






# The formation of the building blocks of peptides on interstellar dust grains

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**Abstract.** The emergence of life on Earth may have its origin in organic molecules formed in the interstellar medium. Molecules with amide and isocyanate groups resemble structures found in peptides and nucleobases and are necessary for their formation. Their formation is expected to take place in the solid state, on icy dust grains, and is studied here by far-UV irradiating a CH<sub>4</sub>:HNCO mixture at 20 K in the laboratory. Reaction products are detected by means of infrared spectroscopy and temperature programmed desorption - mass spectrometry. Various simple amides and isocyanates are formed, showing the importance of ice chemistry for their interstellar formation. Constrained by experimental conditions, a reaction network is derived, showing possible formation pathways of these species under interstellar conditions.

**Keywords.** Astrochemistry, methods: laboratory, Astrobiology

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## 1. Introduction

Prebiotic molecules are species that resemble functional groups of biogenic molecules and are thought to be involved in the formation of molecules that are relevant to life, such as amino acids, nucleobases and sugars (Herbst & van Dishoeck 2009). The interstellar presence of prebiotic molecules supports the idea that the building blocks of life may have an extraterrestrial origin, for example glycolaldehyde, the simplest “sugar” (Hollis *et al.* 2004; Jørgensen *et al.* 2016). Among these prebiotics, molecules with an amide (–NH–C(O)–) or amide-like structure, such as isocyanic acid (HNCO), hereafter generally called amides, are of particular interest because they resemble structures found in peptide bonds and nucleobases. In terrestrial biochemistry amino acids are connected by peptide bonds resulting in long chains which eventually form proteins, the engines of life. Reactions involving molecules with an amide functional group offer alternative pathways to form peptide chains.

Amides are widespread throughout the ISM. HNCO, NH<sub>2</sub>CHO (formamide), CH<sub>3</sub>NCO (methyl isocyanate), CH<sub>3</sub>CONH<sub>2</sub> (acetamide) and NH<sub>2</sub>CN (cyanamide) have all been detected in various interstellar environments, ranging from star forming regions to comets (Rubin *et al.* 1971; Hollis *et al.* 2006; Bisschop *et al.* 2007; Goesmann *et al.* 2015; Ligterink *et al.* 2017; Ligterink *et al.* 2018; Coutens *et al.* 2018). Due to the high interstellar abundances of HNCO and NH<sub>2</sub>CHO, many studies have been dedicated to elucidating their formation mechanism, both in the solid-state (e.g. Raunier *et al.* 2004, Jones *et al.* (2011), Noble *et al.* 2015) and in the gas-phase (e.g. Barone *et al.* 2015). Less extensively studied are the formation of the more complex amides (Agarwal *et al.* (1985), Henderson & Gudipati 2015), and in particular how their formation pathways are linked is still an open question.

In this proceeding we summarize results from Ligterink *et al.* 2017 and Ligterink *et al.* 2018, showing the formation of several amides in far-UV irradiated interstellar ice analogues. Various interlinked radical recombination reactions are shown to be at the basis of the formation of these species.

