani et al. 2011); dust temperature, \( T_{\text{dust}} \) (Mininni et al. submitted); and \( n(\text{H}_2) \) is an average value within \( 28'' \) computed from the column density of \( \text{H}_2 \) given in Fontani et al. (2018) assuming spherical sources for simplicity. Based on this plot, the different behaviour of cold and warm sources is very clear: colder and less dense objects have \( N_{\text{tot}}(\text{HCN}^+) / N_{\text{tot}}(\text{HCN}) \) ratios higher than warmer and denser ones by about an order of magnitude.

5. Chemical modelling

In this Section we investigate the main routes of formation and destruction of HCNH\(^+\) and HCN, together with their possible chemical relation with HCO\(^+\), for two different chemical models, which represent the colder and warmer conditions of the sample of high-mass star-forming regions studied in this work.

### Table 2. Initial abundances with respect to \( n_{\text{H}} \). Adapted from Semenov et al. (2010).

| Species | Initial abundance |
|---------|-------------------|
| H\(_2\)  | 0.5               |
| He      | \(9.00 \times 10^{-2}\) |
| C\(^+\) | \(1.20 \times 10^{-4}\) |
| N       | \(7.60 \times 10^{-5}\) |
| O       | \(2.56 \times 10^{-4}\) |
| S\(^+\) | \(8.00 \times 10^{-8}\) |
| Si\(^+\) | \(8.00 \times 10^{-9}\) |
| Na\(^+\) | \(2.00 \times 10^{-9}\) |
| Mg\(^+\) | \(7.00 \times 10^{-9}\) |
| Fe\(^+\) | \(3.00 \times 10^{-9}\) |
| P\(^+\)  | \(2.00 \times 10^{-10}\) |
| Cl\(^+\) | \(1.00 \times 10^{-9}\) |
| F       | \(2.00 \times 10^{-9}\) |

ortho-para (o/p) \(10^{-3}\)

5.1. Description of the models

For the chemical simulations we use our gas-grain chemical code, recently described in Sipilä et al. (2019a, 2019b). The chemical networks used here contain deuterium and spin-state chemistry (see Sipilä et al. 2019b and references therein). While we do not explicitly consider deuterium chemistry in this paper, the inclusion of spin-state chemistry is important due to its effect on nitrogen chemistry (e.g. Dislaire et al. 2012). The chemical network contains a combined total of 881 species and 40515 reactions (37993 gas-phase reactions and 2519 grain-surface reactions). We have excluded all molecules that contain more than five atoms so that the chemical simulations can run faster; this is justified in the present context where we study the chemistry of molecules with four atoms or fewer. The initial abundances adopted in the models are summarised in Table 2.

To discuss the results obtained from the observations, we have decided to model two types of molecular clouds defined dividing the sample of sources in two sub-groups:

- Cold Model (CM): defined from the sources with a \( T_{\text{dust}} \) of about 10 K (see right panel of Fig. 6). These sources are the HMSCs G034–G2, G034–F1, G034–F2, and G028–C1.
- Warm Model (WM): defined from all of the other sources, which have \( T_{\text{dust}} > 10 \) K.

For both chemical model types we fixed the cosmic-ray ionization rate \( \zeta \), the visual extinction \( A_V \), the grain radius \( a_g \), the grain material density \( \rho_g \), the ratio between the diffusion and the binding energy of a species on dust grains \( \epsilon_g \), and the dust-to-gas mass ratio \( R_d \) to the values given in Table 3. The gas temperature \( T_{\text{gas}} \) and total number density of H nucleus \( n(\text{H}) \) of the two models have been defined from the average \( T_{\text{dust}} \) and \( n(\text{H}_2) \) of the two sub-groups of sources, respectively. We have decided to use the dust temperatures, instead of the kinetic temperatures, because they were all derived with the same method (Mininni et al., submitted), while the kinetic temperatures were not.

