Discovery of new interstellar molecules: expected and unexpected

Marcelino Agúndez
Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain

J. Cernicharo, M. Guélin, P. De Vicente, N. Marcelino, E. Roueff, A. Fuente, M. Gerin
and the Yebes team

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Sensitive observations of cold dark clouds

IRAM 30m project to make deep observations at λ 3 mm to search for molecular anions in cold dark clouds

No detection of molecular anions

… but detections of other interesting molecules

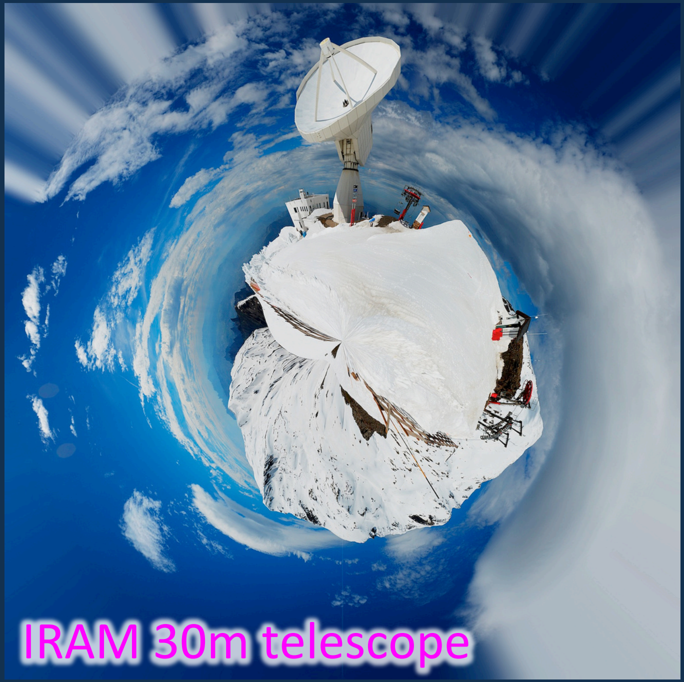
Lupus-1A
L483
L1495B
L1521F
Serpens South 1a
L1389
L1172
L1251A
L1512

IRAM 30m λ 3 mm line surveys
(PI Núria Marcelino)

TMC-1
B1

Yebes 40m observations at 44 GHz taken in 2015 by Pablo de Vicente

TMC-1
L483



What came up from these observations ?

- Detection of $NCCNH^+$ in TMC-1, L483
  First detection in space
  Agúndez et al. (2015), A&A, 579, L10

- Detection of HCCO in Lupus-1A, L483
  First detection in space
- Detection of H_2CCO and CH_3CHO in Lupus-1A, L483, L1495B, L1521F, Serpens South 1a
- Detection of HCO in Lupus-1A, L483, L1495B, L1521F, Serpens South 1a, L1389, L1172, L1251A, L1512
  Detected previously only in three cold dense clouds: L1448, TMC-1, B1
- Detection of CH_2CHCH_3 in Lupus-1A, L1495B, L1521F, Serpens South 1a (non detection in L483)
  Detected previously only in TMC-1
  Agúndez et al. (2015), A&A, 577, L5

- Detection of HCCCHO and *c*-C_3H_2O in various dark clouds
  Loison et al. (2016), MNRAS, 406, 4101

- Detection of cyclic and linear C_3H and C_3H_2 in various dark clouds
  Loison et al. (2017), MNRAS, 470, 4075

