Isotopic fractionation of complex organic molecules: Results from the ALMA-PILS survey

Audrey Coutens (University College London)
and the PILS team*

*Jes Jørgensen (PI), Per Bjerkeli, Tyler Bourke, Audrey Coutens, Maria Drozdovskaya, Cécile Favre, Edith Fayolle, Rob Garrod, Steffen Jacobsen, Julie Lykke, Holger Müller, Karin Öberg, Magnus Persson, Matthijs van der Wiel, Ewine van Dishoeck, Susanne Wampfler

Image credit: ESO/B. Tafreshi

Complex organic molecules (COMs)

COMs detected in a lot of astrophysical environments, especially in the warm inner regions of star-forming regions (**hot cores, hot corinos**) where molecules formed on grain surfaces desorb in the gas phase

Similar COMs detected in star-forming regions and comets

Are the COMs formed early in star-forming regions preserved until incorporation into comets?

How do they form?

Molecules detected on the comet 67P with Rosetta-COSAC (Goesmann et al. 2015)

Name	Formula
Water	H_2O
Methane	CH_4
Methanenitrile (hydrogen cyanide)	HCN
Carbon monoxide	CO
Methylamine	CH_3NH_2
Ethanenitrile (acetonitrile)	CH_3CN
Isocyanic acid	$HNCO$
Ethanal (acetaldehyde)	CH_3CHO
Methanamide (formamide)	$HCONH_2$
Ethylamine	$C_2H_5NH_2$
Isocyanomethane (methyl isocyanate)	CH_3NCO
Propanone (acetone)	CH_3COCH_3
Propanal (propionaldehyde)	C_2H_5CHO
Ethanamide (acetamide)	CH_3CONH_2
2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$

Complex organic molecules (COMs)

COMs detected in a lot of astrophysical environments, especially in the warm inner regions of star-forming regions (**hot cores, hot corinos**) where molecules formed on grain surfaces desorb in the gas phase

Similar COMs detected in star-forming regions and comets

Are the COMs formed early in star-forming regions preserved until incorporation into comets?

How do they form?

Isotopic fractionation (D, ^{13}C, ^{15}N) can help

➡ chemical link between species
➡ formation timescales of molecules

Molecules detected on the comet 67P with Rosetta-COSAC (Goesmann et al. 2015)

Name	Formula
Water	H_2O
Methane	CH_4
Methanenitrile (hydrogen cyanide)	HCN
Carbon monoxide	CO
Methylamine	CH_3NH_2
Ethanenitrile (acetonitrile)	CH_3CN
Isocyanic acid	HNCO
Ethanal (acetaldehyde)	CH_3CHO
Methanamide (formamide)	$HCONH_2$
Ethylamine	$C_2H_5NH_2$
Isocyanomethane (methyl isocyanate)	CH_3NCO
Propanone (acetone)	CH_3COCH_3
Propanal (propionaldehyde)	C_2H_5CHO
Ethanamide (acetamide)	CH_3CONH_2
2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$

Isotopic fractionation of COMs

However observations of the less abundant isotopologues of COMs can be challenging.

It requires :

- a high sensitivity

- a high spatial resolution : region of emission of COMs in star-forming regions is compact (< a few ʹʹ)

- a high spectral resolution : needed to distinguish lines in the relatively dense spectra of hot cores/corinos

Isotopic fractionation of COMs

However observations of the less abundant isotopologues of COMs can be challenging.

It requires :

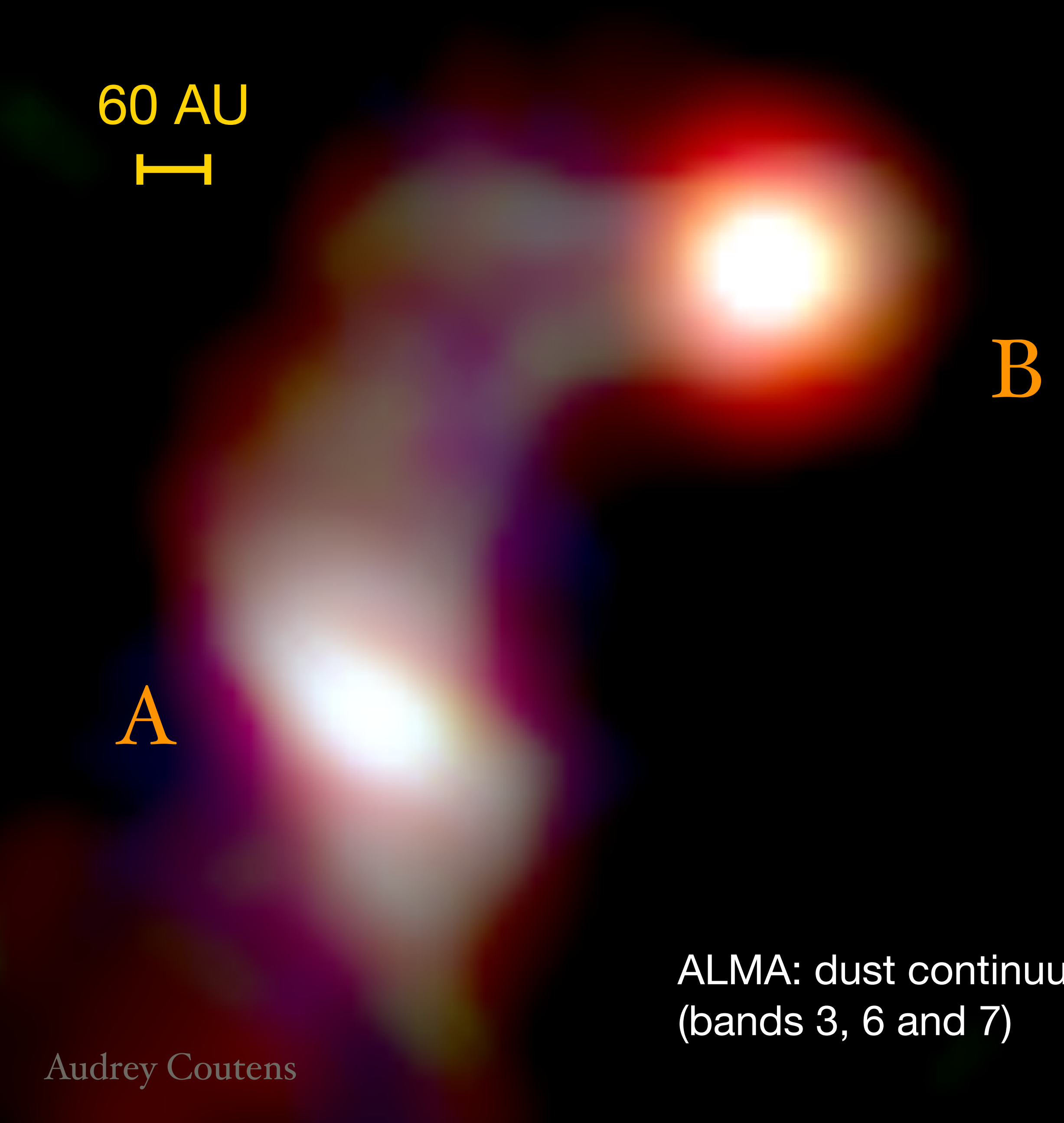
- a high sensitivity
- a high spatial resolution : region of emission of COMs in star-forming regions is compact (< a few ʹʹ)
- a high spectral resolution : needed to distinguish lines in the relatively dense spectra of hot cores/corinos

➡ **Not a lot of studies on isotopic fractionation of COMs in star-forming regions** (mainly deuteration and ^{13}C of CH_3OH)

The PILS Survey

PILS

- Protostellar interferometric line survey (Jørgensen et al. 2016)
- An unbiased spectral survey with ALMA of the solar-type protostellar binary IRAS 16293-2422 between 329 and 363 GHz



