The ALMA-PILS survey: detection of CH$_3$NCO towards the low-mass protostar IRAS 16293$-$2422 and laboratory constraints on its formation

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ABSTRACT
Methyl isocyanate (CH$_3$NCO) belongs to a select group of interstellar molecules considered to be relevant precursors in the formation of larger organic compounds, including those with peptide bonds. The molecule has only been detected in a couple of high-mass protostars and potentially on comets. A formation route on icy grains has been postulated for this molecule but experimental evidence is lacking. Here we extend the range of environments where methyl isocyanate is found and unambiguously identify CH$_3$NCO through the detection of 43 unblended transitions in the ALMA Protostellar Interferometric Line Survey (PILS) of the low-mass solar-type protostellar binary IRAS 16293$-$2422. The molecule is detected towards both components of the binary with a ratio HNCO/CH$_3$NCO $\sim$ 4$-$12. The isomers CH$_3$CNO and CH$_3$OCN are not identified, resulting in upper abundance ratios of CH$_3$NCO/CH$_3$CNO $>$ 100 and CH$_3$NCO/CH$_3$OCN $>$ 10. The resulting abundance ratios compare well with those found for related N-containing species towards high-mass protostars. To constrain its formation, a set of cryogenic UHV experiments is performed. VUV irradiation of CH$_4$:HNCO mixtures at 20 K strongly indicate that methyl isocyanate can be formed in the solid state through CH$_3$ and (H)NCO recombinations. Combined with gas-grain models that include this reaction, the solid-state route is found to be a plausible scenario to explain the methyl isocyanate abundances found in IRAS 16293$-$2422.

Key words: astrochemistry – molecular processes – techniques: spectroscopic – ISM: individual objects: IRAS 16293$-$2422 – ISM: molecules.

1 INTRODUCTION
Complex organic molecules, defined in astrochemistry as molecules that consist of six or more atoms of which at least one is a carbon atom, are widely found in star-forming regions (Herbst & van Dishoeck 2009). A special category of complex molecules is that of the prebiotics, molecules that can be linked via their chemical structures or reactivity to life bearing molecules, such as amino acids and sugars. Methyl isocyanate (CH$_3$NCO), also known as isocyamethane, is a molecule that falls in this category because of its structural similarity with a peptide bond (Fig. 1). This type of bond connects amino acids to form proteins and as such is interesting because it connects to chemistry relevant to the formation of the building blocks of life.

The majority of identified complex molecules has mainly been detected towards high-mass hot cores, such as Orion KL and Sgr B2 (e.g. Blake et al. 1987; Nummelin et al. 2000; Belloche et al. 2013, 2014; Tercero et al. 2013; Crockett et al. 2014; Neill et al. 2014), but over the past decades detections towards low-mass, sun-like, protostars such as IRAS 16293$-$2422 (hereafter IRAS16293) have been regularly reported as well. IRAS16293 (d = 120 pc) is considered as a protostellar template for
low-mass sources and is particularly rich in organic molecules (van Dishoeck et al. 1995; Cazaux et al. 2003; Bottinelli et al. 2004; Kuan et al. 2004; Bisschop et al. 2008; Jaber et al. 2014). Jørgensen et al. (2012) demonstrated the capabilities of the Atacama Large Millimeter/submillimeter Array (ALMA) with the detection of the prebiotic molecule glyceraldehyde (see also Jørgensen et al. 2016, for a history of chemical studies of this source). More recently, other complex molecules (acetone, propanal and ethylene oxide) were identified in the framework of the Protostellar Interferometric Line Survey (PILS) (Lykke et al. 2017). Even the deuterated isotopologues of several complex molecules were detected towards this source (Parise et al. 2003; Coutens et al. 2016; Jørgensen et al. 2016).

Unlike other molecules such as isocyanic acid (HNCO) and formamide (NH₂CHO; Bisschop et al. 2007; López-Sepulcre et al. 2015; Coutens et al. 2016), which have a similar peptide-like structure as methyl isocyanate, CH₃NCO only recently started to attract attention in the astrochemistry community. This activity was inspired by a report from Goesmann et al. (2015) that CH₃NCO may be abundantly present on the surface of comet 67P/Churyumov-Gerasimenko, as measured with the Cometary Sampler and Composition (COSAC) instrument of Rosetta’s Philae lander. Its measured high abundance of 1.3 per cent with respect to H₂O and CH₃NCO/HNCO = 4.3 was based on the assumption that the mass peak recorded at m/z = 57 is dominated by CH₃NCO, as COSAC’s low-mass resolution does not allow discrimination of different species with nearly identical mass. Recent measurements with the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) at much higher mass resolution showed that the CH₃NCO coma abundance is significantly lower (K. Altwegg, private communication). Nevertheless, the possibility of linking complex molecules in star- and planet-forming regions with those present in comets triggered the search for methyl isocyanate in the interstellar medium.