Detection of $NCCNH^+$:
The quest for non-polar molecules in interstellar clouds

Agúndez et al. (2015), A&A, 579, L10

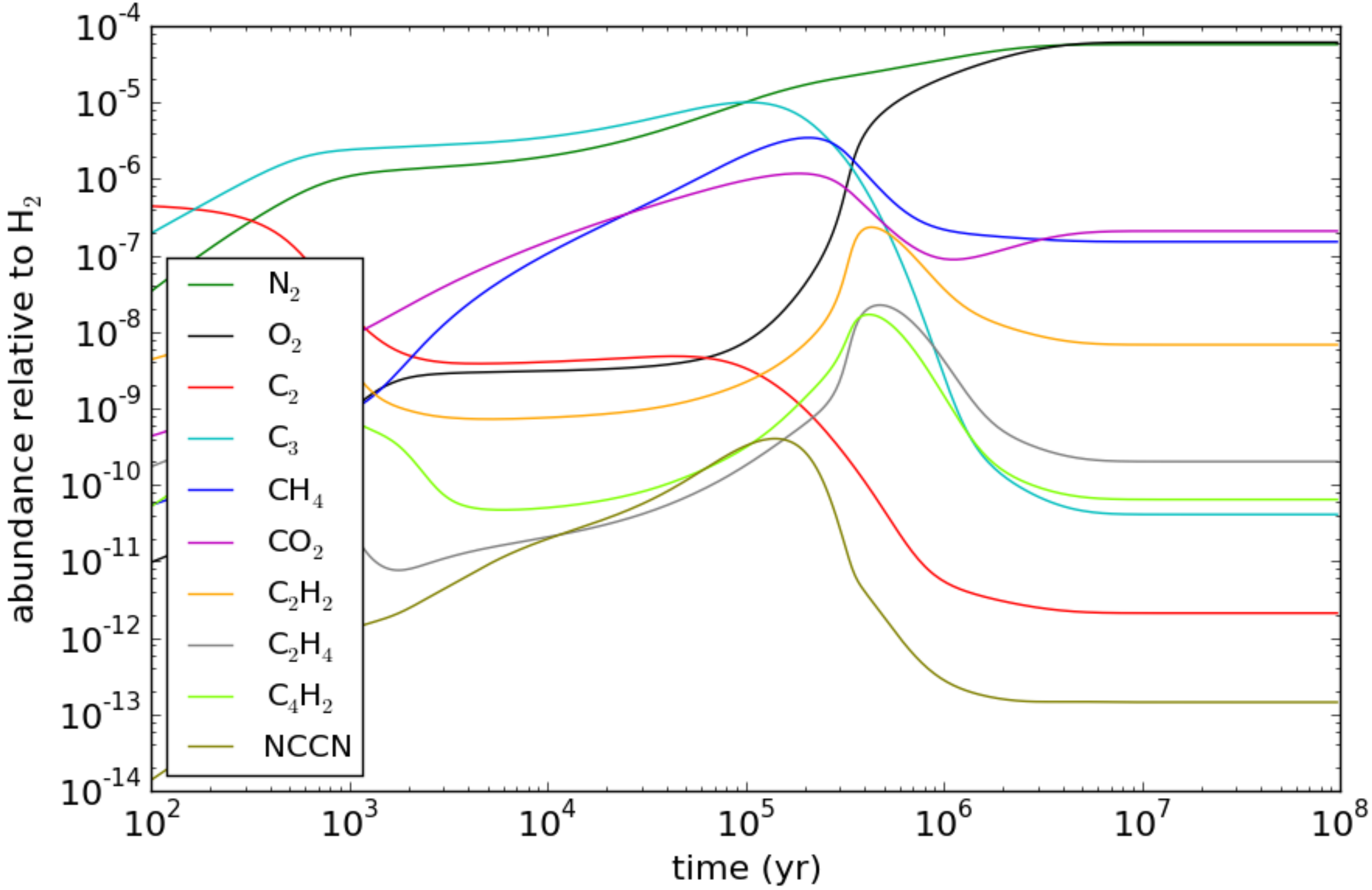
Non-polar molecules are the invisible content of cold interstellar clouds

Not observable through rotational spectrum (μ=0), and thus almost impossible to detect directly in cold clouds

However, there are (theoretical/observational) evidences of their presence

Theoretical evidences

Abundances of non polar molecules predicted by dark cloud chemical model



Observational evidences: direct detection in special cases

O_2: Rotational spectrum at (sub-)mm wavelengths (magnetic-dipole allowed transitions).
Line strengths are weak.
Detected with *Herschel* in Orion and ρ Ophiuchi A.
Abundance upper limits observed in dark clouds much lower than the abundance predicted by chemical models (e.g., Hincelin et al. 2011).

H_2: Rotational spectrum at IR wavelengths (quadrupole allowed transitions).
High energy lying levels (only observable in warm sources).

N_2: No rotational spectrum.
Observable through electronic transitions at ultraviolet wavelengths.
Detected in absorption in diffuse media towards HD 124314 (Knauth et al. 2004).

Usually non polar molecules can only be detected through vibrational or electronic transitions, but these are not adequate for cold interstellar clouds.

Observational evidences: indirect detection through protonated form

H_2: Detection of H_3^+ (μ=0) is very difficult in cold sources (Oka 2013).

N_2: Indirect evidence through detection of N_2H^+ (e.g., Maret et al. 2006).

CO_2: Indirect evidence through detection of HCO_2^+ (e.g., Sakai et al. 2008).

C_3: Protonated C_3 detected in PDRs (Pety et al. 2012) but not in dark clouds.

CH_4: Could be indirectly detected through CH_5^+ (lack of laboratory spectroscopic data).

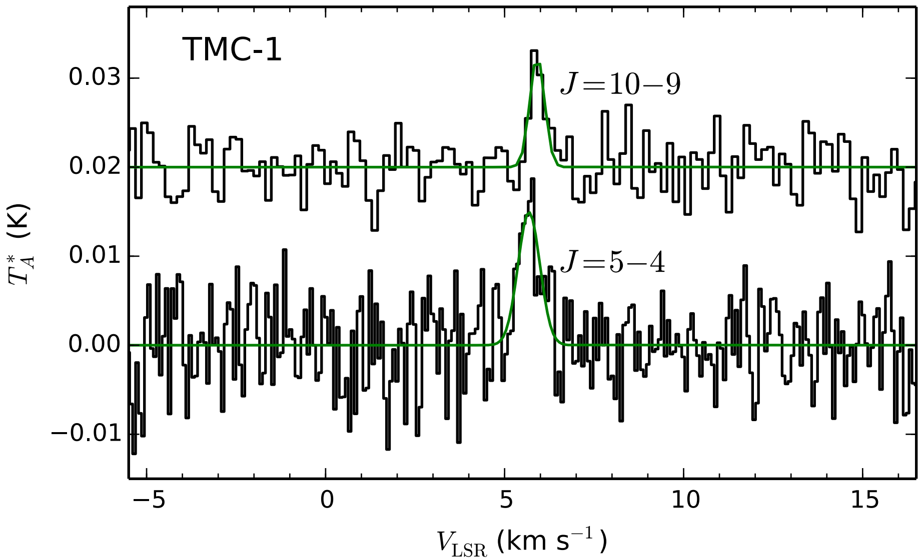
C_2H_2: Could be indirectly detected through $C_2H_3^+$ (need for astronomical searches).
Most favourable line at 368.6 GHz difficult to reach from ground.