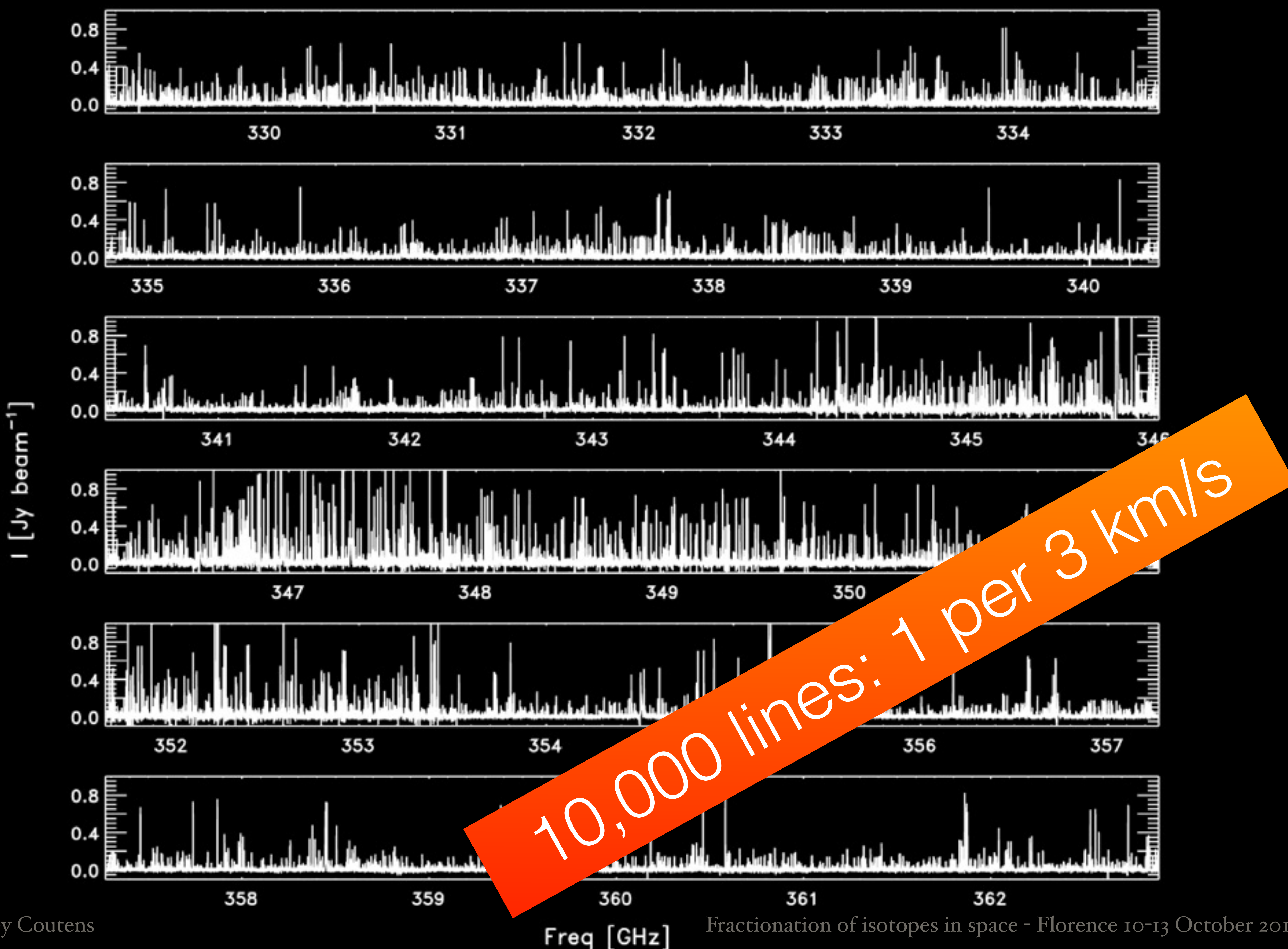
ALMA: dust continuum
(bands 3, 6 and 7)

Nearby (120 pc) low-mass protostellar binary and astrochemical template source.

First detections of complex organic molecules toward solar-type protostars (e.g. Cazaux et al. 2003) as well as prebiotic molecules (Jørgensen et al. 2012).

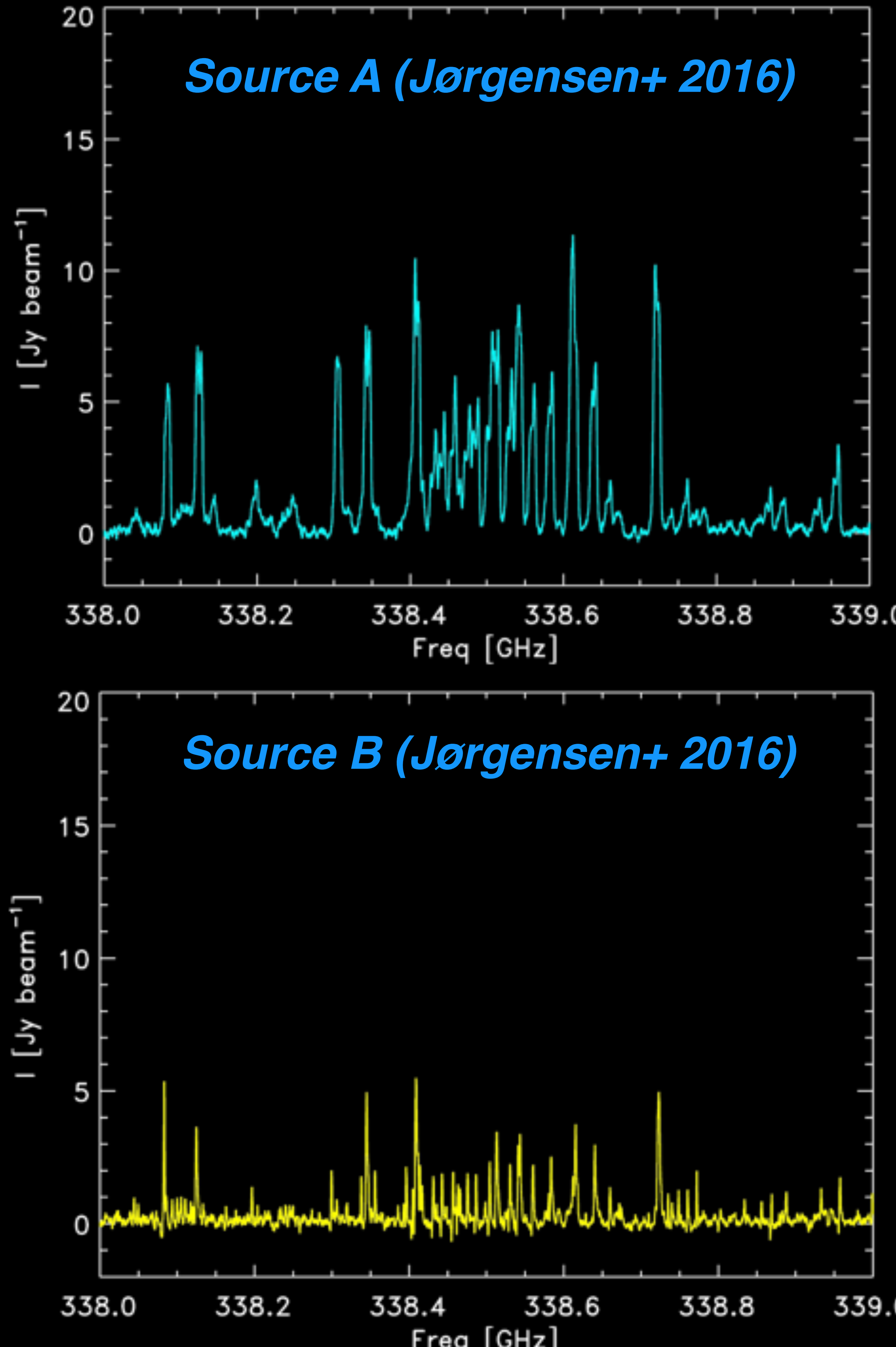
- Spectral resolution 0.2 km/s
- 0.5″ (60 AU) angular resolution
- RMS ~ 5 mJy (1 km/s)

Spectra of IRAS 16293–2422 (Jørgensen+ 2016)



