Interstellar detection of the simplest aminocarbyne H$_2$NC: an ignored but abundant molecule\textsuperscript{*}

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ABSTRACT

We report the first identification in space of H$_2$NC, a high-energy isomer of H$_2$CN that has been largely ignored in chemical and astrochemical studies. This observation of various unidentified lines around 72.2 GHz in the cold dark cloud L483 motivated the search and successful detection of additional groups of lines in harmonic relation. Following an exhaustive high-level ab initio screening of possible carriers, we confidently assign the unidentified lines to H$_2$NC based on the good agreement between the astronomical and theoretical spectroscopic parameters alongside sound spectroscopic and astrochemical arguments. The observed frequencies are used to precisely characterize the rotational spectrum of H$_2$NC. This species is also detected in the cold dark cloud B1-b and the $z=0.89$ galaxy in front of the quasar PKS 1830–211. We derive H$_2$NC/H$_2$CN abundance ratios $\sim$1 in L483 and B1-b and 0.27 toward PKS 1830–211. Neither H$_2$NC nor H$_2$CN are detected in the dark cloud TMC-1, which seriously undermines the previous identification of H$_2$CN in this source. We suggest that the H$_2$NC/H$_2$CN ratio behaves as the HNC/HCN ratio, with values close to one in cold dense clouds and below one in diffuse clouds. The reactions N + CH$_3$ and C + NH$_3$ emerge as strong candidates for the production of H$_2$NC in interstellar clouds. Further studies on these two reactions are needed to evaluate the yield of H$_2$NC. Due to the small number of atoms involved, it should be feasible to constrain the chemistry behind H$_2$NC and H$_2$CN, just as has been done for HNC and HCN, as this could allow for the H$_2$NC/H$_2$CN ratio to be applied as a probe of chemical or physical conditions of the host clouds.

Key words. astrochemistry – line: identification – molecular processes – ISM: molecules – radio lines: ISM

1. Introduction

Line surveys of molecular clouds at high spectral resolution are invaluable tools for carrying out molecular spectroscopy in space and for studying fundamental chemical processes. Since the discovery of HCO$^+$, first assigned to an unidentified line (Buhl & Snyder 1970) based on ab initio calculations (Wahlgren et al. 1973) and subsequently confirmed in the laboratory (Woods et al. 1975), several molecular species have been detected in space prior to their characterization in the laboratory, in most cases aided by state-of-the-art ab initio calculations. Examples of this kind are HCS$^+$ (Thaddeus et al. 1981), C$_2$H ($Guelin$ et al. 1978), C$_6$H (Suzuki et al. 1986), and C$_3$H$^+$ (Pety et al. 2012), all of which were subsequently confirmed in the laboratory, as well as the cases of C$_3$N$^+$ (Cernicharo et al. 2008), MgC$_2$N and MgC$_2$H (Cernicharo et al. 2019), and HCN$^+$ (Marcelino et al. 2020), which have not been yet observed in the laboratory. If the source displays narrow lines and the spectral resolution is high enough, it is possible to resolve the hyperfine structure and derive very precise spectroscopic parameters (e.g., Cernicharo et al. 1987). Here, we present a new case of molecular spectroscopy in space. Thanks to sensitive high-spectral resolution observations of the cold dark cloud L483 at mm wavelengths, we detected various groups of unidentified lines, revealing a complex hyperfine structure, which we confidently assign to H$_2$NC. This species is the simplest member of the family of aminocarbyne ligands, well known in organometallic chemistry (Pombeiro et al. 2001). It is also a high-energy metastable isomer of the methylene amidogen radical (H$_2$CN) and, as such, it has been largely ignored in many chemical and astrochemical studies. We however find that in the cold dark clouds L483 and B1-b, H$_2$NC has the same abundance as H$_2$CN itself. These results illustrate nicely how the chemical composition of cold interstellar clouds is driven by chemical kinetics rather than by thermochemical considerations, contrary to the suggestion from Lattelais et al. (2009). In this work, we discuss which chemical reactions could be behind the formation of H$_2$NC, which is a topic that has been overlooked in the literature.

2. Astronomical observations

We recently carried out a line survey of the cold dark cloud L483 in the 80–116 GHz frequency range with the IRAM 30 m telescope (Agúndez et al. 2019). Additional observations of L483 were carried out in December 2018 to cover the 72–80 GHz range. A group of lines spread over a frequency interval of 45 MHz around 72.2 GHz, close to the hyperfine components of the $N=1–0$ transition of CCD, caught our attention when we found we could not assign them using the CDMS$^1$ (Müller et al. 2005), JPL$^2$ (Pickett et al. 1998), nor MADEX$^3$ (Cernicharo 2012) catalogues. The spectral pattern is typical of a molecule.