NCCN: Protonated form recently detected in dark clouds (Agúndez et al. 2015).

To use the protonated form of a non polar molecule and constraint its abundance:
- There must be a clear chemical link between protonated and non-protonated form
- Need of a precise knowledge of the chemistry of interconversion involved

M ➔ MH+

Probing NCCN through the detection of the protonated form in dark clouds



NCCNH$^+$

Rotational spectrum measured

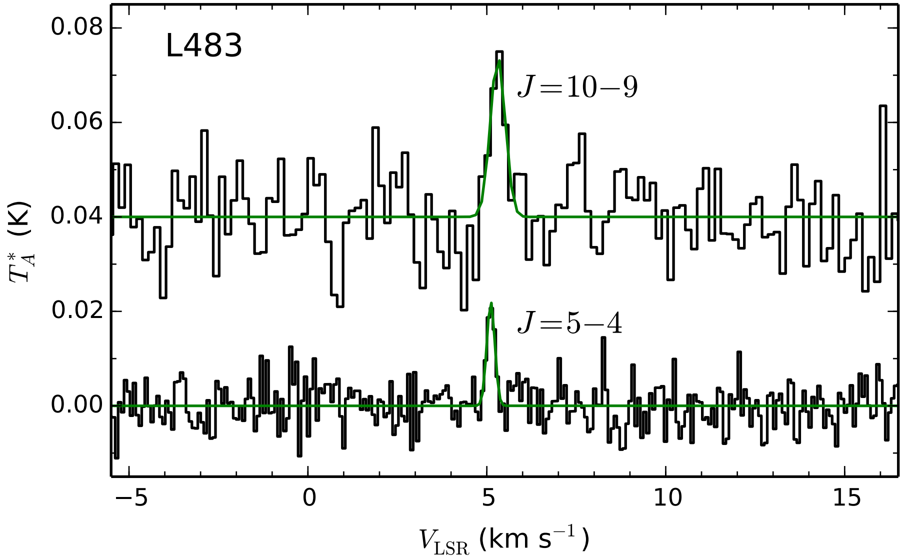
(Amano & Scappini 1991; Gottlieb et al. 2000)

High dipole moment, calculated to be 6.448 D

(Botschwina & Sebald 1990)

$N(\mathrm{NCCNH^+}) = 8.6\times10^{10}$ cm^{-2}

$f = 8.6\times10^{-12}$



$N(\mathrm{NCCNH^+}) = 3.9\times10^{10}$ cm^{-2}

$f = 1.3\times10^{-12}$

Probing NCCN through the detection of the protonated form in dark clouds

Chemical scheme between species M and protonated form MH$^+$

$XH^+ + M \xrightarrow{k_{PT}} MH^+ + X,$ Main formation route of MH$^+$ (proton transfer)

$MH^+ + e^- \xrightarrow{k_{DR}} \text{products},$ Main destruction route of MH$^+$ (dissociative recombination)