The PILS Survey

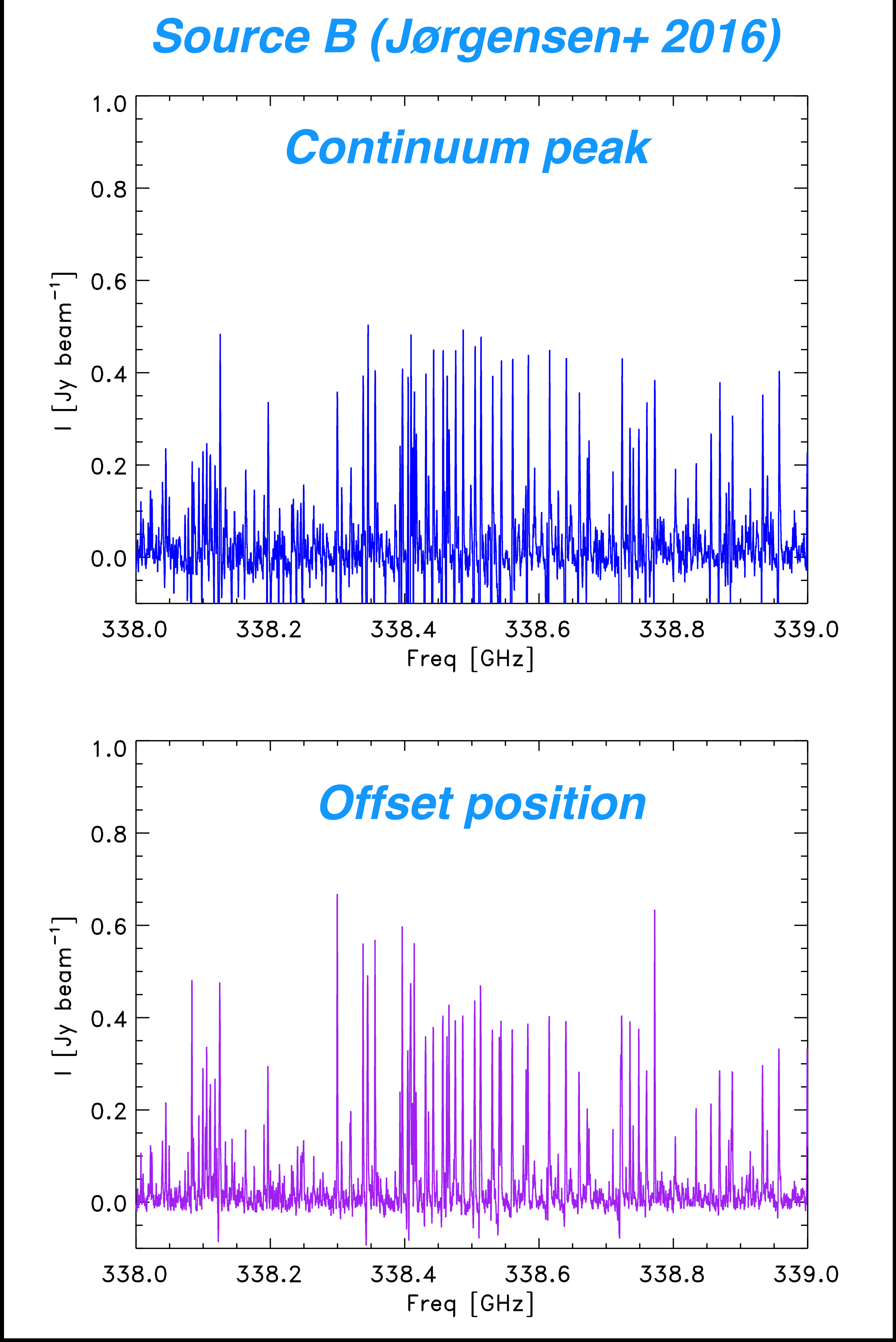
- FWHM ~ 1 km/s towards source B
- FWHM ~ 5 km/s towards source A
- Less line confusion in source B
- Source B ideal to search for new molecules and isotopologues



The PILS Survey

- FWHM ~ 1 km/s towards source B
- FWHM ~ 5 km/s towards source A
- Less line confusion in source B
- Source B ideal to search for new molecules and isotopologues

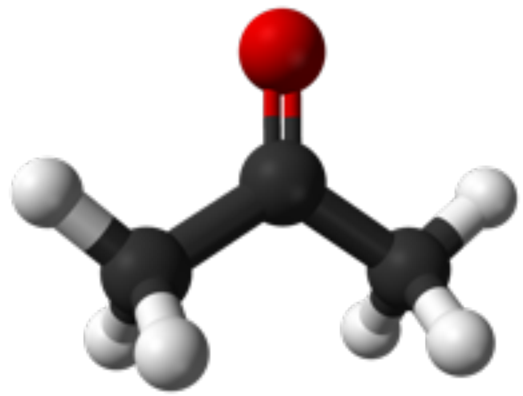
- Lines in absorption towards the continuum peak position of B
- Best position shifted by ~ 0.5″ from continuum peak position
- Bright lines but little absorption



New detections of COMs in IRAS 16293

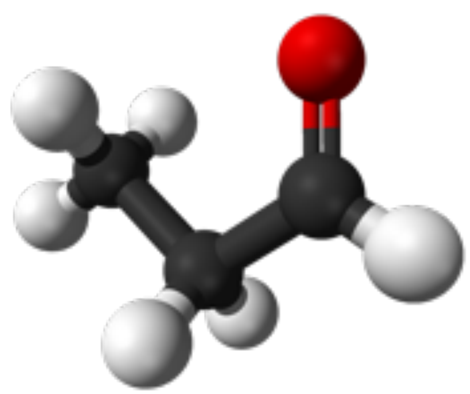
Acetone (CH_3COCH_3)

(detected in comet 67P)

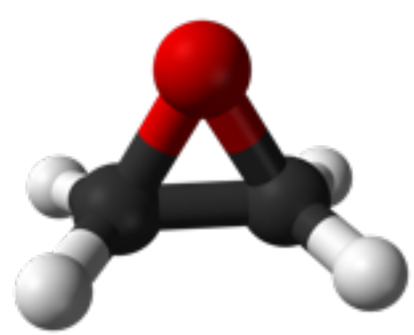


Propanal (CH_3CH_2CHO)

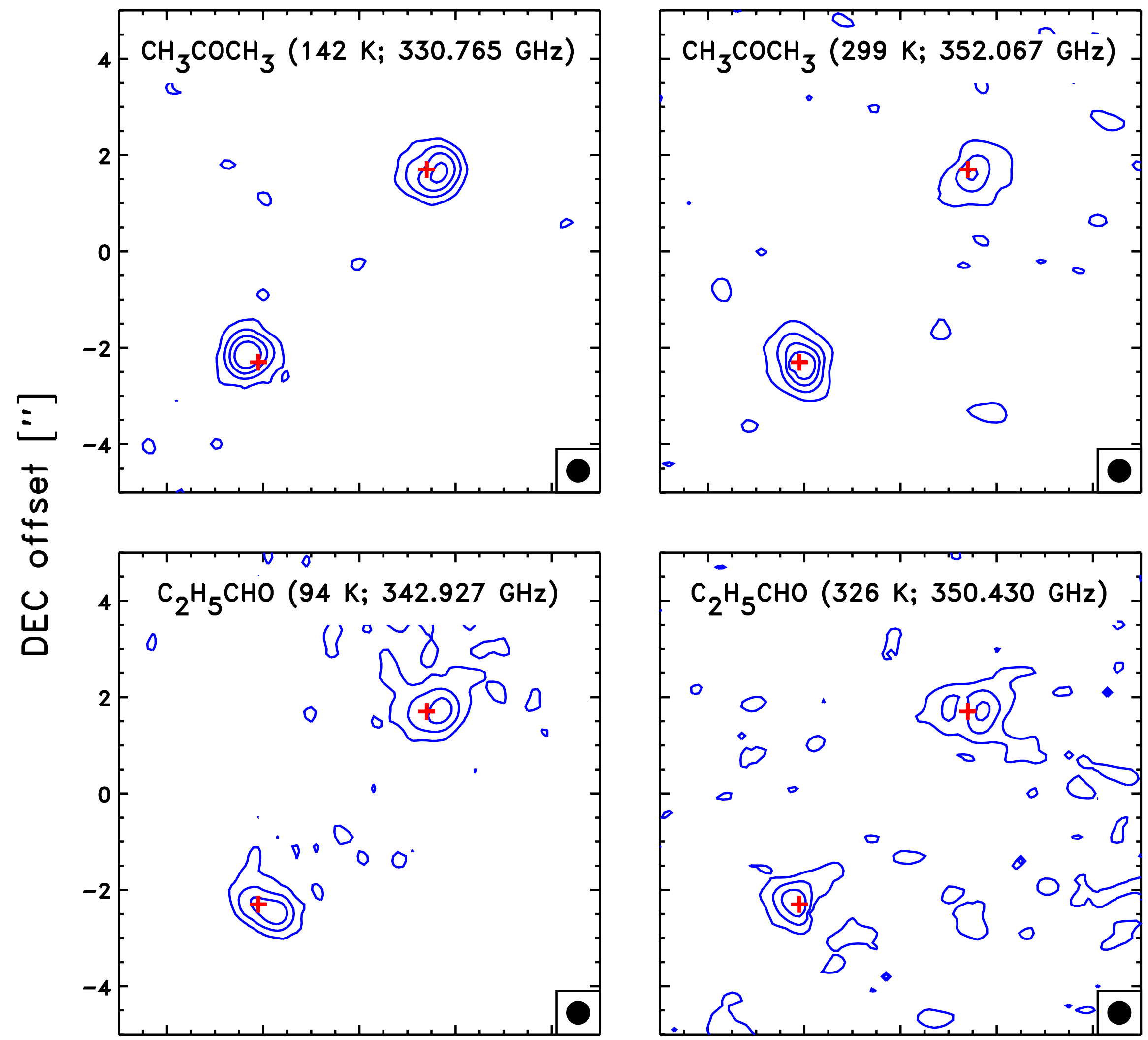
(detected in comet 67P)