Interstellar CH₃NCO was first detected towards Sgr B2(N) by Halfen, Ilyushin & Ziurys (2015) at low rotational temperatures of ~25 K with a column density ratio of N(HNCO)/N(CH₃NCO) = 35–53 depending on the specific velocity component. Cernicharo et al. (2016) detected methyl isocyanate towards Orion KL at N(HNCO)/N(CH₃NCO) ≃ 15 and T_{ex} = 150 K. Their observations towards the cold pre-stellar core B1-b did not yield a detection of the molecule down to an upper column density limit of <2 × 10^{11} cm⁻² or N(HNCO)/N(CH₃NCO) > 42 (based on an HNCO detection towards the same source by López-Sepulcre et al. 2015). In the same paper, publicly accessible Sgr B2 observations from Belloche et al. (2013) were re-analysed with an updated spectral line list and, interestingly, yielded a detection of warm methyl isocyanate at T_{ex} ≃ 200 K and N(HNCO)/N(CH₃NCO) ≃ 40. Attempts to also identify the methyl isocyanate isomer CH₃CNO were unsuccessful down to N(CH₃NCO)/N(CH₃CNO) > 100.

The astrochemical origin of methyl isocyanate is not yet understood and this is partly due to the limited number of laboratory studies that have been performed. Henderson & Gudipati (2015) tentatively assigned a mass fragmentation peak to CH₃NCO after Vacuum UV (VUV) irradiating solid-state mixtures of NH₂CH₃OH. In other experiments by Ruiz & Anderson (2012) UV irradiation of frozen n-methylformamide (CH₃NHCHO) also yielded methyl isocyanate, although it was concluded to represent a minor product channel.

A number of formation routes have been hypothesized by astrochemists. Halfen et al. (2015) postulated gas-phase formation by HNCO or HOCN methylation:

\[ \text{HNCO/HOCN(g)} + \text{CH}_3(g) \rightarrow \text{CH}_3\text{NCO}(g) + \text{H}(g) \]  

or reactions of HNCO or HOCN with protonated methane, followed by electron recombination:

\[ \text{HNCO/HOCN(g)} + \text{CH}_3^+ (g) \rightarrow \text{CH}_3\text{NCOH}^+(g) + \text{H}_2(g) \]  

\[ \text{CH}_3\text{NCOH}^+(g) + e^- \rightarrow \text{CH}_3\text{NCO}(g) + \text{H}(g) \]  

Cernicharo et al. (2016) favoured solid-state formation mechanisms based on the detection of CH₃NCO towards hot cores and its non-detection in the cold-dark cloud B1-b. Particularly, the methylation of HNCO has been mentioned as a possible route to form methyl isocyanate in the solid state, i.e. on the surface of an icy dust grain:

\[ \text{HNCO(s)} + \text{CH}_3(s) \rightarrow \text{CH}_3\text{NCO(s)} + \text{H(s)} \]  

Belloche et al. (2017) used the grain-surface radical-addition reaction CH₃ + NCO → CH₃NCO in their models, with most of the NCO formed via H-abstraction of HNCO:

\[ \text{HNCO(s)} + \text{H}(s) \rightarrow \text{NCO(s)} + \text{H}_2(g) \]  

\[ \text{NCO(s)} + \text{CH}_3(g, s) \rightarrow \text{CH}_3\text{NCO(s)} \]  

These postulated routes require the reactants to be present in sufficient amounts. Gaseous HNCO is detected in high abundances in protostellar environments and has been imaged in IRAS16293, showing it to be prominent in both sources A and B (Bisschop et al. 2008; Coutens et al. 2016). It likely results from sublimation of OCN⁻, known to be a major iced component in low-mass protostellar envelopes (van Broekhuizen et al. 2005). A significant abundance of CH₃ gas is a more speculative assumption since the molecule can only be observed by infrared spectroscopy and has so far only been seen in diffuse gas towards the Galactic Center (Feuchtgruber et al. 2000). Alternatively, CH₃ radicals can be produced in situ in ices by photodissociation of known abundant ice components like CH₃OH or CH₃NCO and then react with HNCO or OCN⁻. This is the solid-state route that is investigated here.

In this work, we present the first detection of methyl isocyanate towards both components of the low-mass protobinary IRAS16293 on scales of <100 au. An independent detection towards source B is also reported by Martín-Doménech et al. (2017). A set of systematic laboratory experiments is presented in order to validate the solid-state formation routes of CH₃NCO. The observational work is presented in Section 2 and the laboratory work in Section 3. In Section 4, the results of the observations and laboratory experiments are compared and discussed in the context of recent astrochemical models. The conclusions of this paper are given in Section 5.
### 2 OBSERVATIONS

#### 2.1 The ALMA PILS survey

We searched for methyl isocyanate in the PILS data, an unbiased spectral survey of the low-mass protostellar binary IRAS16293 with ALMA. A full description and data reduction of the survey is presented in Jørgensen et al. (2016). Briefly, this survey covers a spectral range from 329.147 to 362.896 GHz and was obtained with both the 12 m array and the Atacama Compact Array (ACA). The beam size ranges between ~0.4 and 0.7 arcsec depending on the configuration at the time of the observations. The rms of the combined data sets is about 7–10 mJy beam$^{-1}$ channel$^{-1}$, i.e. approximately 4–5 mJy beam$^{-1}$ km s$^{-1}$. To facilitate the analysis, the combined data set used in this paper was produced with a circular restoring beam of 0.5 arcsec at a spectral resolution of 0.2 km s$^{-1}$.