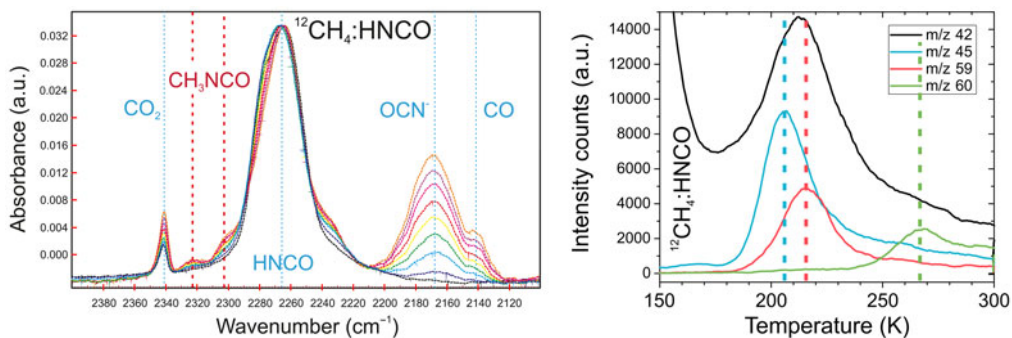
## 2. Experimental

The formation of amides is studied using the CryoPAD2 set-up (Ligterink *et al.* 2017; Ligterink *et al.* 2018). In short, it consists of a central chamber at ultra-high vacuum conditions ( $P \leq 10^{-10}$  mbar). A gold-coated, reflective surface is positioned at the center of the chamber, which is cryogenically cooled to temperatures as low as 12 K. Gases are directly deposited on this surface, forming an ice layer that simulates the ice mantles on interstellar dust grains. The output of a Microwave Discharge Hydrogen-flow Lamp (MDHL, Ligterink *et al.* 2015) is directed at the surface and used to energetically process the ice with far-UV radiation (10.2 – 7.3 eV). Gas mixtures of CH<sub>4</sub> (Linde Gas, 99.995% purity) and HNCO (Sigma-Aldrich, 98% purity) are prepared in a gas mixing line and deposited on the substrate at 20 K. The ice layers are UV irradiated for 20 minutes, corresponding to a total fluence of  $(1.3 \pm 0.1) \times 10^{17}$  photons cm<sup>-2</sup>, which in turn equals the far-UV exposure in a dark cloud lifetime of about  $3 \times 10^5$  years, assuming a dark cloud far-UV flux of  $10^4$  photons s<sup>-1</sup>. Chemical changes within the ice are monitored by Reflection Absorption IR Spectroscopy (RAIRS) and mass spectrometry in combination with Temperature Programmed Desorption (TPD).

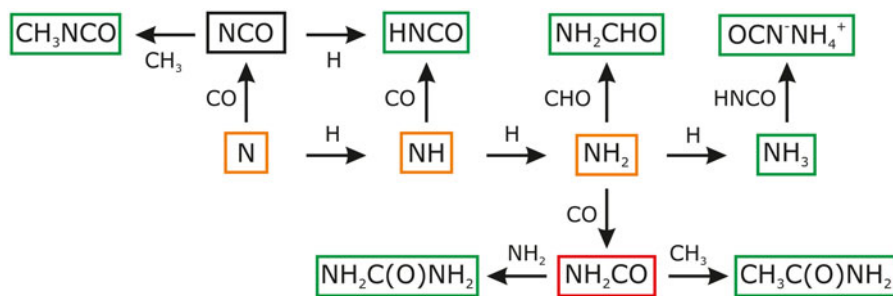
## 3. Results and implications

The left side of Figure 1 presents the IR spectra recorded during the first  $10^{17}$  photons impacting on a CH<sub>4</sub>:HNCO ice mixture at 20 K, with a mixing ratio of 1:1. All spectra are normalized to the HNCO peak. Three known spectroscopic features of CO<sub>2</sub>, OCN<sup>-</sup> and CO (blue) show up during irradiation. Also, two new features become visible around 2300 cm<sup>-1</sup> (red lines), which do not show up while processing samples of pure HNCO or CH<sub>4</sub>. A red shift of about 10 cm<sup>-1</sup> of the two features is seen between samples with <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub>. These spectroscopic features are therefore the result of a product formed in the reaction between CH<sub>4</sub> and HNCO. These features are found very close to reported CH<sub>3</sub>NCO values (e.g. Sullivan *et al.* 1994) and therefore assigned as due to this species.

On the right side of Figure 1 the TPD traces between 150 and 300 K of the main masses of the simplest, or primary, amides that can be formed from CH<sub>4</sub>:HNCO ice mixtures are shown. These masses are  $m/z$  45 for NH<sub>2</sub>CHO,  $m/z$  59 for either CH<sub>3</sub>C(O)NH<sub>2</sub> or CH<sub>3</sub>NHCHO and  $m/z$  60 for NH<sub>2</sub>CONH<sub>2</sub>. The secondary mass channel of HNCO,  $m/z$  42, is included as well to trace HNCO. A prominent trailing slope of  $m/z$  42 between 150 and 300 K, with a superimposed desorption feature at  $\sim 210$  K is seen. The trailing slope is due to residual gas of the main HNCO desorption peak at 130 K, while the desorption