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\bibitem{madex} https://nanocosmos.iff.csic.es/madex

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Fig. 1. Lines of H$_2$NC observed in L483 (see parameters in Table 1). In red we show the computed synthetic spectra for a column density of H$_2$NC of $10^{12}$ cm$^{-2}$, ortho-to-para ratio of 3, rotational temperature of 4.0 K, full width at half maximum of 0.35 km s$^{-1}$ (except for the $3_{0,3} - 2_{0,2}$ lines, in which case a value of 0.19 km s$^{-1}$ was adopted), and an emission size that fills the IRAM 30 m main beam. Vertical blue lines indicate the position of CCD lines (see Appendix A).
Table 1. Line parameters of H$_2$NC observed in L483.

| $N'$ | $K'_v$ | $K''_v$ | $J'$ | $F'_v$ | $F''_v$ | $F''''$ | $v_{\text{obs}}$ (MHz) | $v_{\text{calc}} - v_{\text{obs}}$ (MHz) | $\Delta v$ (mK) | $T'^*_\text{peak}$ (mK km s$^{-1}$) | $\int T'_{\text{d}v}$ (mK km s$^{-1}$) |
|------|--------|---------|------|--------|---------|---------|----------------------|---------------------|----------|---------------------|---------------------|
| 1    | 0      | 1       | 1.5  | 2.5    | 1.5     | 0       | 0                   | 0.5                 | 0.5     | 1.5                 | 0                   |
| 2    | 2      | 2.5     | 1    | 1      | 1.5     | 1.5     | 0       | 0                   | 0.5                 | 1.5     | 1.5                 | 1.5                 |
| 3    | 3      | 3.5     | 1    | 1      | 1       | 1.5     | 0       | 0                   | 0.5                 | 1.5     | 1.5                 | 1.5                 |
| 4    | 4      | 4.5     | 1    | 0      | 0.5     | 1.5     | 1.5     | 0                   | 0.5                 | 1.5     | 1.5                 | 1.5                 |
| 5    | 5      | 5.5     | 1    | 0      | 0.5     | 1.5     | 1.5     | 0                   | 0.5                 | 1.5     | 1.5                 | 1.5                 |

Notes. Numbers in parentheses are 1σ uncertainties in units of the last digits. Line parameters were derived from a Gaussian fit to the line profile. Observed frequencies are derived adopting $V_{\text{LSR}} = 5.30$ km s$^{-1}$ (Agúndez et al. 2019). Errors in the observed frequencies are estimated from the Gaussian fit and range between 10 kHz, for the lines detected with high signal-to-noise ratios, and 20 kHz, for the weakest lines. $v_{\text{calc}} - v_{\text{obs}}$ is the observed minus calculated frequency, where the calculated frequency comes from the fit described in Sect. 3. $\Delta v$ is the full width at half maximum.
We note that the frequencies of some of the hyperfine components of the \( N = 1–0 \) transition of CCD observed in L483 differ significantly from those given in the CDMS catalogue (Müller et al. 2005). This was already noticed by Yoshida et al. (2019) in their observations of L1527. We therefore used the new frequencies to improve the spectroscopic parameters of CCD (see Appendix A).

We also make use of observations of the cold dark clouds B1-b and TMC-1, as well as observations of the quasar PKS 1830–211. The observations of B1-b and TMC-1 were carried out with the IRAM 30 m telescope in the 72–74 GHz range in August 2018 and are part of a J3 mm line survey of these two sources (see Cernicharo et al. 2012 for more details), while those of PKS 1830–211 were done using the Yebes 40 m telescope in the Q band in a monitoring campaign of this source from April 2019 to July 2020 (see Tercero et al. 2020 for more details). Here, we added data taken during eight observing sessions from October 2019 to the data presented in Tercero et al. (2020). All the data were reduced using the program CLASS of the GILDAS software.

### Table 2. Calculated molecular data for the candidates considered.

| Species | \((B+C)/2\) | G.S. Species | \((B+C)/2\) | G.S. |
|---------|-------------|--------------|-------------|------|
| NNH     | 44.968      | \(^2\)A' H\(_2\)CN\(^*\) | 31.626 | \(^3\)A\(_2\) |
| NNH\(^-\) | 37.605      | \(^3\)A' H\(_2\)CN\(^-\) | 35.117 | \(^1\)A\(_1\) |
| cis-HNNH | 36.763      | \(^1\)A' cis-HCNH\(^+\) | 34.271 | \(^3\)A' |
| H\(_2\)NN  | 36.558      | \(^1\)A' trans-HCNH\(^*\) | 33.004 | \(^3\)A' |
| H\(_2\)NN\(^+\) | 37.971      | \(^2\)B\(_2\) H\(_2\)CN\(^+\) | 38.369 | \(^1\)A\(_1\) |
| HCN\(^+\) | 40.073 \(^{(a)}\) | \(^1\)T\(_1\) cis-HCOH\(^+\) | 36.654 | \(^2\)A' |
| HCN\(^-\) | 44.432 \(^{(a)}\) | \(^2\)Σ trans-HCOH\(^-\) | 36.534 | \(^2\)A' |
| trans-HCNH | 37.125      | \(^2\)A' H\(_2\)NO\(^-\) | 36.815 | \(^1\)A\(_1\) |
| cis-HHCNH | 37.330      | \(^2\)A' cis-HNOH\(^-\) | 35.312 | \(^1\)A' |
| H\(_2\)NC | 36.214      | \(^2\)B\(_2\) tran-HNOH\(^-\) | 35.591 | \(^1\)A' |

**Notes.** \((B+C)/2\) in units of GHz. G.S. stands for ground electronic state.

\(^{(a)}\) Value corresponds to B because this species is linear.