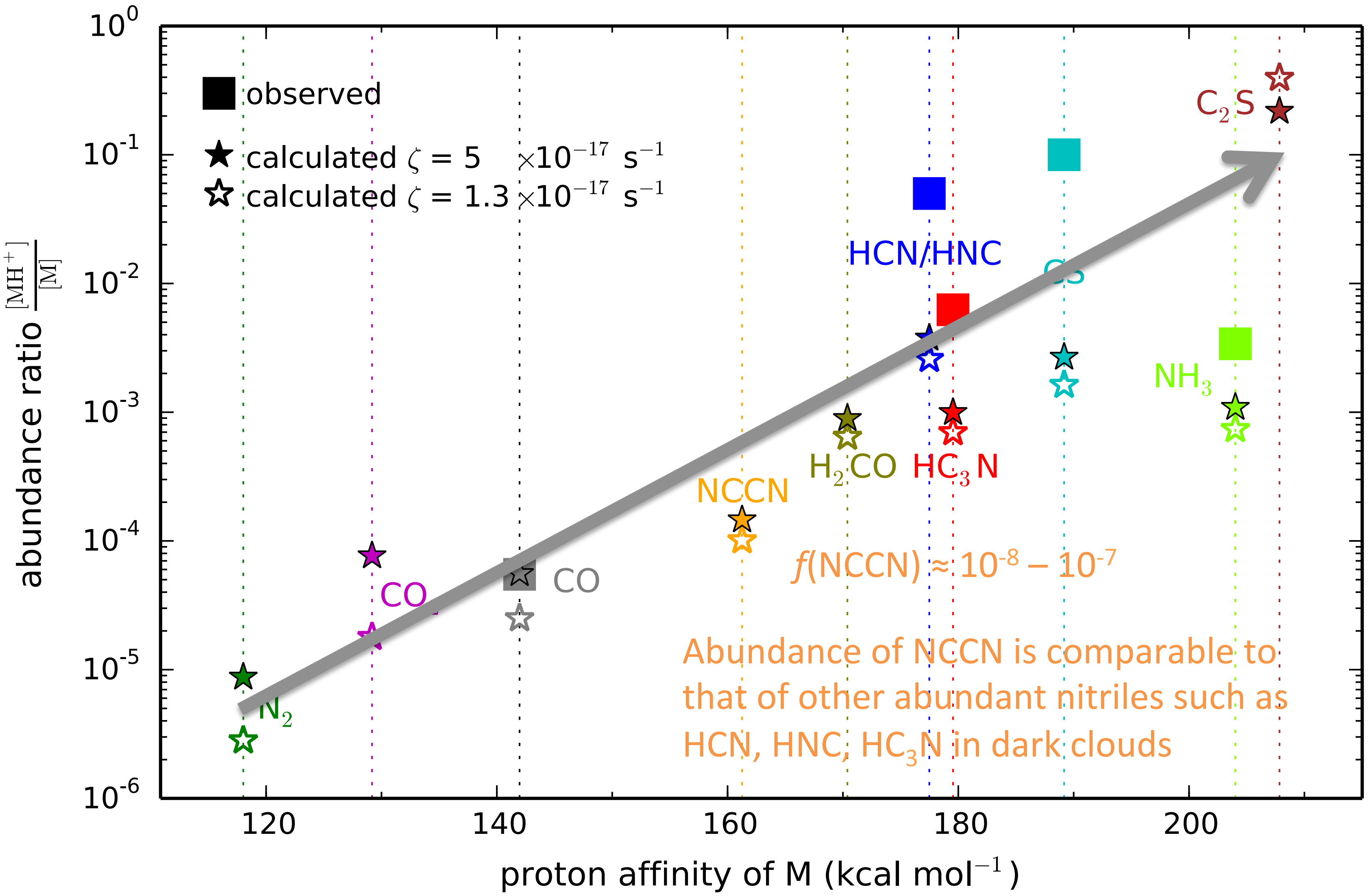
proton transfer by proton donors

At steady state:

$$\frac{[MH^+]}{[M]} = \frac{k_{PT}}{k_{DR}} \frac{[XH^+]}{[e^-]},$$

⇧ proton affinity of M → ⇧ number of proton donors → ⇧ [MH$^+$]/[M]

Protonated molecules in dark clouds



f(NCCN) ≈ 10^{-8} – 10^{-7}

Abundance of NCCN is comparable to that of other abundant nitriles such as HCN, HNC, HC_3N in dark clouds

NCCN and dicyanopolyynes in space

Molecules with 1 cyano (–CN) group are widespread in space

Molecules with two cyano groups ?

NCCN is thought to be the precursor of the CN observed in cometary comae

NCCN observed in the atmosphere of Titan (NC_4N likely to be present as well)

NCCN very likely abundant in dark clouds (evidence after detection of $NCCNH^+$)

Chemistry of NCCN

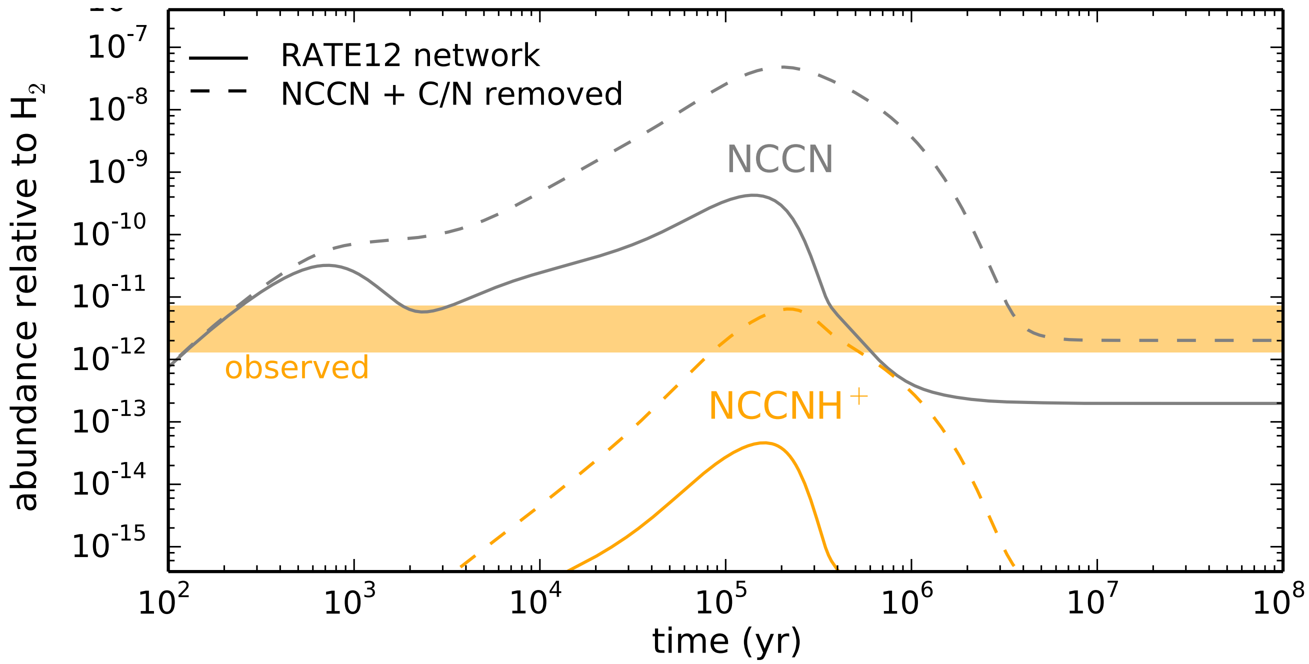
Chemistry of NCCN in dark clouds according to UMIST:

Formation:

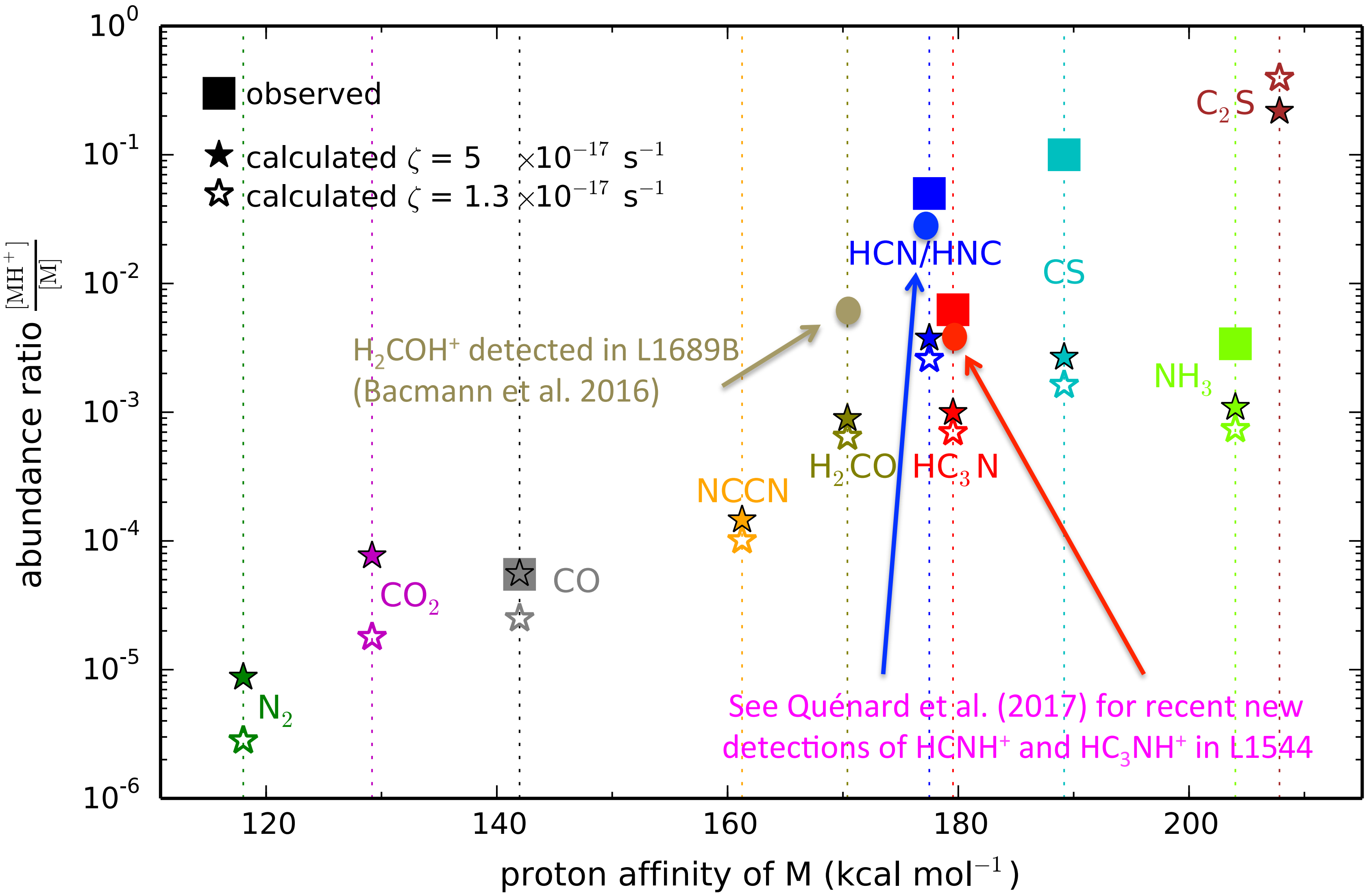
CN + HNC → NCCN + H	$k \approx 2\times10^{-10}$ cm^3 s^{-1} (Petrie et al. 2003)	KIDA ✗ No