**Figure 1.** Left: IR spectra of far-UV irradiated CH<sub>4</sub>:HNCO ice mixture (1:1 ratio) at 20 K over time. Prominent peaks of OCN<sup>-</sup> and CO are seen to appear, but also two peaks in the wing of HNCO, which can be assigned to CH<sub>3</sub>NCO. Right: TPD-MS trace taken after irradiation of the same CH<sub>4</sub>:HNCO mixture. Desorption of HNCO (*m/z* 42, black), NH<sub>2</sub>CHO (*m/z* 45, blue), CH<sub>3</sub>CONH<sub>2</sub> (*m/z* 59, red) and NH<sub>2</sub>CONH<sub>2</sub> (*m/z* 60, green) is seen.



**Figure 2.** Proposed solid-state formation network of various small amides. The atomic nitrogen hydrogenation chain, eventually leading to NH<sub>3</sub> is shown in orange and at the basis of these reactions. Reactions with CO and HCO lead to HNCO, NH<sub>2</sub>CHO and the intermediate radicals NCO and NH<sub>2</sub>CO, while further reactions with CH<sub>3</sub> result in CH<sub>3</sub>NCO, NH<sub>2</sub>CONH<sub>2</sub> and CH<sub>3</sub>CONH<sub>2</sub>.

feature is caused by the thermal decomposition of the OCN<sup>-</sup>NH<sub>4</sub><sup>+</sup> salt complex and subsequent desorption of HNCO.

Three desorption peaks of *m/z* 45, 59 and 60 are visible at ~205, ~215 and ~265 K, respectively. *m/z* 45 and 60 do not shift when <sup>13</sup>CH<sub>4</sub> is used and therefore are photo-products directly resulting from HNCO. They are identified as NH<sub>2</sub>CHO for *m/z* 45 and NH<sub>2</sub>CONH<sub>2</sub> for *m/z* 60. When isotopes are used, *m/z* 59 is seen to shift by one mass unit and therefore a product of a reaction between CH<sub>4</sub> and HNCO, which realistically can either be CH<sub>3</sub>NHCHO or CH<sub>3</sub>C(O)NH<sub>2</sub>. To distinguish between these two products, TPD traces of the pure species are taken and peak desorption temperatures of 184 K and 219 K for CH<sub>3</sub>NHCHO and CH<sub>3</sub>C(O)NH<sub>2</sub>, respectively, are found. Therefore *m/z* is identified as CH<sub>3</sub>C(O)NH<sub>2</sub>, aided by fitting its fragmentation pattern with other masses recorded in the TPD (see Ligterink *et al.* 2018 for details).

In the TPD traces the desorption of higher masses is also seen, which is associated with the formation of more complex species. These masses at *m/z* 73, 74 and 88, are tentatively identified as CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub> (propionamide), NH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> (2-amino acetamide) and NH<sub>2</sub>C(O)C(O)NH<sub>2</sub> (oxamide), but secure identification of these species requires more information on their desorption temperatures and fragmentation patterns.

With the data obtained from these experiments and combined with literature data, a solid-state formation network for amides and isocyanates can be derived, see Figure 2.

This reaction network starts from the nitrogen (N) hydrogenation chain. N, NH and NH<sub>2</sub> can react with CO and HCO to form NCO, HNCO, NH<sub>2</sub>CHO and NH<sub>2</sub>CO. Subsequently, the two radicals NCO and NH<sub>2</sub>CO react with CH<sub>3</sub> radicals to form CH<sub>3</sub>NCO and CH<sub>3</sub>CONH<sub>2</sub>. NH<sub>2</sub>CO can also react with NH<sub>2</sub> to form NH<sub>2</sub>CONH<sub>2</sub> and with other radicals to form larger amides.

These experiments clearly show that a large variety of amides can be formed in interstellar ice analogues, starting from simple and abundant species, making it likely that their interstellar formation takes place on icy dust grains. Various amides are intimately linked in their formation, which could explain observational links found between certain molecules, such as HNCO / NH<sub>2</sub>CHO and NH<sub>2</sub>CHO / CH<sub>3</sub>CONH<sub>2</sub> (Bisschop *et al.* 2007, Ligterink *et al.* 2018, and references therein).

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