3. **Spectroscopic assignment to H\(_2\)NC**

Potential carriers of the unidentified lines observed in L483 are N\(_2\)H\(_2\), CNH\(_2\), COH\(_2\), NOH\(_2\), CH\(_2\), and O\(_2\)H\(_2\), including neutral or ionic forms. To obtain precise spectroscopic parameters that help in the assignment of the observed lines, we carried out high-level ab initio calculations for all plausible candidates. The geometry optimization calculations for all the candidates considered were done using the spin-restricted coupled cluster method with single, double, and perturbative triple excitations (CCSD(T); Raghavachari et al. 1989), with all electrons (valence and core) correlated and the Dunning’s correlation consistent basis sets with polarized core-valence correlation quadruple-\(\zeta\) (cc-pCVQZ; Woon & Dunning 1995). These calculations were carried out using the Molpro 2020.2 program (Werner et al. 2020). In addition to the rotational constants, we calculated the other parameters necessary for interpreting the rotational spectrum. At the optimized geometries of each species, we calculated the fine and hyperfine constants. They are the three spin–rotation coupling constants \(\epsilon_{a\alpha}, \epsilon_{b\beta}, \text{and } \epsilon_{c\epsilon}\), the magnetic hyperfine constants for the non zero nuclear spin nuclei \(\epsilon_{T_{a\alpha}}, \epsilon_{T_{b\beta}}, \text{and } \epsilon_{T_{c\epsilon}}\), and the nuclear electric quadrupole constants for the nitrogen nucleus \(\epsilon_{Q_{a\alpha}}\) and \(\epsilon_{Q_{b\beta}}\), if the molecule contains any. The spin–rotation coupling constants were calculated using the second order Möller-Plesset perturbation (MP2; Möller & Plesset 1934) with the aug-cc-pVQZ basis set. On the other hand, the other hyperfine constants were calculated at the quadratic configuration interaction with single and double excitations (QCISD; Pople et al. 1987) level of calculation with the aug-cc-pVQZ basis set.

Harmonic frequencies were computed at UCCSD/aug-cc-pVQZ level of theory (Čizek 1969) to estimate the centrifugal distortion constants. These calculations were done using the Gaussian16 program (Frisch et al. 2016).

Given the observed splitting of \(\sim 45\) MHz, it is very unlikely that the carrier is a closed-shell species. Even if the molecule has two N nuclei, the hyperfine splitting would be of a few MHz and the number of lines would be smaller than the observed ones. Hence, the carrier should be an open-shell species containing at least two nuclei with a non zero nuclear spin, so that rotational transitions have fine and hyperfine structure. Taking this into account, closed-shell species such as cis-HNNH, H\(_2\)NN\(^-\), H\(_2\)CN\(^-\), cis-HNOH\(^-\), and trans-HNO\(^-\) were discarded. The value of \((B+C)/2\) derived from astronomical observations is 36.1 GHz, and thus the rotational constants calculated for NNH, HCN\(^+\), HCN\(^-\), H\(_2\)CN\(^+\), cis-HCNH\(^+\), trans-HCNH\(^-\), and H\(_2\)NC\(^-\) clearly exclude them as carriers. In the cases of NNH\(^-\), H\(_2\)NN\(^-\), trans-HCNH, and cis-HCNH, the calculated \((B+C)/2\) are closer to the astronomical value, although the differences are larger than 2.5%. These four candidates can be discarded because the level of calculation used provides errors that are not larger than 1%. In addition, their predicted splitting does not agree with the observed one. For NNH\(^-\), H\(_2\)NN\(^-\), and trans-HCNH, the hyperfine components of the \(1_0,1_0\) transition span over 100–200 MHz, whereas for cis-HCNH, the splitting is very small at around 10 MHz. At this point, only three species show a \((B+C)/2\) value compatible with the observed one, 36.1 GHz. H\(_2\)NC has the closest \((B+C)/2\) value, while cis-HCOH\(^+\) and trans-HCOH\(^+\) have values a bit larger, but also compatible taking into account the accuracy of the calculations. However, cis-HCOH\(^+\) and trans-HCOH\(^+\) have only two nuclei with non zero nuclear spin, and thus, the number of hyperfine components and their splitting pattern cannot explain all the unidentified lines observed in L483. In contrast, H\(_2\)NC has three nuclei with non zero nuclear spin and its predicted splitting is consistent with the observed one. To obtain accurate spectroscopic parameters for our best candidate, H\(_2\)NC, we scaled the calculated values using experimental to theoretical ratios derived for the isoelectronic species H\(_2\)CN, for which experimental rotational parameters are known (Yamamoto & Saito 1992). This procedure has been found to provide rotational constants with an accuracy better than 0.1% (e.g., Cabezas et al. 2021). The theoretical rotational constants \(A, B, \text{and } C\) obtained by this way are given in Table 3. It is seen that the calculated \((B+C)/2\), 36.092 GHz, is very similar to the observed value, which prompted us to consider H\(_2\)NC as the starting point in our data analysis.