We have assumed the value of \( T_{\text{gas}} = 10 \) K and \( n(\text{H}_2) = 3.4 \times 10^4 \) cm\(^{-3}\), and for the warm model \( T_{\text{gas}} = 27 \) K and \( n(\text{H}_2) = 2.4 \times 10^5 \) cm\(^{-3}\). We adopt as initial conditions the same used by Colzi et al. (2020) with an initial condition the same used by Colzi et al. (2020) with an
ortho-para (o/p) ratio of $10^{-3}$. Since in warm regions (20 K) the o/p ratio could be higher, and because N chemistry may be affected by it, we tried also to assume a o/p ratio for the WM of $10^{-2}$ and of $10^{-1}$. This test was done with a fixed temperature of 27 K and we do not take into account the possibility that the o/p ratio could be even higher while the temperature increases. In both cases, the results that will be discussed in the next section do not change.

It has to be noted that for this work, both for the observations and for the chemical modelling we discard any possible effect from chemical isotopic fractionation of carbon, which could modify the observed and modelled abundances of HCN and HCO$^+$ at most by a factor three (see Colzi et al. 2020). Gas-grain chemistry is followed in our chemical models and it is important in the differentiation between the warm and cold sources, as in the former ones CO can be mainly maintained in the gas phase (27 K is indeed just above the sublimation temperature of CO), thus contributing to the larger HCO$^+$ abundances in warm regions.

5.2. Model predictions

Figure 7 shows the predicted abundances for HCNH$^+$, HCN, and HCO$^+$. These predictions are plotted together with the range of the observed abundances, derived as explained in Sect. 3.2. The predicted abundances are shown as a function of time, with the abundances at $t_{CM} = 4 \times 10^5$ yr and $t_{WM} = 5 \times 10^4$ yr for the CM and WM, respectively. The figure shows that the abundances predicted by the model are in agreement with the observed values.

Table 3. Values of the physical parameters fixed in each model.

| Parameter | Value |
|-----------|-------|
| $\zeta$ | $1.3 \times 10^{-17}$ s$^{-1}$ |
| $A_V$ | 10 mag |
| $\omega$ | 0.6 |
| $a_g$ | $10^{-5}$ cm |
| $\rho_g$ | 3 g cm$^{-3}$ |
| $e = E_{\text{diff}}/E_b$ | 0.6 |
| $R_d$ | 0.01 |
| $T_{\text{gas}}$ | 10 K (CM) |
| | 27 K (WM) |
| $n_H$ | $3.4 \times 10^4$ cm$^{-3}$ (CM) |
| | $2.4 \times 10^5$ cm$^{-3}$ (WM) |

For the CM the three abundances can be partially reproduced at about $t_{CM} = 4 \times 10^5$ yr. For the WM this happens at two times, $5 \times 10^4$ yr and $3 \times 10^6$ yr, but we have decided to take into account for the discussion only the earlier one ($t_{WM} = 5 \times 10^4$ yr), which is more representative of the life-time of massive star-forming regions (e.g. Motte et al. 2018). Moreover, at these times the abundance of HCN is equal to that of HCO$^+$, as it is observed towards the sources studied in this work (see Figs. 3 and 4).
Fig. 7. Time evolution of HCNH$^+$, HCN, and HCO$^+$ abundances with respect to H$_2$ for the CM (left panel) and for the WM (right panel). In both panels the coloured horizontal areas represent the range of observed abundances, for HCNH$^+$ in red, for HCN in green, and for HCO$^+$ in blue, for the two sub-groups of sources.

Fig. 8. HCNH$^+$/HCN ratio predicted for the CM (green solid line), and for the WM (dashed green line). The grey coloured areas represent the range of observed HCNH$^+$/HCN ratios for the CM (filled area), and for the WM (striped area). The purple vertical lines indicates the times in which the abundances of HCNH$^+$, HCN and HCO$^+$ are reproduced by the CM ($t_{\text{CM}}=4\times10^5$ yr, solid line), and by the WM ($t_{\text{WM}}=5\times10^4$ yr, dashed line).