Two positions are analysed in this study. The first position is offset by one beam diameter (~0.5 arcsec) from the continuum peak of source B in the south-west direction ($\alpha_{\text{J2000}} = 16^h32^m22.58^s$, $\delta_{\text{J2000}} = −24°28′32″$) (see high-resolution images in Baryshev et al. 2015).

Source B presents narrow lines (FWHM ~ 1 km s$^{-1}$). This position is found to be optimal for line identifications, as the lines are particularly bright, do not have strong absorption features towards the bright continuum of source B and do not suffer from high continuum optical depth (Coutens et al. 2016; Jørgensen et al. 2016; Lykke et al. 2017). In this paper, we also analyse source A, which exhibits broader lines than source B making the line identification quite challenging (Pineda et al. 2012). The linewidth varies, however, depending on the spatial separation from this source. With an average FWHM of ~2.5 km s$^{-1}$, the position $\alpha_{\text{J2000}} = 16^h32^m22.90^s$, $\delta_{\text{J2000}} = −24°28′36″$ appears to be one of the best positions to search for new species towards source A (0.3 arcsec offset). At this position, the emission is centred at $v_{\text{LSR}} = 0.8$ km s$^{-1}$, blueshifted from the source A velocity of $v_{\text{LSR}} = 3.2$ km s$^{-1}$ (Jørgensen et al. 2011).

Bisschop et al. (2008) found HNCO and other nitrogen containing species such as CH$_3$CN to be more prominent towards source A than source B. Consequently, it is also interesting to check whether there exists a small-scale chemical differentiation amongst the N-bearing species for the two sources.

#### 2.2 Results

Methyl isocyanate is detected towards both components A and B of IRAS16293. The identification is based on spectroscopic data from the Cologne Database for Molecular Spectroscopy (CDMS, Müller et al. 2001, 2005), taken from Cernicharo et al. (2016) as well as from Koput (1986). CH$_3$NCO is an asymmetric rotor with the NCO group lying at an angle of 140° and a low-lying (~182 cm$^{-1}$) C–N–C stretching mode ($v_b$). Moreover, the barrier to internal rotation of the CH$_3$ group is low, only 21 cm$^{-1}$. The pure rotational spectrum therefore has A and E torsional states and vibrationally excited transitions can become detectable at temperatures of a few hundred K.

The labelling of the states used here refers to the quantum numbers $J$ (rotational angular momentum), $K_a$ and $K_c$ (projection of angular momentum on the respective inertial axes) with internal rotation interactions indicated by the quantum number $m$, with $m= 0$ and ±3 for the A states and $m= 1, −2$ and 4 for the E states (Halfen et al. 2015; Cernicharo et al. 2016).

Using the CASSIS software, we have been able to identify 43 unblended lines of CH$_3$NCO in the bending ground state ($v_b = 0$) with upper energy levels $E_{\text{up}}$ ranging from 320 to 670 K towards source B (see Table A1). Fig. 3 shows the unblended lines detected towards this component as well as the LTE modelling for two different excitation temperatures at 100 and 300 K. Both excitation temperatures allow us to reproduce the observations; only predicted transitions are observed. Our data are not sensitive to any cold CH$_3$NCO component since lines with low $E_{\text{up}}$ values are missing in the spectral range of the PILS survey. Amongst the complex molecules that were detected and analysed towards source B, some (acetaldehyde and ethylene oxide) exhibit a relatively low excitation temperature of ~125 K (Lykke et al. 2017), while others (formamide, isocyanic acid, methanol, methyl formate, glycolaldehyde and ethylene glycol) show a higher excitation temperature of ~300 K (Jørgensen et al. 2012; Coutens et al. 2016; Jørgensen et al. 2016). Their spatial distribution is however rather similar and it is not possible to determine to which category CH$_3$NCO belongs. The methyl isocyanate column density is not very sensitive to the exact value of the excitation temperature: assuming the same source size of 0.5 arcsec as used in the previous PILS studies (Coutens et al. 2016; Jørgensen et al. 2016; Lykke et al. 2017), the CH$_3$NCO column density is found to be about $3 \times 10^{15}$ and $4 \times 10^{15}$ cm$^{-2}$ for $T_{\text{ex}} = 300$ and 100 K, respectively. All lines are optically thin. It is expected that for the same assumptions all column densities towards source B are accurate to better than 30 per cent.

Towards source A, most of the lines are blended due to the larger linewidths (~2.5 km s$^{-1}$). We can, however, identify 11 unblended lines of CH$_3$NCO (see Fig. 4). A column density of ~6 $\times 10^{15}$ and ~9 $\times 10^{15}$ cm$^{-2}$ (assuming a source size of 0.5 arcsec) is in good agreement with observations for excitation temperatures of 300 and 100 K, respectively, again with an uncertainty of about 30 per cent.

At high excitation temperatures, rotational levels in the first excited bending state ($v_b = 1$) may be populated as well and predictions for possible transitions are shown in Fig. B1. For $T_{\text{ex}} = 300$ K, some faint lines can indeed be tentatively attributed to CH$_3$NCO $v_b = 1$ transitions towards source B. An integrated intensity map of one of the brightest CH$_3$NCO lines, the 39$_0,39,0–380,38,0$ transition at 336 339.9 MHz, is presented in Fig. 2. Similarly to other complex molecules, the emission is quite compact with a size of ~60 arc radius and centred near the two sources, with little difference between them (Coutens et al. 2016; Jørgensen et al. 2016; Lykke et al. 2017). For source B, the emission is somewhat offset due to the continuum becoming optically thick on source.