The observed frequencies (see Table 1) were analyzed with the SPFIT program (Pickett 1991) using an appropriate Hamiltonian for an asymmetric top with a doublet electronic state \(\Xi\) and \(C\) symmetry. The employed Hamiltonian has the following form:

\[
\mathbf{H} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{sr}} + \mathbf{H}_{\text{nhf}} + \mathbf{H}_{Q}.
\]

where \(\mathbf{H}_{\text{rot}}\) contains rotational and centrifugal distortion parameters, \(\mathbf{H}_{\text{sr}}\) is the spin-rotation term, \(\mathbf{H}_{\text{nhf}}\) represents the
Table 3. Spectroscopic parameters of H$_2$NC (all in MHz).

| Parameter | Astronomical (L483) fit (a) | Theoretical (b) |
|-----------|-----------------------------|-----------------|
| $A$       | 339.669.82                  | 339.669.82      |
| $B$       | 38.085.559(74)              | 38.102.01       |
| $C$       | 34.124.301(74)              | 34.082.34       |
| $\Delta_N$ | 0.13463(16)                | 0.101           |
| $\Delta_K$ | 2.367                      | 2.367           |
| $\delta_N$ | 26.907                     | 26.907          |
| $\delta_K$ | 0.012                      | 0.012           |
| $\epsilon_{aa}$ | 1.758              | 1.758           |
| $\epsilon_{bb}$ | 2319.573               | 2319.573        |
| $\epsilon_{cc}$ | 1.885(59)                | 9.221           |
| $\epsilon_{bc}$ | $-57.17(58)$            | $-54.056$       |
| $\alpha_{(N)}$ | $-22.8656(59)$          | $-21.248$       |
| $\beta_{(N)}$ | 3.417(14)                 | 3.464           |
| $\gamma_{(N)}$ | 0.581                     | 0.581           |
| $\chi_{aa}$ | 0.2125(83)                | 0.212           |
| $\chi_{bb}$ | 1.594                     | 1.594           |
| $\epsilon_{aa}$ | 169.90(23)                | 170.360         |
| $\epsilon_{bb}$ | 9.345(13)                | 8.648           |
| $\epsilon_{cc}$ | $-2.675$                  | $-2.675$        |
| $|\mu|$ | 3.83 (c)                   |                 |

Notes. (a) Numbers in parentheses are 1σ uncertainties in units of the last digits. Parameters without uncertainties were fixed to the theoretical values. (b) The values of the rotational constants $A$, $B$, and $C$ were corrected using the experimental and theoretical constants of H$_2$CN. (c) Calculated using the RCCSD(T)/cc-pCVQZ level of theory, in units of Debye.

magnetic hyperfine coupling interaction term due to the N and H nuclei, and H$_2$O represent the nuclear electric quadrupole interaction due to the N nucleus. The coupling scheme used is $J = N + S$, $F_1 = J + I_1$, and $F = F_1 + I_2$, where $I_1 = I(N)$ and $I_2 = (I(H_1) + I(H_2))$. H$_2$NC has two equivalent H nuclei and it is thus necessary to discern between the ortho and para species. The ortho levels are described by $K_a + K_c$, while the para levels by $K_a + K_c$ odd. The hyperfine interaction term $H_{\text{hf}}$ is thus written explicitly as a two spin system:

$$H_{\text{hf}} = a_F^{(N)} \cdot S \cdot I_1 + I_1 \cdot T^{(N)} \cdot S + a_F^{(H_1)} \cdot S \cdot I_2 + I_2 \cdot T^{(H_1)} \cdot S,$$

(2)

where $a_F^{(N)}$ and $T^{(N)}$ stand for the Fermi contact constant and the dipole-dipole interaction tensor for the N nucleus, respectively, and $a_F^{(H_1)}$ and $T^{(H_1)}$ are averages of the coupling constants for the two H nuclei. There is a term proportional to the difference of the coupling constants for the dipole-dipole interaction. However, the term connects levels only off-diagonal in $K_a$, and thus it can be ignored, treating the two H nuclei as if they are equivalent. In this manner, each energy level is denoted by six quantum numbers: $N, K_a, K_c, J, F_1$, and $F$. The results obtained from the fit are shown in Table 3. We experimentally determined the values for a total of thirteen molecular parameters, considering the two equivalent H nuclei. These parameters are the rotational constants $B$ and $C$, the centrifugal distortion constant $\Delta_T$, the electron spin-rotation coupling constants $\epsilon_{bb}$ and $\epsilon_{cc}$, the magnetic hyperfine constants for the nitrogen and hydrogen nuclei $\alpha_F$ and $T_{aa}$, and the nuclear electric quadrupole constant for the nitrogen nucleus $\gamma_{aa}$. Other constants were kept fixed to the theoretical values calculated in this work. The standard deviation of the fit is 15.2 kHz.