Ethylene oxide (C_2H_4O)

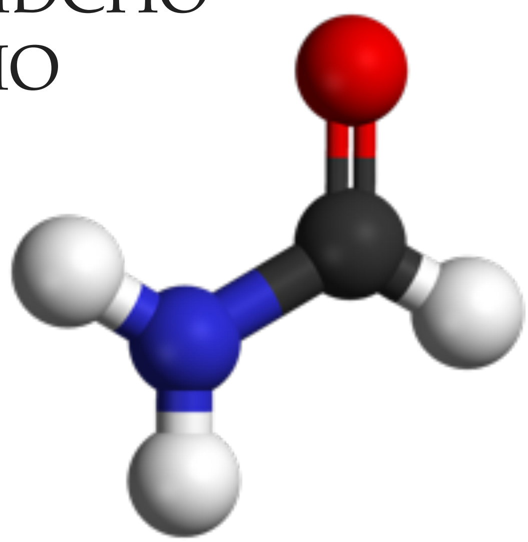


Lykke et al. submitted

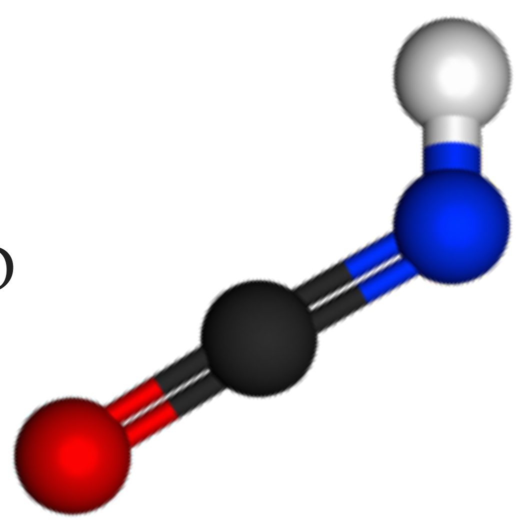


Detections of deuterated and ^{13}C isotopologues

Formamide (NH_2CHO):
NH_2CDO
cis-NHDCHO
trans-NHDCHO
$NH_2{}^{13}CHO$



HNCO:
DNCO
$HN^{13}CO$



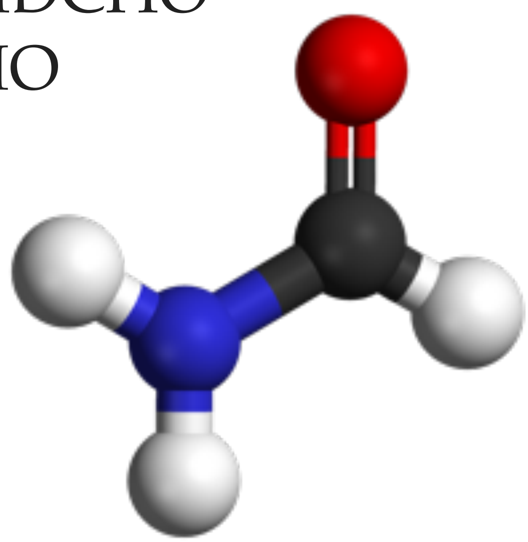
- **Molecules with peptide bond**
  Precursors of metabolic and genetic material (e.g., RNA bases)

- **Formation route unclear :**
  - correlation with HNCO (Bisschop+ 2007, Mendoza+ 2014, Lopez-Sepulcre+ 2015)
  - hydrogenation of HNCO on grain surface (Noble+ 2015, Song+ 2016)
  - radical association on grains NH_2 + HCO, NH_2 + H_2CO (Fedoseev+ 2016)
  - gas phase formation NH_2 + H_2CO (Barone+ 2015)

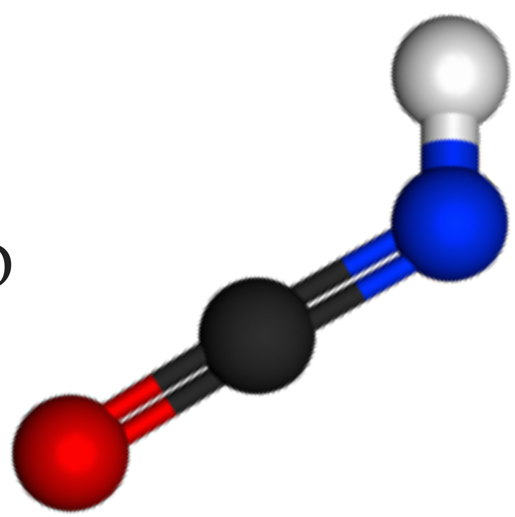
- **Possibly different D/H ratios between the functional groups** (-NH, -CH) that could reveal the presence of **hydrogen isotope exchanges on grain surfaces**

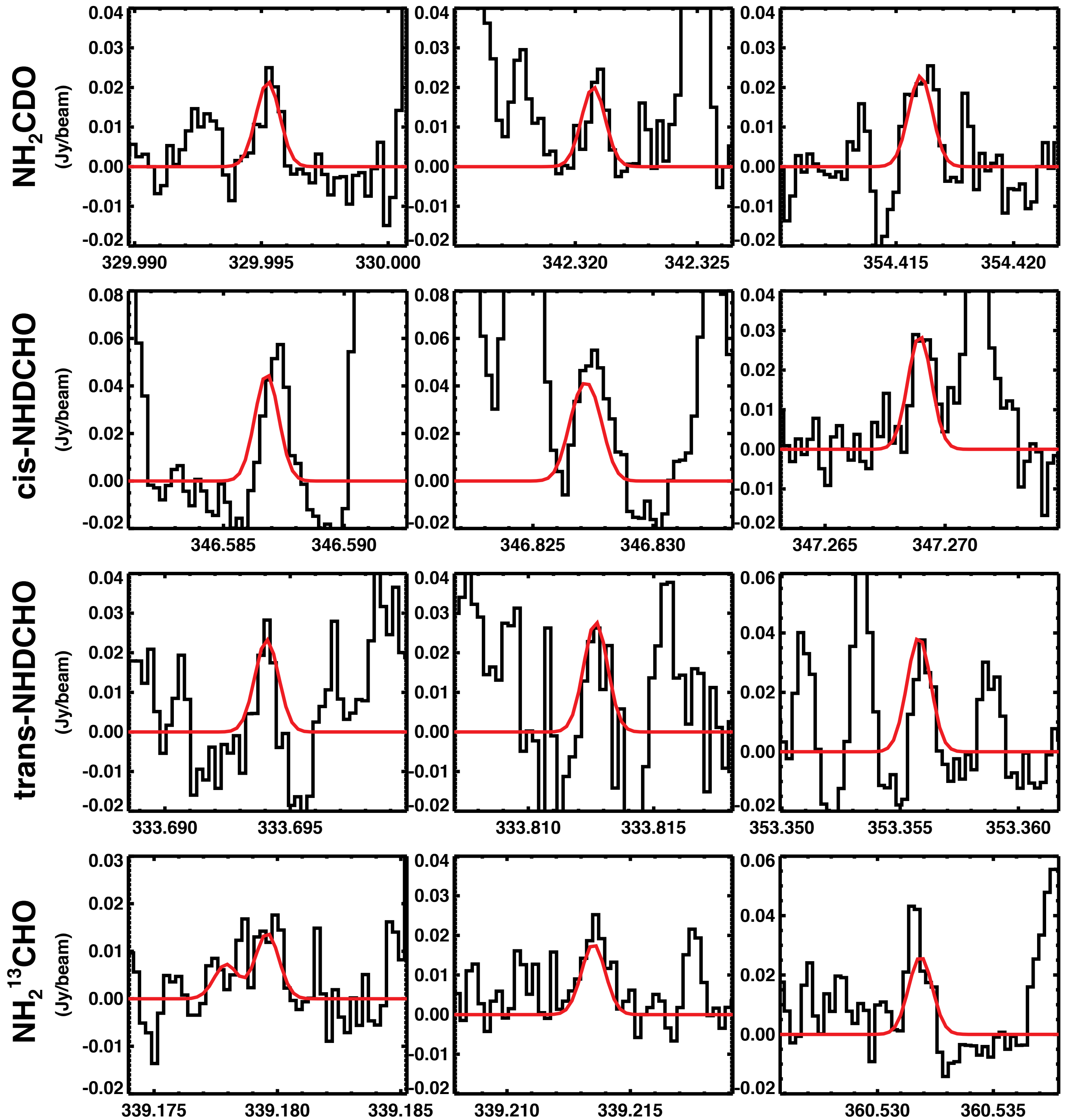
Detections of deuterated and ^{13}C isotopologues