We also searched for spectral evidence of two isomers of methyl isocyanate – acetonitrile oxide (CH$_3$CNO; Winnewisser et al. 1982) and methyl cyanate (CH$_3$OCN; Sakaizumi et al. 1990; Kolesniková et al. 2016) – but the corresponding transitions were not found in the PILS data set. From this non-detection, 3σ upper limits of 5 $\times 10^{13}$ and 5 $\times 10^{14}$ cm$^{-2}$ are derived, respectively (assuming an excitation temperature of 100 K). These isomers are consequently less abundant than methyl isocyanate by at least two and one orders of magnitude, in agreement with recent findings towards Orion KL (Cernicharo et al. 2016; Kolesniková et al. 2016).

In view of the important role that HNCO and HOCN may play in the formation of CH$_3$NCO, we also searched for spectral signatures of these precursor species. The analysis of the PILS data for HOCN towards source B is presented in Coutens et al. (2016). The HNCO lines are optically thick, so lines of the isotopologue HN$^{13}$CO were analysed and the HNCO column density was derived assuming a $^{12}$C/$^{13}$C ratio of 68 (Milam et al. 2005). To get precise abundance ratios, we re-analysed the HN$^{13}$CO data using the same data set (with the circular restoring beam of 0.5 arcsec) and obtained
an HNCO column density of $3.7 \times 10^{16}$ cm$^{-2}$, which is within the 30 per cent uncertainty range. The resulting HNCO/CH$_3$NCO abundance ratio is about 12 towards source B with an uncertainty of less than a factor of 2. Within the error margins, this is similar to the value derived in Orion KL (Cernicharo et al. 2016) or Sgr B2(N2) (Belloche et al. 2016, 2017). For source A, the column density of HNCO is estimated to be about $3.4 \times 10^{16}$ cm$^{-2}$ ($T_{ex} = 100$ K). The corresponding HNCO/CH$_3$NCO ratio is consequently about 4 towards this component, with a somewhat larger uncertainty of a factor of 3 due to the difficulty of deriving a precise column density for HNCO because of line blending. Overall, we can conclude that the two HNCO/CH$_3$NCO ratios are comparable towards the two components of the binary.

Whereas HNCO is readily identified, this is not the case for HOCN. No HOCN lines were detected and a $3\sigma$ upper limit of $3 \times 10^{13}$ cm$^{-2}$ is derived towards source B. HOCN is consequently less abundant than HNCO and CH$_3$NCO by at least three and two orders of magnitude, respectively. Therefore, it is highly unlikely that the gas-phase formation pathway involving HOCN, as proposed by Halfen et al. (2015) in equations (1) and (2), contributes significantly to the production of methyl isocyanate in this source.

We have also determined the abundance ratios of CH$_3$NCO with respect to CH$_3$OH and CH$_3$CN for comparison with other sources in which methyl isocyanate has been detected (see Table 1). The column density of CH$_3$OH was estimated based on CH$_3^+$OH by Jørgensen et al. (in preparation) for the one beam offset position towards source B ($\sim 1 \times 10^{19}$ cm$^{-2}$) using a $^{16}$O/$^{18}$O ratio of 560 (Wilson & Rood 1994). With the same assumptions, we estimate a column density of CH$_3$OH of $\sim 2 \times 10^{19}$ cm$^{-2}$ in source A. CH$_3$CN was analysed by Calcutt et al. (in preparation) towards both source A ($\sim 8 \times 10^{16}$ cm$^{-2}$) and source B ($\sim 3 \times 10^{16}$ cm$^{-2}$). Similarly to the HNCO/CH$_3$NCO ratio, the abundance ratio of CH$_3$CN/CH$_3$NCO is comparable to the values found in Orion KL (Cernicharo et al. 2016) and lower than towards Sgr B2(N1), but again comparable to Sgr B2(N2) (Belloche et al. 2016, 2017). Methanol is, however, clearly more abundant than methyl isocyanate towards IRAS16293 than towards Orion KL and Sgr B2.

The HNCO/CH$_3$NCO and CH$_3$CN/CH$_3$NCO abundance ratios derived in IRAS16293 are much larger than the lower limits found in comet 67P ($\sim 0.2$). A proper comparison awaits the new results derived with the ROSINA instrument (Altwegg et al. in preparation).

3 LABORATORY EXPERIMENTS

Grain-surface formation routes of complex molecules have been investigated experimentally for many years using cryogenic set-ups to mimic specific chemical processes under fully controlled laboratory conditions (see Herbst & van Dishoeck 2009; Linnartz, Ioppolo & Fedoseev 2015, for reviews). In the present work, the formation of methyl isocyanate is investigated by energetically processing solid-state CH$_3$NCO mixtures with vacuum-UV radiation. VUV irradiated methane ice is known to efficiently yield methyl radicals (Bossa et al. 2015), and these radicals are expected to further react through surface diffusion with HNCO to form CH$_3$NCO, as proposed by Goesmann et al. (2015) and Cernicharo et al. (2016), reaction (4). The Cryogenic Photoproduction Analysis Device 2 (CryoPAD2) in the Sackler Laboratory for Astrophysics is used to perform the measurements to investigate the role of methylation of HNCO in methyl isocyanate formation. A short description of this set-up, experimental procedure and reference data is given below.