The results in Table 3 show an excellent agreement between the theoretical and astronomical values of the rotational constants $B$ and $C$. The relative errors are 0.01 and 0.06% for $B$ and $C$, respectively. These errors are slightly larger if we compare with the unscaled theoretical values of $B$ and $C$, 0.04 and 0.58%, respectively. The rotational constants provide information on the mass distribution of the molecular species and, thus, the good accordance between observed and calculated values could serve by itself to identify the spectral carrier. Moreover, the high resolution of our survey allows us to completely scrutinize the fine and hyperfine structure of the rotational transitions. This structure depends strongly on the electronic environment of the molecular species, which is related to the number of nuclei with a non zero nuclear spin and their relative positions. Hence, the fine and hyperfine coupling constants determined are ideal fingerprints for the spectral carrier, providing key information for its identification. The results from our fit indicate that our carrier must have two equivalent hydrogen nuclei and one nitrogen nucleus, whose $\alpha_F$ and $T_{aa}$ constants are in very good agreement with those predicted for H$_2$NC. The $\alpha_F$ and $T_{aa}$ values for the two H nuclei are comparable to those of H$_2$CN, 233.152 MHz and 8.294 MHz, respectively (Yamamoto & Saito 1992), which is reasonable since their electronic environment is almost similar in both molecules. However, the $\alpha_F$ and $T_{aa}$ for the N nucleus are very different in H$_2$NC and H$_2$CN. First, the $T_{aa}$ values for H$_2$NC and H$_2$CN are 3.413 MHz and $-45.143$ MHz, respectively, which indicates that the spin density on the N nucleus is much smaller in H$_2$NC. Secondly, the Fermi constants $\alpha_F$ have opposite signs, $-22.8660$ MHz for H$_2$NC and 25.916 MHz for H$_2$CN. This is explained by the different mechanisms for spin polarization due to the unpaired electron on both systems. Figure 2 shows the molecular orbital of the unpaired electron in the two species. In the case of H$_2$NC, the orbital has a node at the location of the N atom, while for H$_2$CN the N atom is completely covered by this orbital. The rest of parameters determined from our fit, $\Delta_T$, $\epsilon_{bb}$, and $\epsilon_{cc}$, agree reasonably well with the values calculated theoretically for H$_2$NC. However, it should be mentioned that the accuracy of the prediction of the constants $\epsilon_{aa}$, $\epsilon_{bb}$, and $\epsilon_{cc}$ is usually much smaller than for the rotational or hyperfine constants. In the light of all these arguments we definitively conclude that the carrier of the unidentified lines observed in L483 is H$_2$NC.

4. Discussion

4.1. H$_2$NC/H$_2$CN ratio in the interstellar medium

We computed synthetic spectra assuming local thermodynamic equilibrium to derive the column density of H$_2$NC in L483. The relative intensities of the various rotational transitions observed
constrain the rotational temperature to a low value, 4.0 ± 0.2 K, which is consistent with a highly polar carrier like H$_2$NC. The calculated dipole moment of H$_2$NC is 3.83 D (see Table 3). As full width at half maximum (FWHM) we adopted the average of the observed values, 0.19 km s$^{-1}$ for the $J_{0,0}$-$2_{0,2}$ lines and 0.35 km s$^{-1}$ for the rest (see Table 1). We derived a beam-averaged column density of $(1.0 ± 0.2) \times 10^{12}$ cm$^{-2}$ for H$_2$NC in L483 (see synthetic spectrum in Fig. 1). The ortho-to-para ratio is fully consistent with the statistical value of three.

H$_2$NC is the highest energy member of the isomeric family composed of H$_2$CN, trans-HCNH, cis-HCNH, and H$_2$NC. Our calculations predict that H$_2$CN is the most stable isomer, with trans-HCNH and cis-HCNH lying above by 7.9 kcal mol$^{-1}$ and 12.8 kcal mol$^{-1}$, respectively, while H$_2$NC lies 29.9 kcal mol$^{-1}$ higher in energy with respect to H$_2$CN. These results are in agreement with those reported by Puzzarini (2010).

A further argument in support of the assignment to H$_2$NC comes from astronomical observations that have indicated that the carrier is related to H$_2$CN. This radical is also observed in L483 (see Agúndez et al. 2019 and Fig. 3). From the observed intensities of the $0_{1,1}$-$0_{0,0}$ and $2_{0,2}$-$1_{0,1}$ lines of H$_2$CN in L483, we derived a rotational temperature of 4 K and a column density of $(8 ± 2) \times 10^{11}$ cm$^{-2}$. This value is somewhat lower than that given by Agúndez et al. (2019) because at that time line absorption at the position of the strongest hyperfine components comes from astronomical observations that have indicated that the carrier is related to H$_2$CN.