Formamide (NH_2CHO):
NH_2CDO
cis-NHDCHO
trans-NHDCHO
$NH_2{}^{13}CHO$



HNCO:
DNCO
$HN^{13}CO$



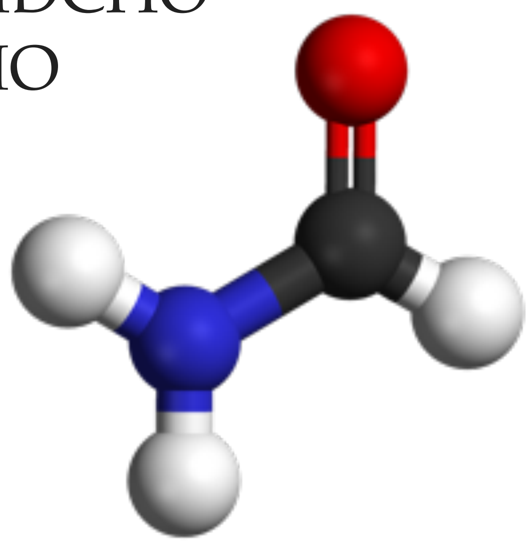


Coutens et al. 2016

Detections of deuterated and ^{13}C isotopologues

Formamide (NH_2CHO):

NH_2CDO
cis-NHDCHO
trans-NHDCHO
$NH_2{}^{13}CHO$

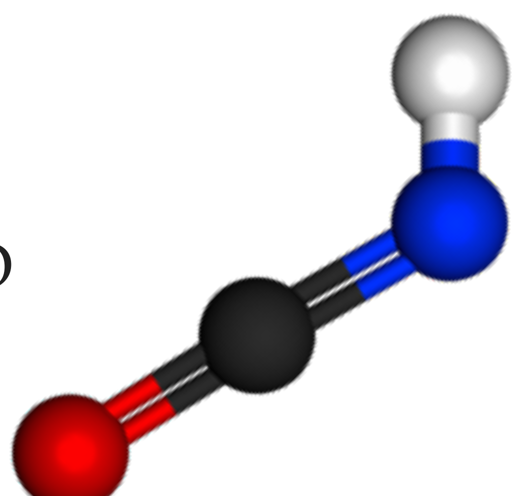


$N(NH_2CDO) = 1.2 \times 10^{14}$ cm^{-2}
N(cis-NHDCHO) $= 1.2 \times 10^{14}$ cm^{-2}
N(trans-NHDCHO) $= 1.0 \times 10^{14}$ cm^{-2}
$N(NH_2{}^{13}CHO) = 9 \times 10^{13}$ cm^{-2}

D/H ~ 2% for any form
based on a standard $^{12}C/^{13}C$ ratio ~68

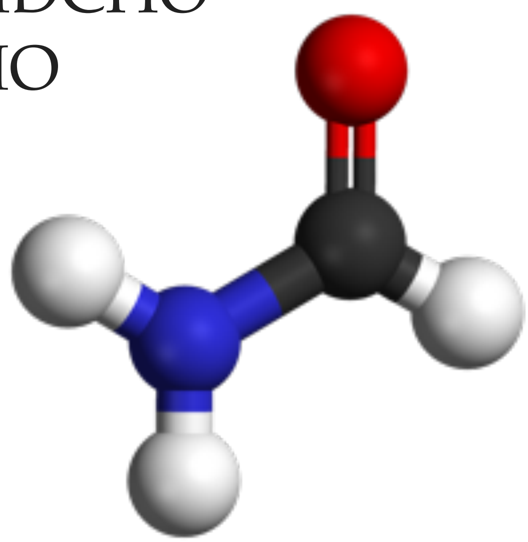
HNCO:

DNCO
$HN^{13}CO$



Detections of deuterated and ^{13}C isotopologues

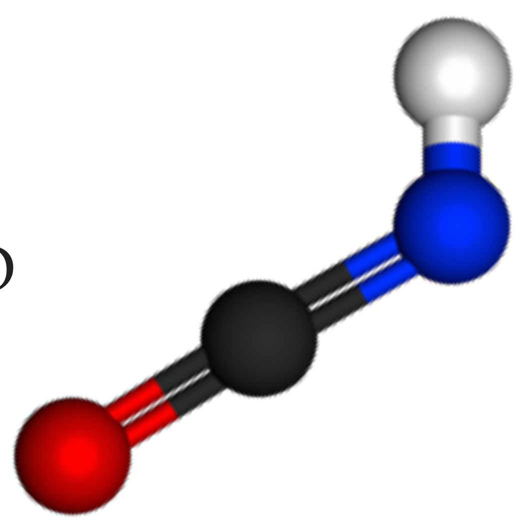
Formamide (NH_2CHO):
NH_2CDO
cis-NHDCHO
trans-NHDCHO
$NH_2{}^{13}CHO$



$N(NH_2CDO) = 1.2 \times 10^{14}\ cm^{-2}$
$N(cis\text{-}NHDCHO) = 1.2 \times 10^{14}\ cm^{-2}$
$N(trans\text{-}NHDCHO) = 1.0 \times 10^{14}\ cm^{-2}$
$N(NH_2{}^{13}CHO) = 9 \times 10^{13}\ cm^{-2}$