Destruction:

NCCN + C → CN + C_2N	$k \approx 10^{-11}$ cm^3 s^{-1} at 300 K (NIST)	KIDA ✔ Yes
NCCN + N → N_2 + C_2N	$k \approx 10^{-11}$ cm^3 s^{-1} at 300 K (NIST)	KIDA ✗ No



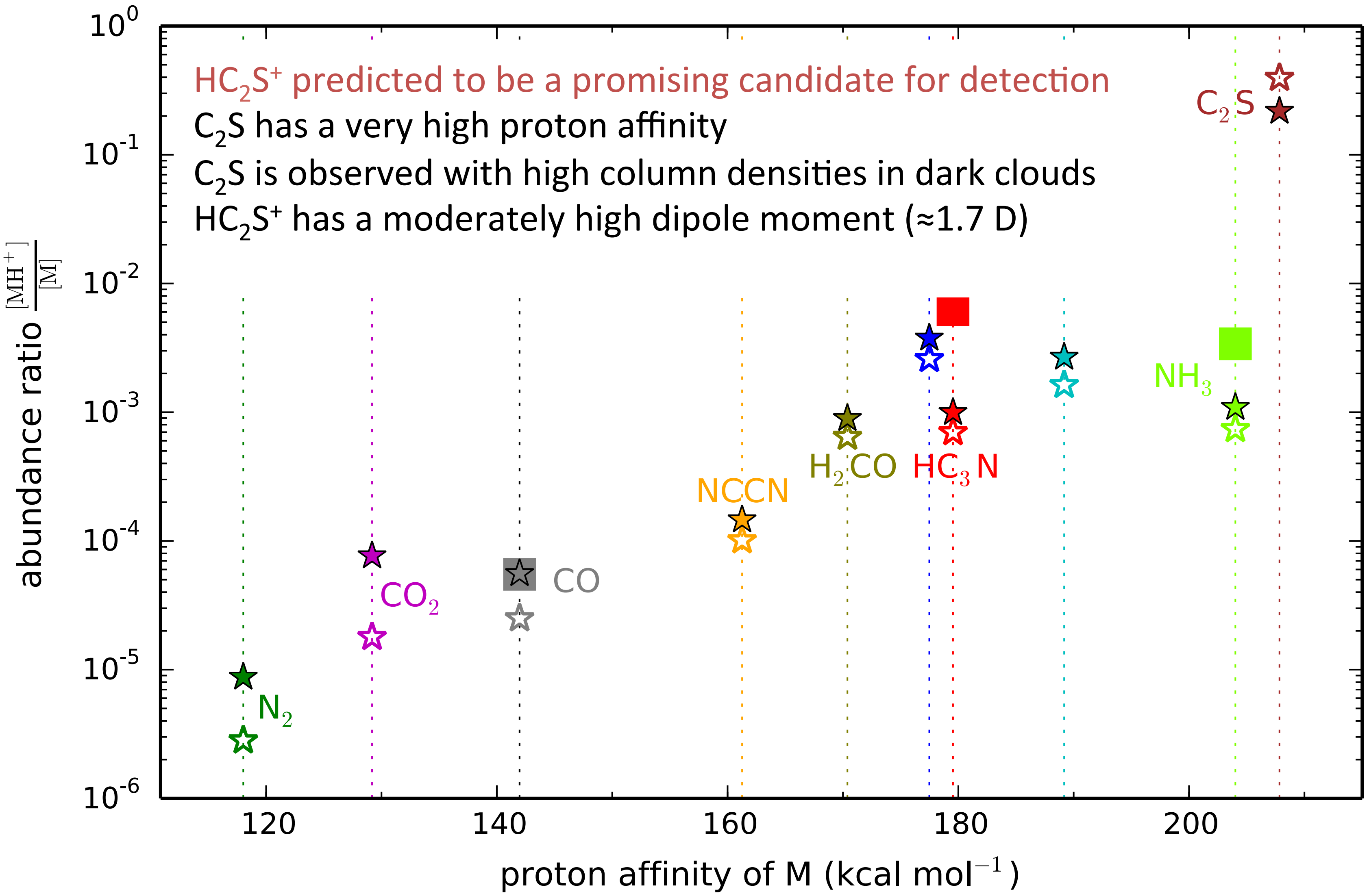
Protonated molecules in dark clouds



H_2COH^+ detected in L1689B (Bacmann et al. 2016)

See Quénard et al. (2017) for recent new detections of $HCNH^+$ and HC_3NH^+ in L1544