The fact that the strongest hyperfine component of H$_2$NC is 3–4 times more intense than the strongest one of H$_2$CN in L483 and B1-b suggests that H$_2$NC could be easily found in those sources where H$_2$NC is detected. H$_2$CN has been reported toward L1544 (Vastel et al. 2019) and the $z = 0.89$ galaxy in front of the quasar PKS 1830–211 (Tercero et al. 2020). We examined our Yebes 40 m data of PKS 1830–211 and find significant absorption at the position of the strongest hyperfine components of H$_2$NC $0_{1,1}$-$0_{0,0}$ (see Fig. 4). We computed synthetic spectra for H$_2$NC and H$_2$CN (red curves in Fig. 4) assuming the same physical parameters of the source reported by Tercero et al. (2020). We derive a H$_2$NC/H$_2$CN abundance ratio of 0.27 ± 0.08. The new data added to the PKS 1830–211 spectrum allow us to clearly distinguish an additional component for H$_2$CN (blue curve; see Tercero et al. 2020). The fact that the H$_2$NC/H$_2$CN ratio is significantly lower than the values found in L483 and B1-b points to a chemical differentiation between this high-redshift galaxy and galactic cold interstellar clouds. In fact, the chemical composition in this lensing galaxy is more characteristic of diffuse or translucent clouds rather than of cold dense clouds, as indicated by the presence of ions such as C$_3$H$^+$. (Tercero et al. 2020). The case of H$_2$NC and H$_2$CN isomers reminds that of HNC and HCN. The HNC/HCN abundance ratio is ~1 in cold dense clouds (Hirot a et al. 1998; Sarrasin et al. 2010) and <1 in diffuse clouds (Liszt & Lucas 2001). In the gravitational lens of PKS 1830–211 the abundance ratio HNC/HCN is 0.4 (Muller et al. 2006), in line with expectations if the source has a diffuse cloud character. Thus, similarly to the case of HNC and HCN, it is likely that in general cold dense clouds show HNC/HCN ratios around one and diffuse clouds H$_2$NC/H$_2$CN ratios below one. The presence of H$_2$NC is therefore a further example of how chemical kinetics, rather than thermodynamics, regulate the chemical composition of interstellar clouds.

### 4.2. Chemistry of H$_2$NC and H$_2$CN

The isomer H$_2$NC is missing in chemical kinetics databases used in astrochemistry, such as UMIST (McElroy et al. 2013) or KIDA.
However, the more stable isomer H$_2$CN is included and it is interesting to look at its main formation reactions. To this end, we ran a pseudo-time-dependent gas-phase chemical model with typical parameters of cold dark clouds (see, e.g., Agúndez & Wakelam 2013). We used the chemical network RATE12 from the UMIST database (McElroy et al. 2013), updated with reactions relevant for the chemistry of H$_2$CN from Loison et al. (2015) and Hickson et al. (2015). According to our calculations, H$_2$CN is formed with a peak abundance relative to H$_2$ of $\sim 10^{-10}$. The main formation reactions are C + NH$_3$, N + CH$_3$, and N + CH$_2$CN, while it is mainly destroyed through reactions with neutral H, C, N, and O atoms. Taking into account that H$_2$NC and H$_2$CN are observed with similar abundances in L483 and B1-b, it is likely that both isomers share a common formation route.

The reaction between N and CH$_3$ has been studied experimentally and theoretically. Experimental studies in the temperature range 200–423 K reveal a rate coefficient around $10^{-10}$ cm$^3$ s$^{-1}$, with a positive temperature dependence, and a branching ratio of 0.9 for production of H atoms (Marston et al. 1991). Computations point to H$_2$CN + H as main channel (Cimas & Largo 2006; Alves et al. 2008). The study of Alves et al. (2008) does not consider H$_2$NC as product, but that of Cimas & Largo (2006) considers H$_2$NC and trans-HCNH. Cimas & Largo (2006) show how the reactants N and CH$_3$ approach via an attractive potential surface leading to an intermediate, H$_2$CN, whose formation does not involve any barrier. This intermediate has two different possibilities for its further evolution. In the first place, elimination of a hydrogen atom would lead to H$_2$CN + H, the most exothermic channel. This process involves a transition state which lies well below the reactants. A second possibility is isomerization into H$_2$CNH, through hydrogen migration from carbon to nitrogen, which proceeds through a transition state also located well below the reactants. H$_2$CNH may lead to trans-HCNH + H involving a lower barrier and a further isomerization into HCNH$_2$ would produce the H$_2$NC + H channel as final product. Although the three isomers, H$_2$CN, trans-HCNH, and H$_2$NC can be formed without any barrier (all the transition states are submerged below the reactants), the elimination of a hydrogen atom from the initially formed intermediate, H$_2$CN, leading to H$_2$CN + H, is the preferred reaction path. Cimas & Largo (2006) state that residual quantities of trans-HCNH can be formed, whereas for H$_2$NC the branching ratio is negligible.

