

# CH<sub>3</sub>NCO detections in observations and the laboratory

N. F. W. Ligterink and the PILS team

Sackler Laboratory, Leiden Observatory, Leiden University,  
PO Box 9513, 2300 RA Leiden, The Netherlands

**Abstract.** Methyl isocyanate (CH<sub>3</sub>NCO) belongs to a select group of peptide-like prebiotic molecules. In this paper we present its first detection toward the solar type low-mass protostar IRAS16293-2422 (hereafter IRAS16293). CH<sub>3</sub>NCO is detected towards IRAS16293 as a warm component with T<sub>ex</sub> > 100 K and HNC/CH<sub>3</sub>NCO ~4-12. Also, its grain surface formation route is investigated in the laboratory. VUV processing of CH<sub>4</sub>:HNC mixtures, investigated by IR spectroscopy and mass spectrometry, revealed that it can be formed by reactions of CH<sub>3</sub> and with (H)NCO. Observations and experiments strongly hint that methyl isocyanate is formed on interstellar dust grains.

---

## 1. INTRODUCTION

Within astrochemistry prebiotic complex organic molecules hold a special place, due to their link to life-bearing molecules such as amino acids. Methyl isocyanate, CH<sub>3</sub>NCO, is a molecule that is structurally similar to a peptide bond, the bond that links amino acids together. It belongs to a larger family of molecules that include isocyanic acid (HNCO) and formamide (NH<sub>2</sub>CHO). These last two molecules have been observed in a variety of sources, including the sun-like low mass protostar IRAS16293-2422 (Bisschop *et al.* 2007; López-Sepulcre *et al.* 2015; Coutens *et al.* 2016). 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). However, methyl isocyanate only started to gather interest in the last two years, after a detection was claimed on the comet 67P/Churyumov-Gerasimenko (Goesmann *et al.* 2015; but see for a rebuttal Altwegg *et al.* 2017). This triggered the interstellar observation of CH<sub>3</sub>NCO toward Sgr B2(N) and Orion KL (Halfen *et al.* 2015; Cernicharo *et al.* 2016).

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 (Ruzi & Anderson 2012; Henderson & Gudipati 2015). A number of formation routes have been hypothesized by astrochemists, with one of the more prominent ones being the solid-state methylation (CH<sub>3</sub> addition) to (H)NCO proposed by Cernicharo *et al.* (2016); Belloche *et al.* (2017):



**Table 1.** Comparison of molecular abundance ratios toward different sources

Source	HNCO/CH <sub>3</sub> NCO	CH <sub>3</sub> CN/CH <sub>3</sub> NCO	CH <sub>3</sub> OH/CH <sub>3</sub> NCO
IRAS16293 B	12	5	3333
IRAS16293 A	4	11	3200
Orion KL A <sup>a</sup>	15	10	400
Orion KL B <sup>a</sup>	15	25	225
Sgr B2(N) <sup>a</sup>	40	50	40
Comet 67P/C-G <sup>b</sup>	>0.2	>0.2	–

<sup>a</sup> Cernicharo *et al.* (2016), <sup>b</sup> Goesmann *et al.* (2015); Altwegg *et al.* (2017)

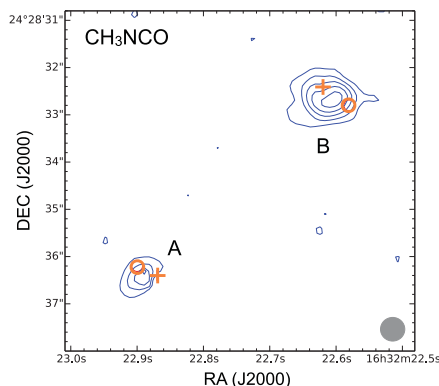
## 2. Observations

We searched for methyl isocyanate in the Protostellar Interferometric Line Survey (PILS) data, an unbiased spectral survey of the low-mass protostellar binary IRAS16293-2422 with ALMA (Jørgensen *et al.* 2016). Methyl isocyanate is detected toward both A and B component. In source B we have been able to identify 43 unblended lines of CH<sub>3</sub>NCO, while in source A 11 unblended lines are found. Excitation temperatures of 100 and 300 K give good agreement with the observations. Our data are not sensitive to any cold CH<sub>3</sub>NCO component since lines with low  $E_{\text{up}}$  values are missing in the spectral range of the PILS survey. The CH<sub>3</sub>NCO column density is found to be  $3\text{--}4 \times 10^{15} \text{ cm}^{-2}$  in source B and  $6\text{--}9 \times 10^{15} \text{ cm}^{-2}$  in source A, for  $T_{\text{ex}} = 300$  and 100 K, respectively in a  $0.5''$  beam. An integrated intensity map of one of the brightest CH<sub>3</sub>NCO lines is presented in Figure 1. The two isomers of methyl isocyanate - acetonitrile oxide (CH<sub>3</sub>CNO) and methyl cyanate (CH<sub>3</sub>OCN) - are not found and are less abundant than methyl isocyanate by at least two and one orders of magnitude, respectively.