D/H ~ 2% for any form
based on a standard $^{12}C/^{13}C$ ratio ~68

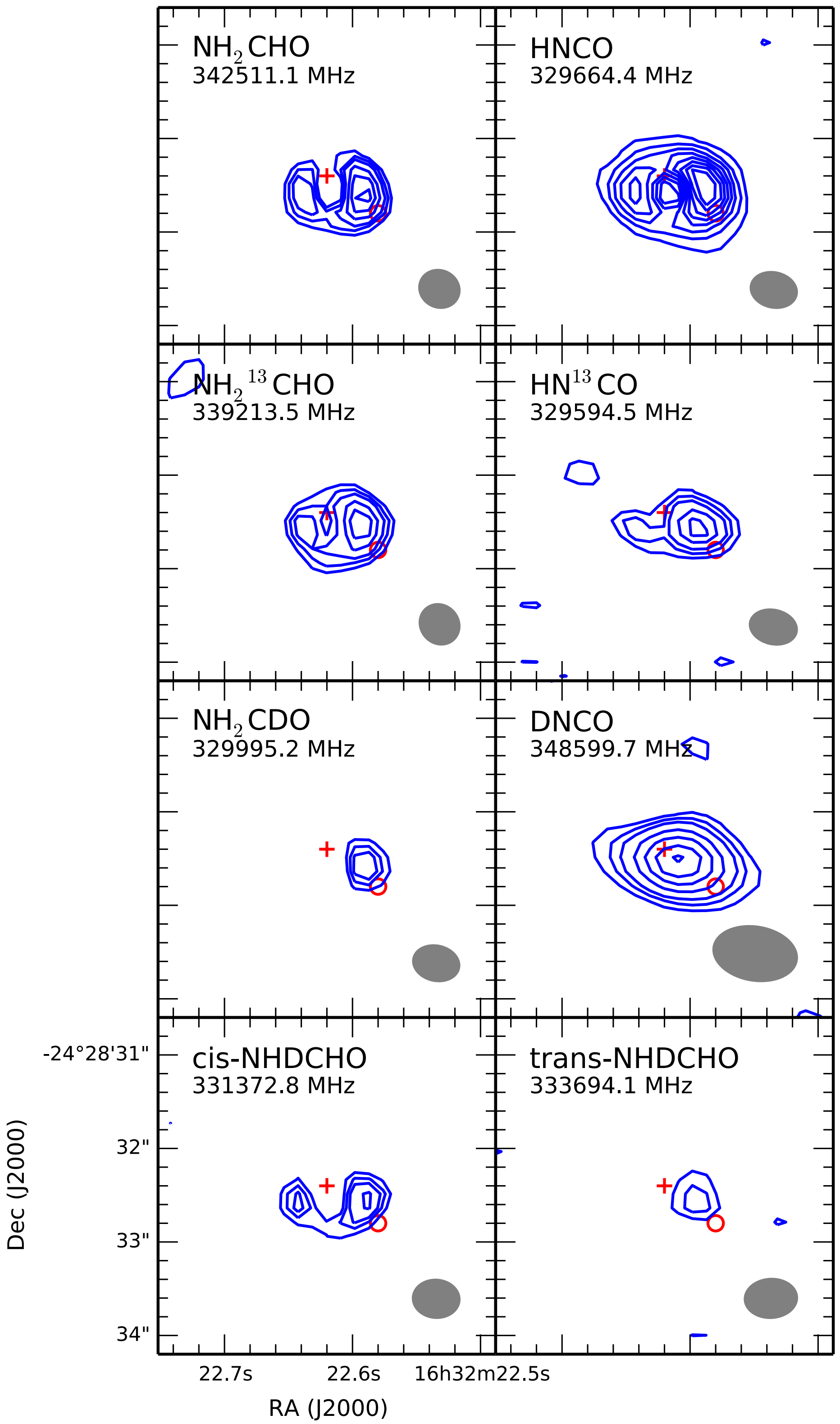
HNCO:
DNCO
$HN^{13}CO$



$N(DNCO) = 3 \times 10^{14}\ cm^{-2}$
$N(HN^{13}CO) = 4 \times 10^{14}\ cm^{-2}$

DNCO/HNCO ~ 1%

Detections of deuterated and ^{13}C isotopologues



Coutens et al. 2016

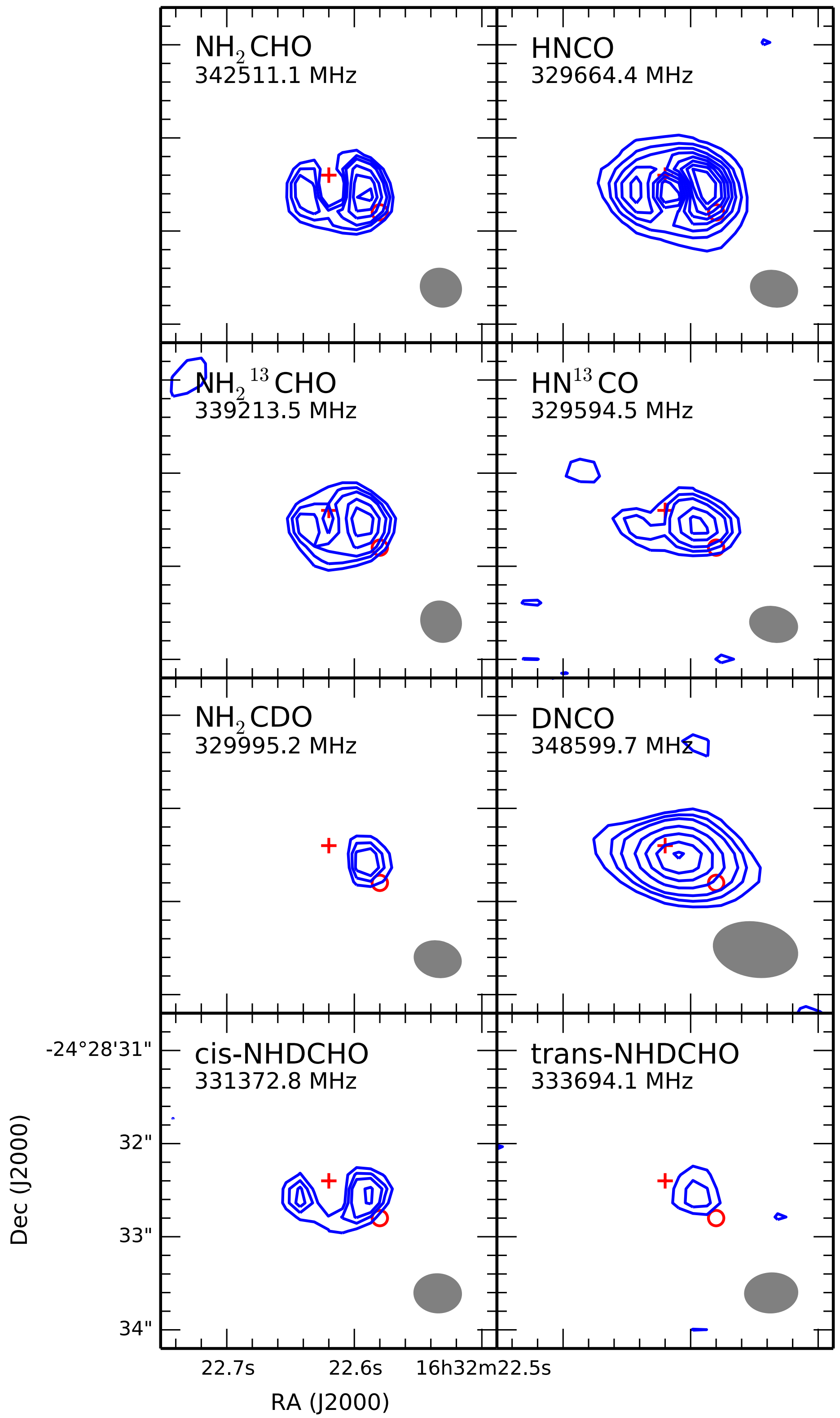
N(NH_2CDO) = 1.2 x 10^{14} cm^{-2}
N(cis-NHDCHO) = 1.2 x 10^{14} cm^{-2}
N(trans-NHDCHO) = 1.0 x 10^{14} cm^{-2}
N($NH_2{}^{13}CHO$) = 9 x 10^{13} cm^{-2}

D/H ~ 2% for any form
based on a standard ^{12}C/^{13}C ratio ~68

N(DNCO) = 3 x 10^{14} cm^{-2}
N($HN^{13}CO$) = 4 x 10^{14} cm^{-2}

DNCO/HNCO ~ 1%

Detections of deuterated and ^{13}C isotopologues



Coutens et al. 2016

N(NH_2CDO) = 1.2 x 10^{14} cm^{-2}
N(cis-NHDCHO) = 1.2 x 10^{14} cm^{-2}
N(trans-NHDCHO) = 1.0 x 10^{14} cm^{-2}
N($NH_2{}^{13}CHO$) = 9 x 10^{13} cm^{-2}

D/H ~ 2% for any form
based on a standard $^{12}C/^{13}C$ ratio ~68

N(DNCO) = 3 x 10^{14} cm^{-2}
N($HN^{13}CO$) = 4 x 10^{14} cm^{-2}

DNCO/HNCO ~ 1%

Confirmation for a link between HNCO and NH_2CHO (spatial distribution + deuteration)

Detections of deuterated and ^{13}C isotopologues

Need for deuteration of potential precursors to constrain formation of formamide

Gas phase :

$NHD + H_2CO \longrightarrow NHDCHO + H$

$NH_2 + HDCO \longrightarrow NH_2CDO + H$

$\longrightarrow NH_2CHO + D$

Grain surface :