The reaction C + NH$_3$ has been studied more recently and it has been found that it is rapid at 50 K, with a rate coefficient of $1.8 \times 10^{-10}$ cm$^3$ s$^{-1}$ (Hickson et al. 2015). In a related study, Bourgalais et al. (2015) combined photoionization and LIF experiments supported by theoretical calculations and showed that the H$_2$CN + H channel represents 100% of the product yield for this reaction. These authors rule out that trans-HCNH or cis-HCNH are formed, but do not discuss whether H$_2$NC can be produced. The theoretical calculations reported by Bourgalais et al. (2015) show that the first step is the formation of a reaction intermediate, CNH$_3$, in a process without any barrier. As in the case of the H$_2$CN intermediate in the N + CH$_3$ reaction discussed above, CNH$_3$ can proceed through two different pathways. The first one, the elimination of a hydrogen atom, would lead to H$_2$NC + H, through a transition state which lies below the reactants. This reaction path is illustrated in Fig. 5. On the other hand, the isomerization of the CNH$_3$ intermediate through hydrogen migration from nitrogen to carbon can lead to HCN$_2$. This isomerization proceeds through a transition state also located below the reactants. HCNH$_2$ can further evolve to form H$_2$NC + H or trans-HNCN. A second hydrogen migration from nitrogen to carbon in HCN$_2$ produces H$_2$CNH, which ultimately leads H$_2$CN + H, that is the most exothermic channel. Although H$_2$NC + H is not the most exothermic product channel, it could be the most favored channel if we consider the elimination of a hydrogen atom from CNH$_3$ as the preferred reaction path, analogously to the N + CH$_3$ results of Cimas & Largo (2006).

Another fact that reinforces the credibility of the previous statement is that the identification of H$_2$CN as main product in the C + NH$_3$ reaction by Bourgalais et al. (2015) is based exclusively in the agreement between their measured photoionization spectrum and that measured and attributed to H$_2$CN by Nesbitt et al. (1991). However, as discussed by Holzmeier et al. (2013), the ionization energy measured by Nesbitt et al. (1991) is derived from an ion yield curve and it is therefore afflicted with a rather large uncertainty. In fact, Holzmeier et al. (2013) measured an excitation energy of 12.32 eV for H$_2$CN, very different from the value derived by Nesbitt et al. (1991), 10.8 eV. This can be attributed to the fact that the method used by Nesbitt et al. (1991) contains less information than the threshold photoelectron spectra of Holzmeier et al. (2013), which precluded Nesbitt et al. (1991) from distinguishing between isomers. Since the experimental methods employed by Bourgalais et al. (2015) and Nesbitt et al. (1991) are quite similar, it is reasonable to think that both have the same limitations. Hence, if H$_2$NC is formed in the experiment of Bourgalais et al. (2015), it could have escaped detection with their experimental setup.

The reaction between N and CH$_3$CN was considered by Loison et al. (2015) to yield H$_2$CN with a moderately high rate coefficient by analogy to the reaction N + CH$_3$. However, no dedicated studies have been carried out on this particular reaction and thus it is uncertain whether H$_2$CN or any of its metastable isomers are formed. Other plausible routes to H$_2$CN and H$_2$NC are the reactions between radicals NH + CH$_3$ and NH$_2$ + CH, although they are probably less efficient than N + CH$_3$ and C + NH$_3$ because the reactants are expected to have
lower abundances. Formation routes involving ions are also possible, in particular those leading to the various possible isomers \(\text{H}_2\text{CNH}_x\)\(^{(x=0-3)}\), which upon dissociative recombination with electrons can form \(\text{H}_2\text{CN}\) and \(\text{H}_2\text{NC}\). A plausible such route could involve the reaction \(\text{NH}_2^+ + C\), although its rate coefficient and products are not known.

In summary, the two isomers \(\text{H}_2\text{CN}\) and \(\text{H}_2\text{NC}\) can be produced in a barrierless process in the reactions: \(\text{N} + \text{CH}_3\) and \(\text{C} + \text{NH}_3\), with \(\text{H}_2\text{NC}\) being a more likely product of the latter reaction. In the light of our results, it would be interesting to revisit these two reactions and evaluate the yields of the different isomers: \(\text{H}_2\text{CN}\), trans- and cis-\(\text{H}_2\text{NC}\), and \(\text{H}_2\text{NC}\). Other routes are also possible, however the relevant theoretical or experimental information is missing.

5. Conclusions

We observed various sets of unidentified lines in the cold dark cloud L483, which we confidently assign to \(\text{H}_2\text{NC}\), a high-energy metastable isomer of \(\text{H}_2\text{CN}\). The astronomical lines are used to precisely characterize the rotational spectrum of \(\text{H}_2\text{NC}\). Both \(\text{H}_2\text{NC}\) and \(\text{H}_2\text{CN}\) are detected, in addition to L483, in the cold dark cloud B1-b and the high redshift lensing galaxy in front of the quasar PKS 1830–211. Neither \(\text{H}_2\text{NC}\) nor \(\text{H}_2\text{CN}\) are detected in the dark cloud TMC-1, which calls into question a previous claim of detection of \(\text{H}_2\text{CN}\) in this source. We derived \(\text{H}_2\text{NC}/\text{H}_2\text{CN}\) abundance ratios \(\sim 1\) in the cold dense clouds L483 and B1-b and 0.27 in the high-redshift galaxy. It appears that the \(\text{H}_2\text{NC}/\text{H}_2\text{CN}\) ratio behaves as the \(\text{HNC}/\text{HCN}\) ratio, with values around one in cold dense clouds and below one in diffuse and translucent media. The most obvious formation routes to \(\text{H}_2\text{CN}\) and \(\text{H}_2\text{NC}\) are the reactions \(\text{N} + \text{CH}_3\) and \(\text{C} + \text{NH}_3\). The latter is particularly favorable for production of \(\text{H}_2\text{NC}\). Further studies of these reactions able to constrain the yield of each isomer would allow us to improve our understanding of the chemistry behind \(\text{H}_2\text{NC}\) and \(\text{H}_2\text{CN}\). This could open the door to the use of the \(\text{H}_2\text{NC}/\text{H}_2\text{CN}\) ratio as a proxy for the chemical or physical parameters of interstellar clouds.