Note that in these experiments CH$_4$ is used as the parent of CH$_3$ but in interstellar space methyl radicals active in the ice may also originate from CH$_3$OH dissociation (Öberg et al. 2009) or from direct CH$_4$ accretion from the gas phase. The main aim of this section is to investigate whether or not the proposed solid-state reaction as shown in reaction (4) can proceed at temperatures typical for dark cloud conditions in the interstellar medium (ISM), i.e. independent of the exact precursor species.

3.1 Set-up and method

CryoPAD2 consists of a central chamber operating under ultrahigh vacuum conditions ($P \approx 10^{-10}$ mbar), to which various instruments are attached. On the top a cryostat is mounted which cools a gold-coated reflective surface down to 12 K. The temperature of this surface can be controlled through resistive heating and varied between 12 and 300 K, with an absolute temperature accuracy better than 1 K. Pure and mixed gases are prepared separately in a gas-mixing system which is attached to a high-precision leak valve to the main chamber and which doses the gases on to the cooled surface. The deposited ice samples are irradiated with VUV radiation from a Microwave Discharge Hydrogen-flow Lamp (MDHL), which emits radiation peaking at 121 nm and a region between 7.5–10.2 eV (Chen et al. 2014; Ligterink et al. 2015). The total lamp flux is $(1.1 \pm 0.1) \times 10^{12}$ photons s$^{-1}$ that is determined using a calibrated NIST diode. CryoPAD2 possesses two diagnostic tools to monitor the VUV-induced processes in the ice. The beam of a Fourier-Transform IR Spectrometer (FTIRS) is directed under grazing incidence on to the gold-coated surface, in order to perform Reflection Absorption IR Spectroscopy (RAIRS). The sample preparation and chemical changes under influence of VUV radiation are monitored by recording vibrational fingerprint spectra of molecules on the surface. To decrease the perturbing role of atmospheric CO$_2$ and H$_2$O, the system is purged with filtered dry air. The second instrument is a highly sensitive Quadrupole Mass Spectrometer (QMS), with an ionization element at 70 eV, which is able to
trace gas-phase molecules in the chamber that are released from the ice surface upon linear heating during a temperature-programmed desorption (TPD) experiment. TPD is a very useful method that allows to identify desorbing species through their specific desorption temperature and mass fragmentation pattern. Unambiguous identifications become possible through the use of isotopologues and searching for the corresponding mass shifts of specific fragments. Obviously, TPD comes with the destruction of the ice.
In the experiments CH₄ (Linde Gas, 99.995 per cent purity), \(^{13}\)CH₂ (Sigma-Aldrich, 99 per cent purity) and HNCO are used. HNCO is produced from cyuranic acid (Sigma-Aldrich, 98 per cent purity), the solid trimer of HNCO, following the protocol described in van Broekhuizen, Keane & Schutte (2004). Impurities of the HNCO production process are removed by freeze–thaw cycles to obtain an HNCO purity of \(>99\) per cent.

For the experiments, samples of pure HNCO and methane and mixtures of \(^{13}\)CH₂/CH₄:HNCO at 5:1 ratio are prepared. This ratio is within a factor of 2 of that observed for interstellar ices (Öberg et al. 2011) but is particularly chosen to create a large abundance of CH₃ radicals to test whether reaction (4) proceeds or not. Homogeneously mixed ices are grown on the surface at 20 K and irradiated with a total fluence of \(\sim 3.3 \times 10^{17}\) photons. During irradiation of the sample, IR spectra are continuously recorded at 1 cm\(^{-1}\) resolution. After the irradiation TPD is started, while still recording IR spectra.

The strongest vibrational features of solid methyl isocyanate are found between 2320 and 2280 cm\(^{-1}\) (\(\sim 4.34\) \(\mu\)m) for the \(-N=C=O\) antisymmetric stretching vibration and overtone 2\(\nu_7\) CH₃ rocking mode. Sullivan et al. (1994) lists these at 2320, 2280, 2270, 2240 and 2228 cm\(^{-1}\), with 2280 cm\(^{-1}\) being the strongest band. Zhou & Durig (2009) positioned all bands around 2300 cm\(^{-1}\) and Revá, Lapinska & Fausto (2010) put the band for methyl isocyanate in a nitrogen matrix at 2334.7, 2307.9, 2288.9, 2265.2 and 2259.7 cm\(^{-1}\), finding the strongest transition at 2288.9 cm\(^{-1}\). The region around these bands is used to monitor CH₃NCO formation in the ice. After the irradiation TPD is started, while still recording IR spectra.

In order to identify methyl isocyanate in the gas phase using TPD, the mass fragmentation pattern available from the NIST data base\(^2\) is used. The fragmentation pattern at 70 eV comprises unique peaks at \(m/z = 57\) and 56 (hereafter also called the primary and secondary mass peaks), which have an \(m/z = 57:56\) ratio of 5:2 and these will be used as main TPD mass tracers. Known products of pure HNCO and methane irradiation do not have a mass fragmentation peak at \(m/z = 57\) (see also Appendix C).