#ND + #CO ⟶ #DNCO

#NHD + #H_2CO ⟶ #NHDCHO + H

#NH_2 + #HDCO ⟶ #NH_2CDO + H

⟶ #NH_2CHO + D

#NH_2 + #DCO ⟶ #NH_2CDO + H

#NHD + #HCO ⟶ #NHDCHO + H

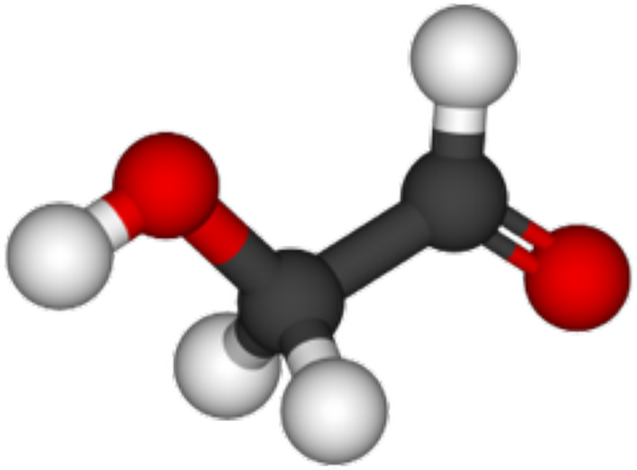
#DNCO $\xrightarrow{H}$ #NHDCHO

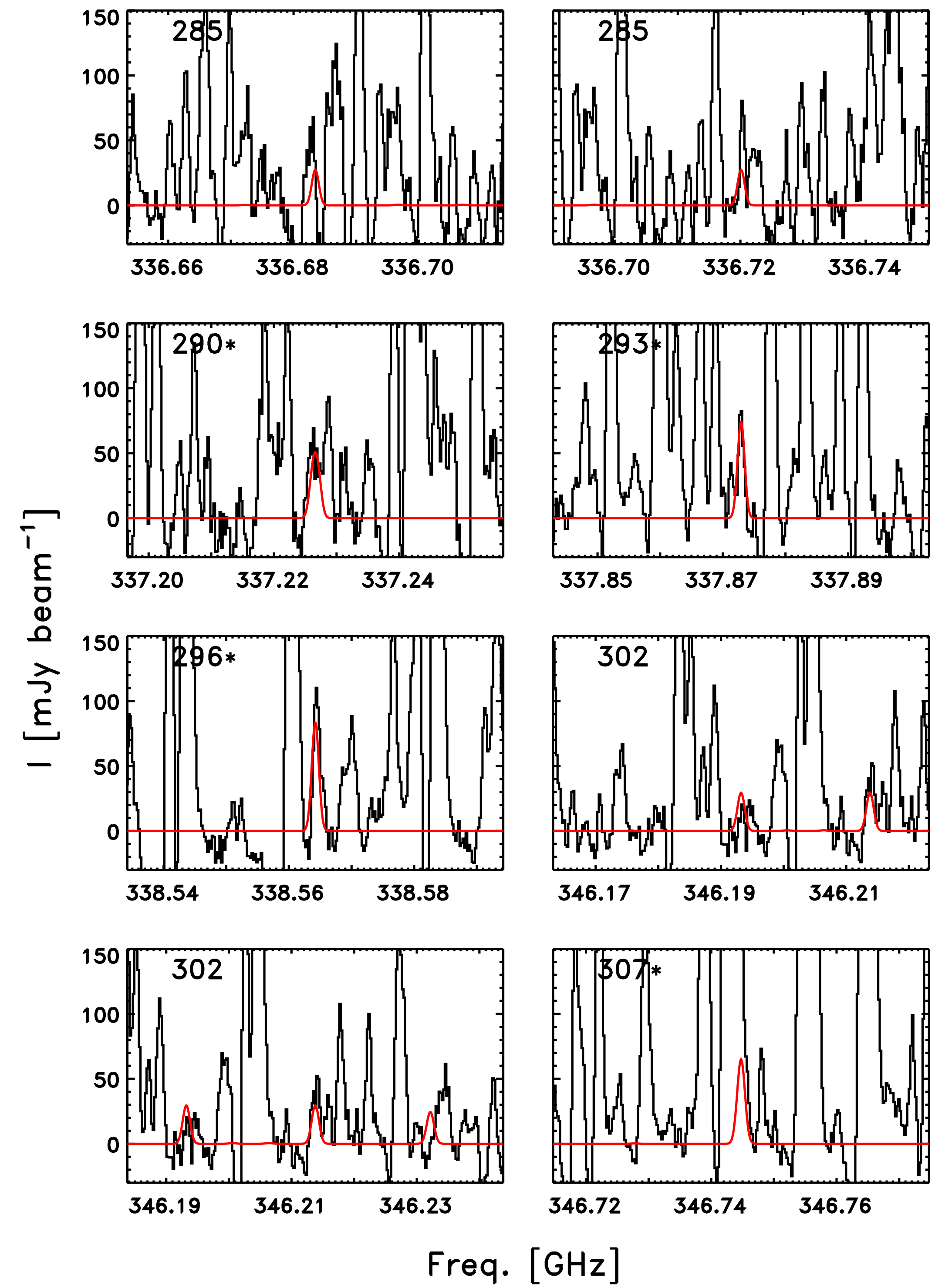
#HNCO $\xrightarrow{H,D}$ #NH_2CDO

$\xrightarrow{H,D}$ #NHDCHO

Detections of deuterated and ^{13}C isotopologues

Glycolaldehyde:
$CH_2OH^{13}CHO$
$^{13}CH_2OHCHO$
CH_2ODCHO
CH_2OHCDO
$CHDOHCHO$

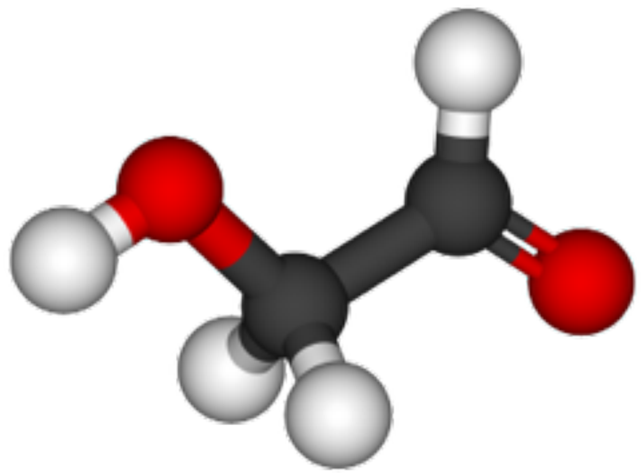




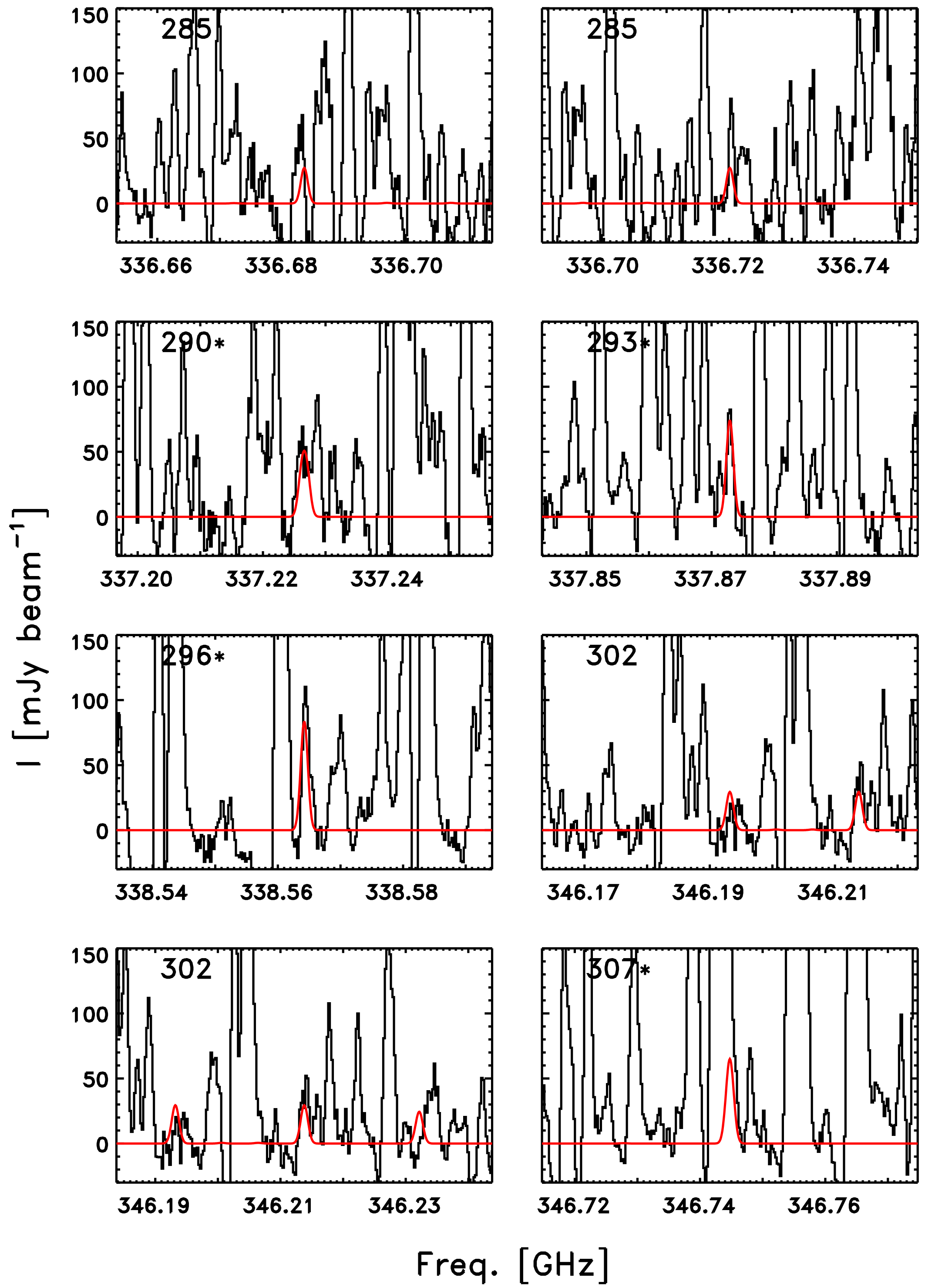
Jørgensen et al. 2016

Detections of deuterated and ^{13}C isotopologues

Glycolaldehyde:
$CH_2OH^{13}CHO$
$^{13}CH_2OHCHO$
CH_2ODCHO
CH_2OHCDO
$CHDOHCHO$



Species	N^a [cm^{-2}]	$N/N(CH_2OHCHO)^b$
CH_2OHCHO	6.8×10^{16}	...
$CHDOHCHO$	7.1×10^{15}	0.10 (9.6)
CH_2ODCHO	3.2×10^{15}	0.047 (21)
CH_2OHCDO	3.5×10^{15}	0.052 (19)
$^{13}CH_2OHCHO$	2.5×10^{15c}	$0.037\ (27)^c$
$CH_2OH^{13}CHO$	2.5×10^{15c}	$0.037\ (27)^c$

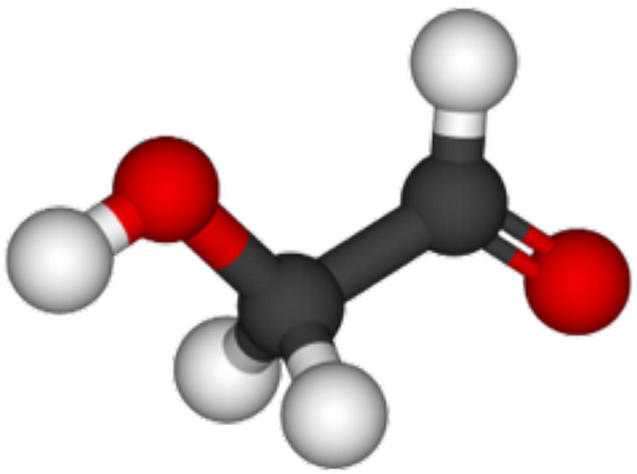


Jørgensen et al. 2016

- **Statistical D/H ratio of 5% for each functional group**
- **Same $^{12}C/^{13}C$ ratio for each C**
- **$^{12}C/^{13}C$ ratio lower than the standard value by a factor 2**

Detections of deuterated and ^{13}C isotopologues

Glycolaldehyde:
$CH_2OH^{13}CHO$
$^{13}CH_2OHCHO$
CH_2ODCHO
CH_2OHCDO
CHDOHCHO



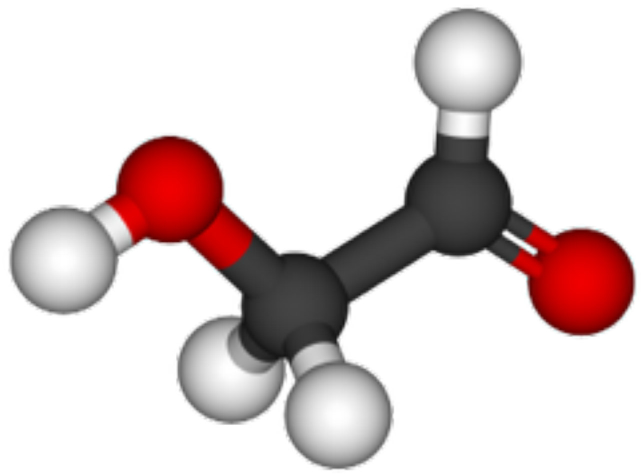
- similar to formamide
- different from single-dish data analysis of methanol ($CH_2DOH/CH_3OD > 3$, Parise et al. 2002, 2006)

Species	N^a [cm^{-2}]	$N/N(CH_2OHCHO)^b$
CH_2OHCHO	6.8×10^{16}	...
CHDOHCHO	7.1×10^{15}	0.10 (9.6)
CH_2ODCHO	3.2×10^{15}	0.047 (21)
CH_2OHCDO	3.5×10^{15}	0.052 (19)
$^{13}CH_2OHCHO$	2.5×10^{15c}	$0.037 (27)^c$
$CH_2OH^{13}CHO$	2.5×10^{15c}	$0.037 (27)^c$

- **Statistical D/H ratio of 5% for each functional group**