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Appendix A: New frequencies and spectroscopic parameters for CCD

Yoshida et al. (2019) pointed out that the frequencies of some of the hyperfine components of the $N=1-0$ transition of CCD, as observed in L1527, are significantly different from those reported in the CDMS catalogue (Müller et al. 2005). The predictions from the CDMS catalogue are based in the experimental data reported by Bogey et al. (1985) and Vrtilk et al. (1985), who observed the $N=2-1$, 3-2, 4-3, and 5-4 transitions, but only one hyperfine component of the $N=1-0$ transition. Yoshida et al. (2019) reported observed frequencies in L1527 for seven hyperfine components of the $N=1-0$ transition, with discrepancies with respect to the CDMS ones of up to 224 kHz. The inaccuracy of the $N=1-0$ frequencies reported in the CDMS catalogue is due to the fact that they are calculated based on the laboratory measurements of higher $N$ transitions with a limited spectral resolution, which makes it difficult to discern between close hyperfine components.

In the analysis of our IRAM 30m data of L483, we also noticed that the observed frequencies of the hyperfine components of the $N=1-0$ and 2-1 transitions of CCD differ from those reported in the CDMS catalogue. In order to provide more accurate predictions of the rotational spectrum of CCD, we carried out a fit in which we only include the astronomical frequencies for the $N=1-0$ and 2-1 transitions, along with another fit in which we also include the laboratory frequencies for the $N=3-2$, 4-3, and 5-4 transitions. The spectroscopic parameters resulting from our fits are given in Table A.1, where they are compared with the original values reported by Bogey et al. (1985) and Vrtilk et al. (1985). The frequencies used in the fits are given in Table A.2.

The spectroscopic parameters derived in our two fits are very similar. The main difference is found in the distortion constant, $D$, which is affected by the inclusion of higher $N$ transitions when moving from the astronomical fit to the astronomical + laboratory fit. There is a notable change in the new value of $B$ derived in our fits compared to those derived by Bogey et al. (1985) and Vrtilk et al. (1985), whereas the value of $D$ obtained in our combined fit agrees with those reported by Bogey et al. (1985) and Vrtilk et al. (1985). The new value for $\gamma$ is determined more accurately and also agrees with what has been previously reported. The larger differences are found for the hyperfine constants $b_F$ and $c$, whose previous values also differ between the two laboratory studies. The high resolution of our measurements is reflected in a higher accuracy determination for these hyperfine constants. The nuclear quadrupole coupling constant $eQq$ is also determined more precisely than before, but the previous values agree with the new one. We recommend the spectroscopic parameters derived in our combined astronomical + laboratory fit to predict the rotational spectrum of CCD.


### Table A.1: Spectroscopic parameters of CCD (all in MHz).

| Parameter | Astronomical | Astronomical + Laboratory | Vrtilk et al. (1985) | Bogey et al. (1985) |
|-----------|--------------|---------------------------|----------------------|---------------------|
| $B$       | 36068.01(625) | 36068.01245(153)          | 36068.035(13)        | 36068.03109(75)     |
| $D$       | 0.06709(40)  | 0.067892(126)             | 0.067892(126)        | 0.06764(40)         |
| $\gamma$  | -55.8334(34) | -55.8349(32)              | -55.843(3)           | -55.880(46)         |
| $b_F^{(D)}$ | 6.9918(51)   | 6.9912(49)                | 6.35(7)              | 7.159(85)           |
| $e^{(D)}$ | 1.8893(133)  | 1.8898(127)               | 1.59(26)             | 0.712(73)           |
| $eQq^{(D)}$ | 0.2145(124)  | 0.2166(134)               | 0.219(9)             | 0.23(11)            |
| rms(kHz)  | 14.99        |                            | 31.61                |                     |

$^a$ The parameter $c$ is denoted as $3\sigma$ in Bogey et al. (1985).

References: (1) Frequencies derived in this work from Gaussian fits to the lines observed in L483, adopting $V_L$ = 5.30 km s$^{-1}$ (Agündez et al. 2019). (2) These two lines are affected by a negative frequency-switching artifact in our L483 data and thus frequencies are taken from the L1527 data of Yoshida et al. (2019). (3) Laboratory data of Vrtilk et al. (1985). (4) Laboratory data of Bogey et al. (1985).