It is important to mention that methyl isocyanate is severely toxic and specialized laboratories and equipment are needed to work with this substance. This complicates the extensive use of this species and for this reason additional experiments, starting from the pure precursor, have not been performed.

\(^2\)NIST Mass Spec Data Center, S.E. Stein, director, ‘Mass Spectra’ in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Lindstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

Table 1. Comparison of molecular abundance ratios towards different sources.

| Source          | HNCO/CH₃NCO | CH₃CN/CH₃NCO | CH₃OH/CH₃NCO | Reference             |
|-----------------|-------------|--------------|---------------|-----------------------|
| IRAS16293 B     | 12          | 8            | 3333          | This work             |
| IRAS16293 A     | 4           | 9            | 3200          |                      |
| Orion KL A      | 15          | 10           | 400           | Cernicharo et al. (2016) |
| Orion KL B      | 15          | 25           | 225           |                      |
| Sgr B2(N1)      | 40          | 50           | 40            |                      |
| Sgr B2(N2)      | 9           | 10           | 182           | Belloche et al. (2016, 2017) |
| Comet 67P/C-G   | >0.2        | >0.2         | –             | Goesmann et al. (2015) |
|                 |             |              |               | Altwegg et al. (in preparation) |
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3.2 Results – IR Spectra

Fig. 5 presents the IR spectra recorded during the first $1 \times 10^{17}$ photons irradiating the $^{12}$/$^{13}$CH$_3$:HNCO samples. All spectra are normalized to the HNCO peak. Three known spectroscopic features of CO$_2$, OCN$^-$ and CO (blue) show up during irradiation. Also, two new features become visible around 2300 cm$^{-1}$ (red), which do not show up while processing samples of pure HNCO or CH$_4$. Also, a clear redshift of about 10 cm$^{-1}$ of the two features is seen between the sample of $^{12}$CH$_4$ and $^{13}$CH$_4$, moving transitions at 2322 and 2303 cm$^{-1}$ to 2313 and 2294 cm$^{-1}$. These spectroscopic features are therefore the result of a product formed in the reaction between methane and isocyanic acid, and, since they are found close to known CH$_3$NCO features (given by Sullivan et al. 1994; Reva et al. 2010), are plausibly identified with methyl isocyanate. Another feature is seen in the wing of the HNCO peak around 2235 cm$^{-1}$, which does not clearly shift with methane isotopologues. The origin of this band is unclear.

Bandstrength values for methyl isocyanate are not available from the literature; however, a rough indication of the amount of formed methyl isocyanate versus lost HNCO can be given by making the assumption that the bandstrength of the NCO antisymmetric stretch vibration of methyl isocyanate equals that of the corresponding vibration of HNCO. To obtain the ratio, the integrated area of the 2303 cm$^{-1}$ feature is divided by the integrated loss area of the 2265 cm$^{-1}$ HNCO band for a number of spectra. A ratio of $N$(HNCO)/$N$(CH$_3$NCO) = 100–200 is found, which is about an order of magnitude higher than the ratio observed towards IRAS16293. It should be noted that it is not apriori clear whether solid-state laboratory and gas-phase astronomical abundances can be directly compared (see e.g. Chuang et al. 2017). It is likely that ongoing gas-phase reactions, for one or the other species, change the solid state to gas-phase ratios. It is also possible that non-linear RAIRS effects can offset the column density (Teolis et al. 2007) or that the CH$_3$NCO bandstrength is significantly different. In a same manner, CH$_3$NCO photodestruction may affect the overall abundances.

3.3 Results – temperature-programmed desorption

The desorption temperature of methyl isocyanate has not been reported in the literature, but the TPD traces of our experiments on UV processed CH$_3$:HNCO ices do show the combined release of the primary and secondary masses of $^{12}/^{13}$CH$_3$NCO. Both the primary and secondary masses are seen being released around 145 K (blue line). The secondary mass shows another release peak around 205 K (green), which is suspected to also contribute to first release peak, thus altering respectively the $m/z$ 57/56 and 58/57 ratio.

The verification experiment of pure HNCO did not show these masses and only $m/z$ = 56 (and no 57) was seen after the irradiation of pure methane ice, releasing at 105 K (Fig. C1 in the Appendix). At the 145 K desorption peak the primary over secondary mass ratio is around 1–1.5, lower than the value of 2.5 suggested by NIST upon 70 eV electron impact ionization. The NIST calibration values are a good indicator of the values to be expected, but are to some extent set-up specific. In such cases, the expected reactant can be deposited directly and the fragmentation pattern can be studied and adapted to the set-up in use. This is
unfortunately not possible here due to the aforementioned toxicity of methyl isocyanate. Moreover, contributions from other reaction products cannot be fully excluded. In Fig. 6B a second desorption peak is found around 205 K, which is seen only as a shoulder in panel A. It is unlikely that this peak is associated with methyl isocyanate, instead it shows that the chemical network involves the formation of other species as well. In fact, since the additional product(s) have a mass fragmentation pattern that contributes to the secondary mass of methyl isocyanate, this could explain why the primary/secondary mass ratio does not exactly match with that given by NIST. Additionally, the unidentified product of pure methane irradiation could be trapped in the ice and contribute to other desorption peaks. Therefore, the 145 K desorption peak is still consistent with methyl isocyanate. There is also no other candidate molecule with a primary mass of 57 in the NIST data base that could plausibly explain the TPD spectra.