Protonated molecules in dark clouds



HC_2S^+ predicted to be a promising candidate for detection

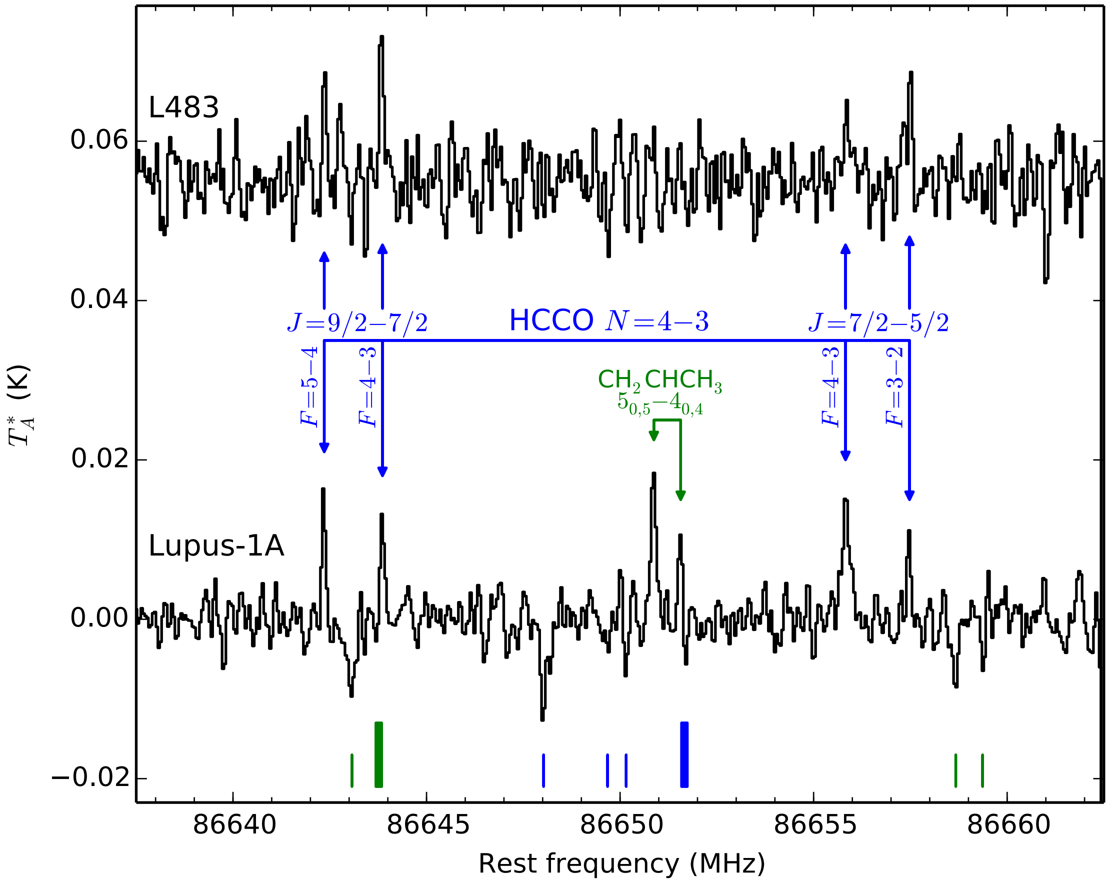
C_2S has a very high proton affinity

C_2S is observed with high column densities in dark clouds

HC_2S^+ has a moderately high dipole moment (≈1.7 D)

Detection of HCCO:
A surprinsingly abundant radical in cold dark clouds

Agúndez et al. (2015), A&A, 577, L5



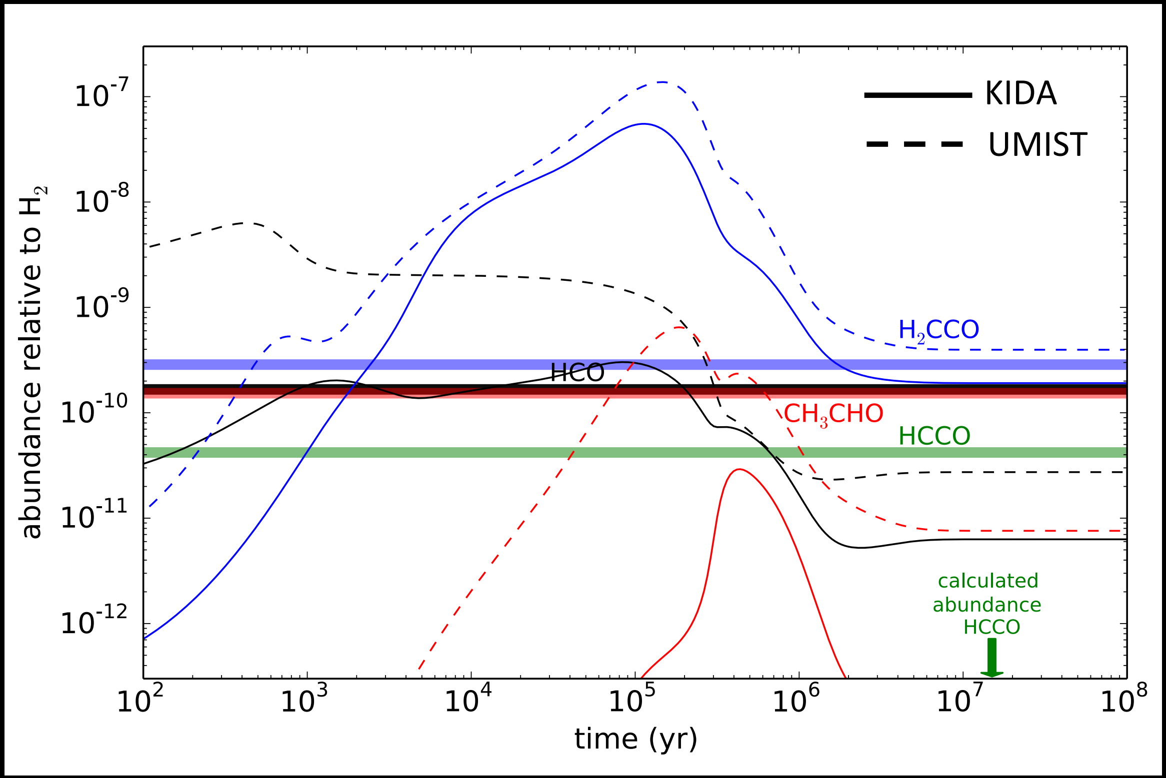
N(HCCO) = 4.3×10^{11} cm^{-2}
f = 1.4×10^{-11}