At these time scales most of the HCN and HCNH$^+$ are already formed through the early-time chemistry (see e.g. Hily-Blant et al. 2010), HCN being mainly formed from:

$$\text{CH}_2 + \text{N} \rightarrow \text{HCN} + \text{H},$$

and HCNH$^+$ from:

$$\text{HCN} + \text{H}_3^+ \rightarrow \text{HCNH}^+ + \text{H}_2.$$  

Indeed, the abundances of both HCN and HCNH$^+$ increase by one order of magnitude at chemical times of $10^5$ yr (Fig. 7).

As shown in Fig. 8 the observed HCNH$^+$/HCN ratio can not be reproduced by our chemical models at time scales in which the abundances are reproduced. In fact, the predicted HCNH$^+$/HCN ratio at $t_{\text{CM}}$ is $\sim 0.02$, lower than the observed ratios, and at $t_{\text{WM}}$ is $\sim 0.01$, slightly higher than what observed. However, observations and model predictions agree with a higher HCNH$^+$/HCN ratio in colder sources with respect to the warmer ones.

Fig. 9. Scheme of the chemical network that connects the main molecular species investigated in this work for the Warm Model (WM in Sect. 5.1). The prefix g- indicates molecules in icy mantles on dust grains. The arrows are colour-coded depending on the involved reactant: H (blue), H$_2$ (red), free electrons (green), H$^+$ (red), other species (black; the reactant is indicated on the side). Dashed arrows refer to transitions from solid to gas phase, or vice-versa. For the reactions forming and destroying HCNH$^+$, we also indicate their relative contribution in percentage.
5.3. Formation and destruction reactions of HCNH$^+\,$

To perform a detailed analysis and discuss the observed differences between the two sub-groups of sources, i.e. cold/early starless cores and warmer/evolved objects, we have studied in detail the main reactions of formation and destruction which involve HCN, HCNH$^+$ and related chemical species. In particular, we have taken into account the $t_{\text{fCM}}$ and $t_{\text{WM}}$ times. HCO$^+$ is in both models formed mainly from CO + H$_2^+$ and mainly destroyed by HCO$^+$ dissociative recombination. However, as will be discussed later, its presence is very important in the cycle of reactions involved in the warm model.

Regarding the cold model, HCNH$^+$ is mainly formed via:

$$\text{HCN}^+ + H_2 \rightarrow \text{HCNH}^+ + H, \quad (3)$$

$$\text{HNC}^+ + H_2 \rightarrow \text{HCNH}^+ + H, \quad (4)$$

and

$$\text{NH}_3 + C^+ \rightarrow \text{HCNH}^+ + H, \quad (5)$$

and mainly destroyed by dissociative recombination forming HCN, HNC and CN with almost the same probability (33.5%, 33.5% and 33%, respectively, Semaniak et al. 2001):

$$\text{HCNH}^+ + e^- \rightarrow \text{HCN} + H, \quad (6)$$

$$\text{HCNH}^+ + e^- \rightarrow \text{HNC} + H, \quad (7)$$

and

$$\text{HCNH}^+ + e^- \rightarrow \text{CN} + H + H. \quad (8)$$

Moreover, HCN$^+$ is mainly formed via CN + H$_2^+$ closing this part of the cycle of reactions (Woon & Herbst 2009). Another cycle of reactions involves HCN which at $t_{\text{fCM}}$ is mainly formed via reaction (6) and mainly destroyed by the presence of HCO$^+$, C$^+$ and H$_2^+$. All of this is in agreement with the predictions of Hily-Blant et al. (2010), and Loison et al. (2014) for low-temperature pre-stellar cores and dark molecular clouds, respectively. More recently, for HCNH$^+$, this was also confirmed by Quénard et al. (2017) towards the pre-stellar core L1544.