- **Same $^{12}C/^{13}C$ ratio for each C**
- **$^{12}C/^{13}C$ ratio lower than the standard value by a factor 2**

Detections of deuterated and ^{13}C isotopologues

Glycolaldehyde:
$CH_2OH^{13}CHO$
$^{13}CH_2OHCHO$
CH_2ODCHO
CH_2OHCDO
CHDOHCHO



Species	N^a [cm^{-2}]	$N/N(CH_2OHCHO)^b$
CH_2OHCHO	6.8×10^{16}	...
CHDOHCHO	7.1×10^{15}	0.10 (9.6)
CH_2ODCHO	3.2×10^{15}	0.047 (21)
CH_2OHCDO	3.5×10^{15}	0.052 (19)
$^{13}CH_2OHCHO$	2.5×10^{15c}	$0.037 (27)^c$
$CH_2OH^{13}CHO$	2.5×10^{15c}	$0.037 (27)^c$

- **Statistical D/H ratio of 5% for each functional group**
- **Same $^{12}C/^{13}C$ ratio for each C**
- **$^{12}C/^{13}C$ ratio lower than the standard value by a factor 2**

- similar to formamide
- different from single-dish data analysis of methanol ($CH_2DOH/CH_3OD > 3$, Parise et al. 2002, 2006)

Enhancement of ^{13}CO in the ice due to :
- ion-molecule reactions in the gas phase before freeze-out ?
- differences where ^{12}CO and ^{13}CO ices sublimate with $T_{sub}(^{12}CO) < T_{sub}(^{13}CO)$?

Conclusions on isotopic fractionation from the ALMA-PILS survey

- Detections of numerous isotopologues of complex organics (high number of lines from wide spectral coverage provide accurate abundance ratios)

- First detections of deuterated forms of formamide (NH_2CHO; *Coutens+ 2016*) and deuterated and ^{13}C-forms of glycolaldehyde (CH_2OHCHO; *Jørgensen+ 2016*) in the ISM

- D/H ratios ~ 1–5% on the scales probed by ALMA observations

- Lower values than inferred in colder gas from single-dish observations

- No significant difference in ratios for different functional groups of molecules.

Thanks

Science & Technology
Facilities Council

Our Astro-Chemical History

cost
European Cooperation in Science and Technology

UCL

STARPLAN

SIGILLVM FACVLTATIS NATVRALIS UNIVERSITATIS HAFNIENSIS