The column densities of CH<sub>3</sub>NCO have been compared with those of HNCO, CH<sub>3</sub>CN and CH<sub>3</sub>OH (see Table 1, Coutens *et al.* 2016, Calcutt *et al.* in prep., Jørgensen *et al.* subm.). Within IRAS16293 no significant differences are seen between source A and B. In general the abundance ratios are comparable to the values found in Orion KL (Cernicharo *et al.* 2016) and slightly lower than toward Sgr B2. Methanol is, however, clearly more abundant than methyl isocyanate toward IRAS16293 than toward Orion KL and Sgr B2.

## 3. Laboratory experiments

Methylation of HNCO was tested in the laboratory by VUV irradiating <sup>12/13</sup>CH<sub>4</sub>:HNCO mixtures at a cryogenic temperature of 20 K under ultra high vac-



**Figure 1.** ALMA integrated intensity map of the CH<sub>3</sub>NCO 39<sub>0,39,0</sub>–38<sub>0,38,0</sub> transition at 336339.9 MHz. The positions of the continuum of source A (South East source) and source B (North West source) are indicated with red crosses, while the positions studied in this paper are indicated with red circles.

uum (UHV) conditions. VUV radiation is used as a tool to form  $\text{CH}_3$  radicals, which can further react with  $\text{HNCO}$ . Chemical changes in the ice are traced by IR spectroscopy and Temperature Programmed Desorption (TPD) mass spectrometry.

The strongest vibrational features of solid methyl isocyanate are found between  $2320$  and  $2280\text{ cm}^{-1}$  for the  $-\text{N}=\text{C}=\text{O}$  antisymmetric stretching vibration and overtone  $2\nu_7$   $\text{CH}_3$  rocking mode (Sullivan *et al.* 1994; Zhou & Durig 2009; Reva *et al.* 2010). The region around these bands is used to monitor  $\text{CH}_3\text{NCO}$  formation in the ice. In order to identify methyl isocyanate in the gas-phase using TPD, the mass fragmentation pattern available in the NIST database is used. The fragmentation pattern at  $70\text{ eV}$  comprises unique peaks at  $m/z = 57$  and  $56$  and these will be used as main TPD mass tracers. When using  $^{13}\text{CH}_4$ , both IR bands and the mass tracers will shift.

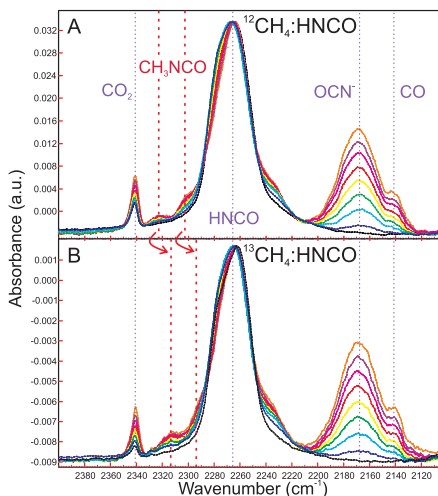
Figure 2 presents the IR spectra of VUV irradiated  $^{12/13}\text{CH}_4:\text{HNCO}$  samples. Three known spectroscopic features of  $\text{CO}_2$ ,  $\text{OCN}^-$  and  $\text{CO}$  (blue) show up during irradiation. However, two new features are seen around  $2300\text{ cm}^{-1}$  (red), which do not show up while processing samples of pure  $\text{HNCO}$  or  $\text{CH}_4$ . Also a clear redshift of about  $10\text{ cm}^{-1}$  of the two features is seen between the sample of  $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$ . These spectroscopic features are therefore the result of a reaction between methane and isocyanic acid, and, since they are found close to the positions of known  $\text{CH}_3\text{NCO}$  features, are plausibly identified with methyl isocyanate.