The main novelty of this work is the study of the main chemical reactions for these chemical species in an environment warmer and denser than in the previous studies. In fact, from the WM we have found that HCNH$^+$ is mainly formed via:

$$\text{HCN} + \text{HNC} + \text{CO}^+ \rightarrow \text{HCNH}^+ + \text{CO}, \quad (9)$$

instead of reactions (3) and (4). The latter reactions are still occurring, but are not efficient enough for the formation of protonated HCN because the abundances of HCN$^+$ and HNC$^+$ decrease by three orders of magnitude with respect to the CM. The cycle of main reactions for the warm model is shown in Fig. 9. These chemical pathways are in agreement with the tentative correlations found for the FWHM between HCNH$^+$ and HCN and HCO$^+.$

5.4. Discussion of the assumed parameters

It is worth noting that the sources have very complex structure, with dense cores embedded in a diffuse envelope, and also with the possible presence of extended outflows from the massive protostellar objects. In these models we are simplifying the physical geometry of the sources, and most of the parameters are assumed to be constant during the chemical evolution, possibly affecting the predicted abundances. Hence, we have checked if changing some of the physical parameters of the two models could lead to a better agreement with the absolute HCNH$^+/\text{HCN}$ ratios observed.

First of all, we tested higher values of the cosmic-ray ionisation rate with respect to the canonical value of 1.3×10$^{-17}$ s$^{-1}$ (e.g. Padovani et al. 2009), of 10$^{-16}$, 10$^{-15}$, and 10$^{-14}$ s$^{-1}$ (e.g. López-Sepulcre et al. 2013, Fontani et al. 2017). We find a higher HCNH$^+/\text{HCN}$ ratio (up to 0.04 already at 10$^{-8}$ yr), at the lower edge of the observed values, for higher $\zeta$ in the CM (see left panel of Fig. 10). In fact, the presence of more ions favours the destruction of HCN over the formation of HCNH$^+.$ Moreover, this trend is the same for the WM, making the observed values reproduced for lower $\zeta$ (see right panel of Fig. 10). However, these trends are hard to understand because the $\zeta$ measured towards HMSCs are lower with respect to those found towards protostellar objects (e.g. Fontani et al. 2017). Another discrepancy is that the observed abundances of the molecules could not be reproduced, for both models, at times in which the HCNH$^+/\text{HCN}$ ratio matches (see Figs. A1, A2, and A3). Thus, cosmic-ray ionisation rate could not help us to explain the observed values.

Secondly, we investigated the possibility of a higher hydrogen nuclei number density for the cold model. In fact, $n_H$ has been found from the H$_2$ column densities, which in turn have been derived in an area with angular dimension 28″. However, the emission is not resolved and in principle it could mainly come from a smaller region (dense cores inside the high-mass clump). This would lead to higher $n_H.$ Assuming a density of one order of magnitude higher ($n_H = 3.4 \times 10^5$ cm$^{-3}$) we find a better agreement with respect to the observed abundances of HCN, which are lower with respect to the predictions of the initial cold model (Fig. 11). In fact, the higher density, together with the low temperature, makes adsorption onto grain surfaces more efficient. However, also the abundance of HCN decreases.

Finally, since high-mass protostellar objects are born in a gas that was previously a starless core, we tried to model the warm sources using as initial conditions the abundances of the CM at 4×10$^5$ yr, time in which the CM observations are reproduced. Interestingly, we found a warm model with almost constant abundances for the three models, well reproduced by the observations of HCN and HCO$^+$, while slightly above with respect to the observed HCNH$^+$ (Fig. 12). This leads to the same result obtained in the original WM, but spread during the chemical evolution.

To conclude, we have found that a change in the initial conditions or in some of the initial parameters of the chemical model would not lead to the absolute observed HCNH$^+/\text{HCN}$ ratios. Many of the relevant reactions in the chemical model are not well constrained, and perhaps some important pathways are missing. For example, reactions (3), (4), and (9) in the KIDA network are just estimated and laboratory measurements are needed to obtain the correct molecular abundances.