CryoPAD2 offers the unique feature to combine IR and TPD data, i.e. at the moment a specific ice feature starts thermally desorbing, the IR signal starts decreasing and simultaneously the mass signal starts increasing. In the measurements presented here, this effect is not as clearly visible as in the previous studies (e.g. Öberg et al. 2009), but this may be partly due to the low final S/N of the feature, making it difficult to link RAIRS and TPD signals. The present data are as accurate as possible, but obviously their interpretation would benefit from focused experiments determining the thermal desorption peak of pure CH₃NCO and the IR band strengths.

4 LINKING OBSERVATIONS AND LABORATORY DATA

Methyl isocyanate is detected in a significant abundance towards both components of IRAS16293 with an excitation temperature of at least 100 K. The two isomers, CH₃CNO and CH₃OCN, are not detected. Abundance ratios with respect to HNCO and CH₃CN are similar to those found towards Orion KL and comparable within a factor of a few to Sgr B2, making a common formation pathway in these three sources likely. Moreover, no chemical differentiation between sources A and B is found. Gas-phase production of CH₃NCO via HOCN (reaction 1) can be seen as insignificant due to the low upper limit on this molecule, but a gas-phase route involving HNCO cannot be excluded.

The laboratory experiments on the formation of CH₃NCO strongly suggest that a solid-state formation scheme is possible, starting from two astronomically relevant precursor species, CH₃ and HNCO. The proposed reaction $\text{CH}_4 + \text{HNCO} \rightarrow \text{CH}_3\text{NCO} + \text{H}$ indeed seems to proceed, confirming a solid-state reaction pathway, but other routes such as hydrogen stripping $\text{CH}_3 + \text{HNCO} \rightarrow \text{CH}_2 + \text{NCO}$ may take place in parallel. Reactions involving the OCN⁻ anion, which is abundantly formed in these experiments, provide alternative routes. Irradiation of a sample of OCN⁻ with VUV light, generating methyl radicals as reactive intermediates to form methyl isocyanate.

The detection of CH₃NCO adds to the growing list of complex molecules known to be present around solar mass protostars, showing that the ingredients for prebiotic molecules are abundant. Future deeper searches for even more complex molecules relevant for the origin of life are warranted.

5 CONCLUSIONS

The main observational and experimental conclusions are listed below:

(i) Methyl isocyanate is detected for the first time towards a low-mass protostar, IRAS16293, on Solar system scales (emission radius of 60 au). Column densities of $\sim (3-4) \times 10^{15}$ and $\sim (6-9) \times 10^{15}$ cm$^{-2}$ are obtained towards sources B and A, respectively, yielding $N(\text{HNCO})/(N(\text{CH}_3\text{NCO}) = 12$ and 4, with no significant variation between the two sources.

(ii) The abundance ratios of CH₃NCO relative to the N-bearing species HNCO and CH₃CN are similar to those found towards Orion KL and deviate by at most an order of magnitude from Sgr B2.

(iii) The isomers of methyl isocyanate, CH₃CNO and CH₃OCN, are not detected. These species are less abundant than CH₃NCO by at least a factor of 100 and 10, respectively.

(iv) HOCN is not found down to $\sim 3 \times 10^{13}$ cm$^{-2}$, giving $N(\text{HOCN})/N(\text{HNCO}) > 1000$, which makes this an insignificant gas-phase precursor to methyl isocyanate in IRAS16293.

(v) Laboratory experiments strongly suggest that it is possible to form CH₃NCO on an icy surface, irradiating CH₄ and HNCO as astronomically relevant precursor species with VUV light, generating methyl radicals as reactive intermediates to form methyl isocyanate.

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### APPENDIX A: LINE LIST

Table A1 contains the full list of detected CH$_3$NCO, $v_b = 0$ transitions towards IRAS16293. A total of 43 lines are observed.