In the TPD trace  $m/z = 57$  and  $56$  are seen to desorb from the ice after irradiation, while the same desorption peak is not seen in control experiments. It is not possible to match the database fragmentation pattern of methyl isocyanate to the observed peaks, due to interference with other species in  $m/z = 56$ , but the assignment to methyl isocyanate is plausible.

#### 4. Conclusion

Methyl isocyanate is detected for the first time toward a low mass protostar, IRAS16293, on solar system scales (emission radius of  $60\text{ au}$ ). The abundance ratios of  $\text{CH}_3\text{NCO}$  relative to the N-bearing species  $\text{HNCO}$  and  $\text{CH}_3\text{CN}$  are similar to those found toward Orion KL and deviate by at most an order of magnitude from Sgr B2, making a common pathway in these sources likely. Laboratory experiments strongly suggest that reactions between  $\text{CH}_3$  radicals and  $(\text{H})\text{NCO}$  form  $\text{CH}_3\text{NCO}$ . Both observations and laboratory results hint that the interstellar formation route of methyl isocyanate should be found in icy grains.

The detection of  $\text{CH}_3\text{NCO}$  adds to the growing list of complex molecules known to be present around solar mass protostars, showing that the ingredients for prebiotic molecules



**Figure 2.** IR spectra taken over time for the  $^{12/13}\text{CH}_4:\text{HNCO}$  mixture. Spectroscopic features that coincide with  $\text{CH}_3\text{NCO}$  are found at the red lines and show a clear shift with the  $^{13}\text{CH}_4$  isotopologue.

are abundant. Future deeper searches for even more complex molecules relevant for the origin of life are warranted.

For more details on this work see Ligterink *et al.* (2017).

## Acknowledgement

This work has been made possible by valuable contributions from A. Coutens, V. Kofman, H. S. P. Müller, R. T. Garrod, H. Calcutt, S. F. Wampfler, J. K. Jørgensen, H. Linnartz and E. F. van Dishoeck.

## References

- Altwegg, K., Balsiger, H., Berthelier, J. J., *et al.* 2017, *MNRAS*, 469, S130
- Belloche, A., Meshcheryakov, A. A., Garrod, R. T., *et al.* 2017, *A&A*, 601, A49
- Bisschop, S. E., Jørgensen, J. K., Bourke, T. L., Bottinelli, S., & van Dishoeck, E. F. 2008, *A&A*, 488, 959
- Bisschop, S. E., Jørgensen, J. K., van Dishoeck, E. F., & de Wachter, E. B. M. 2007, *A&A*, 465, 913
- Bottinelli, S., Ceccarelli, C., Neri, R., *et al.* 2004, *ApJ*, 617, L69
- Cazaux, S., Tielens, A. G. G. M., Ceccarelli, C., *et al.* 2003, *ApJ*, 593, L51
- Cernicharo, J., Kisiel, Z., Tercero, B., *et al.* 2016, *A&A*, 587, L4
- Coutens, A., Jørgensen, J. K., van der Wiel, M. H. D., *et al.* 2016, *A&A*, 590, L6
- Goesmann, F., Rosenbauer, H., Bredehöft, J. H., *et al.* 2015, *Science*, 349
- Halfen, D. T., Ilyushin, V. V., & Ziurys, L. M. 2015, *ApJ*, 812, L5
- Henderson, B. L. & Gudipati, M. S. 2015, *ApJ*, 800, 66
- Jaber, A. A., Ceccarelli, C., Kahane, C., & Caux, E. 2014, *ApJ*, 791, 29
- Jørgensen, J. K., van der Wiel, M. H. D., Coutens, A., *et al.* 2016, *A&A*, 595, A117
- Kuan, Y.-J., Huang, H.-C., Charnley, S. B., *et al.* 2004, *ApJ*, 616, L27
- Ligterink, N. F. W., Coutens, A., Kofman, V., *et al.* 2017, *MNRAS*, 469, 2219
- López-Sepulcre, A., Jaber, A. A., Mendoza, E., *et al.* 2015, *MNRAS*, 449, 2438
- Reva, I., Lapinski, L., & Fausto, R. 2010, *J. Mol. Struct.*, 976, 333–341
- Ruzi, M. & Anderson, D. 2012, *J. Chem. Phys.*, 137, 194313
- Sullivan, J., Heusel, H., Zunic, W., & Durig, J. 1994, *Spectrochimica Acta*, 50
- van Dishoeck, E. F., Blake, G. A., Jansen, D. J., & Groesbeck, T. D. 1995, *ApJ*, 447, 760
- Zhou, S. & Durig, J. 2009, *J. Mol. Struct.*, 924