6. Summary and conclusions

We have presented the first survey of HCNH$^+$ $J = 3 \rightarrow 2$ lines, observed with the IRAM-30 telescope, towards 26 high-mass star-forming regions. We report 14 detections and two tentative detections, for a total detection rate of $\approx 62\%.$ The total column densities, $N_{\text{tot}}(\text{HCNH}^+),$ calculated assuming optically thin lines and local thermodynamic equilibrium conditions, are in the range 0.5 – 10×10$^{14}$ cm$^{-2}$. The abundances of HCNH$^+$ with respect to H$_2$ are in the range 0.9 – 14×10$^{-11},$ and the highest values are found towards the coldest HMSCs, for which [HCNH$^+$]...
Fig. 10. HCNH\(^+\)/HCN ratio predicted for the CM (left panel), and for the WM (right panel), assuming different cosmic-ray ionisation rate, \(\zeta\). The grey coloured areas represent the range of observed HCNH\(^+\)/HCN ratios for the CM (filled area in the left panel), and for the WM (striped area in the right panel).

Fig. 11. Time evolution of HCNH\(^+\), HCN, and HCO\(^+\) abundances with respect to \(H_2\) for the cold model, but assuming a higher \(n_{\text{HI}}\) of \(3.4 \times 10^5\) cm\(^{-3}\). The coloured horizontal areas are the same as in the left panel of Fig. 7.

Fig. 12. Time evolution of HCNH\(^+\), HCN, and HCO\(^+\) abundances with respect to \(H_2\) for the warm model, found assuming as initial conditions the abundances of the CM at \(t_{\text{CM}}\). The coloured horizontal areas are the same as the right panel of Fig. 7.

is of the order of \(10^{-10}\). The abundance ratios [HCNH\(^+\)]/[HCN] and [HCNH\(^+\)]/[HCO\(^+\)] are both \(\leq 0.01\) in all targets except towards the four coldest HMSCs. Hence, the dominant formation pathways of HCNH\(^+\) in cold/early and warm/evolved regions are likely different. We have run two chemical models, a "cold" one and a "warm" one, to attempt to reproduce our results. Besides the different temperature, the two models are also adapted to match as much as possible the average physical conditions of the four cold(est) HMSC and the other sources. In particular, the main chemical reactions leading to the formation and destruction of HCNH\(^+\) in the "warm" model are investigated in this work for the first time. Our predictions indicate that indeed HCO\(^+\) and HCN/HNC are the dominant progenitor species of HCNH\(^+\) in the warm model, while in the cold one HCNH\(^+\) is mainly formed by HCN\(^+\) and HNC\(^+\). Another important result of this study is that the abundance ratios [HCNH\(^+\)]/[HCN] and [HCNH\(^+\)]/[HCO\(^+\)] can be a useful astrochemical tool to discriminate between different evolutionary phases in the process of star formation. Naturally, higher angular resolution observations will allow us to better constrain precise location and extent of the emitting region of HCNH\(^+\) in the sources. More transitions will also help constraining more precisely the excitation conditions, both crucial elements to define better the range of physical parameters appropriate to model the chemistry.

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Appendix A: model predictions for different $\zeta$

We show in this appendix the predictions of our chemical models for $\zeta$ different from the canonical value $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$, adopted in Fig. [7]
Fig. A-1. Same as Fig. 7 assuming a cosmic-ray ionisation rate $\zeta = 1.3 \times 10^{-14}$ s$^{-1}$.

Fig. A-2. Same as Fig. A-1 for $\zeta = 1.3 \times 10^{-15}$ s$^{-1}$.

Fig. A-3. Same as Fig. A-1 for $\zeta = 1.3 \times 10^{-16}$ s$^{-1}$.