| Species      | Transition | Frequency (MHz) | $E_{up}$ (K) | $A_{ij}$ $(s^{-1})$ | $g_{up}$ |
|--------------|------------|----------------|--------------|---------------------|----------|
| CH$_3$NCO, $v_b = 0$ | (38 0 0 2 to 37 0 0 2) | 329 675.6 | 361.3 | $1.71 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 1 0 2 to 37 1 0 2) | 329 732.1 | 367.3 | $1.71 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 0 0 3 to 37 0 0 3) | 329 929.3 | 427.1 | $1.67 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 0 0 4 to 37 0 0 4) | 330 611.8 | 367.3 | $1.71 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 1 0 3 to 37 1 0 3) | 331 251.7 | 423.4 | $1.70 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 2 0 3 to 37 2 0 3) | 331 653.6 | 447.5 | $1.72 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (38 3 0 3 to 37 3 0 3) | 332 234.9 | 477.7 | $1.71 \times 10^{-5}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (39 0 0 0 to 38 0 0 0) | 334 214.7 | 336.5 | $1.82 \times 10^{-5}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 1 0 0 to 38 1 0 0) | 334 470.6 | 327.3 | $1.78 \times 10^{-5}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 1 0 1 to 38 1 0 1) | 335 432.3 | 342.5 | $1.83 \times 10^{-5}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 2 0 2 to 38 2 0 2) | 335 521.3 | 401.3 | $1.83 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 3 0 2 to 38 3 0 2) | 335 973.3 | 431.1 | $1.82 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 0 0 0 to 38 0 0 0) | 336 339.9 | 323.7 | $1.82 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 2 0 0 to 38 2 0 0) | 337 737.4 | 348.4 | $1.83 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 2 0 0 to 38 2 0 0) | 338 235.6 | 377.6 | $1.85 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 2 0 1 to 38 2 0 1) | 339 028.2 | 349.0 | $1.85 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (38 3 1 0 to 37 3 1 0) | 339 705.0 | 374.5 | $1.75 \times 10^{-3}$ | 77 |
| CH$_3$NCO, $v_b = 0$ | (39 1 0 0 to 38 1 0 0) | 339 948.8 | 448.8 | $1.88 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 1 0 1 to 38 1 0 1) | 339 948.0 | 448.0 | $1.88 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 1 0 2 to 38 1 0 2) | 340 327.9 | 333.1 | $1.88 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (39 2 0 0 to 38 2 0 0) | 340 363.3 | 464.6 | $1.87 \times 10^{-3}$ | 79 |
| CH$_3$NCO, $v_b = 0$ | (40 0 0 1 to 39 0 0 1) | 342 747.6 | 353.1 | $1.97 \times 10^{-3}$ | 81 |
| CH$_3$NCO, $v_b = 0$ | (40 1 0 1 to 39 1 0 1) | 344 280.7 | 359.2 | $1.98 \times 10^{-3}$ | 81 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 2 to 39 3 0 2) | 344 650.3 | 447.7 | $1.97 \times 10^{-3}$ | 81 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 0 to 39 3 0 0) | 344 660.0 | 395.0 | $1.97 \times 10^{-3}$ | 81 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 0 to 39 3 0 0) | 344 672.6 | 417.3 | $2.15 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 1 to 39 3 0 1) | 353 345.6 | 464.8 | $2.12 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 2 to 39 3 0 2) | 353 763.0 | 417.3 | $2.15 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 3 to 39 3 0 3) | 357 668.8 | 367.0 | $2.18 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 4 to 39 3 0 4) | 357 766.6 | 498.4 | $2.17 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 0 5 to 39 3 0 5) | 358 444.3 | 671.4 | $2.16 \times 10^{-3}$ | 83 |
| CH$_3$NCO, $v_b = 0$ | (40 3 1 0 to 39 3 1 0) | 360 817.3 | 378.0 | $2.23 \times 10^{-3}$ | 85 |
| CH$_3$NCO, $v_b = 0$ | (40 3 1 1 to 39 3 1 1) | 361 995.5 | 452.2 | $2.52 \times 10^{-3}$ | 85 |
| CH$_3$NCO, $v_b = 0$ | (40 3 1 2 to 39 3 1 2) | 361 425.5 | 393.7 | $2.29 \times 10^{-3}$ | 85 |
| CH$_3$NCO, $v_b = 0$ | (40 3 1 3 to 39 3 1 3) | 361 770.5 | 429.5 | $2.28 \times 10^{-3}$ | 85 |
| CH$_3$NCO, $v_b = 0$ | (40 3 1 4 to 39 3 1 4) | 362 063.6 | 482.2 | $2.28 \times 10^{-3}$ | 85 |
APPENDIX B: CH$_3$NCO $v_b = 1$

Fig. B1 shows the tentative identification of the first excited state of methyl isocyanate.

Figure B1. Predictions for the CH$_3$NCO $v_b = 1$ lines towards source B (red solid: best-fitting model for $T_{ex} = 300$ K; green dashed: best-fitting model for $T_{ex} = 100$ K).

APPENDIX C: m/z = 56, 57 AND 58 UPON VUV IRRADIATION OF PURE CH$_4$ AND HNCO SAMPLES

Several publications address the energetic processing of pure HNCO and CH$_4$ ice and much is known about the chemistry that can be induced in these species (Raunier et al. 2004; Bennett et al. 2006; Bossa et al. 2015). Of the known chemical products, none of them contributes to the primary and secondary masses of methyl isocyanate. To verify this, pure methane and isocyanic acid have been VUV irradiated. The HNCO sample (Fig. C1A) does not show any significant release of these masses. However, after irradiation of methane a substantial amount of $m/z = 56$, coinciding with a lesser amount of $m/z = 58$, is seen releasing at a desorption temperature of 105 K. Some $m/z = 57$ is seen to be released as well, although there is no clear peak found in this case. The resulting contribution of $m/z = 56$ can interfere with the $m/z = 57/56$ amu mass ratio of methyl isocyanate.

Figure C1. TPD trace of $m/z = 57$ (primary mass CH$_3$NCO), $m/z = 56$ (secondary mass CH$_3$NCO) and $m/z = 58$ after the irradiation of pure HNCO (A) and pure CH$_4$ (B). The desorption peak found in the CH$_3$HNOC mixtures is indicated by the dashed line at 145 K.

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