N(HCCO) = 5.4×10^{11} cm^{-2}
f = 3.6×10^{-11}

Chemistry of HCCO (Agúndez et al. 2015)

HCCO chemistry:
combustion chemistry and
literature on chemical kinetics

Calculated HCCO abundance is much less than observed



Formation:

$OH + C_2H \rightarrow HCCO + H$ $k \approx 3\times10^{-11}$ cm^3 s^{-1} (Frenklach et al. 1992)

$O + C_2H_2 \rightarrow HCCO + H$ *important activation barrier* (Balucani et al. 2012)
$OH + H_2CCO \rightarrow HCCO + H_2O$ *rapid but low yield of HCCO* (Brown et al. 1989; Grußdorf et al. 1994)

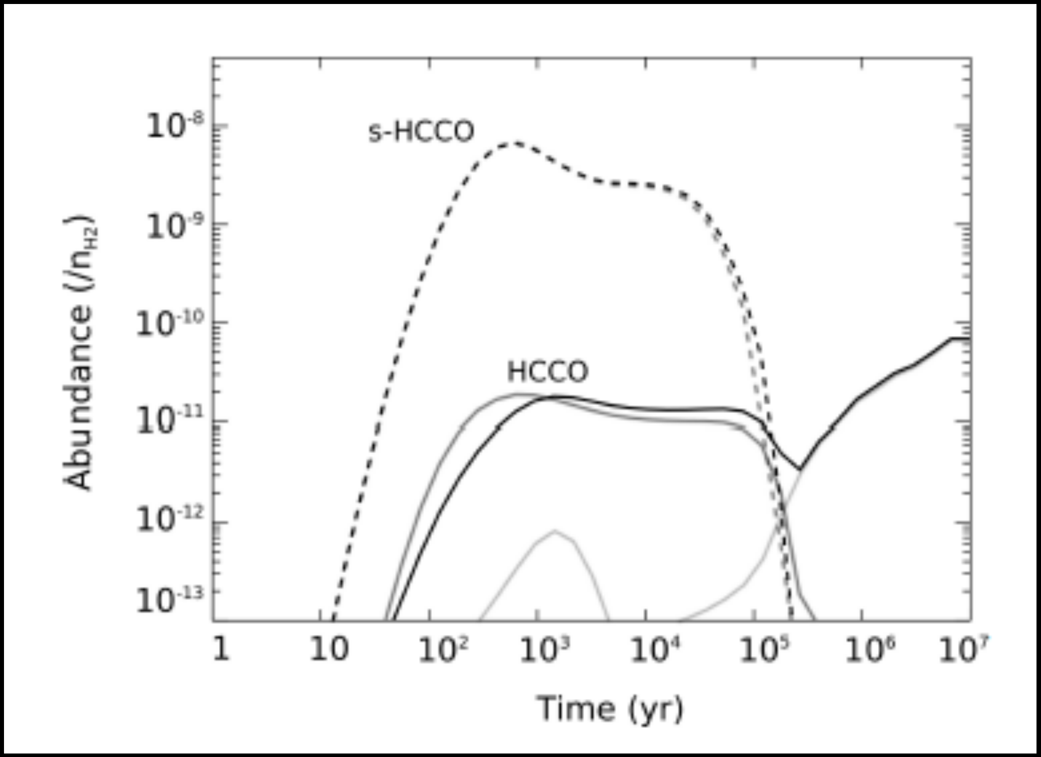
Destruction:

$HCCO + H \rightarrow$ products $k \approx 10^{-10}$ cm^3 s^{-1} at 300 K (NIST)
$HCCO + O \rightarrow$ products $k \approx 10^{-10}$ cm^3 s^{-1} at 300 K (NIST)
$HCCO + N \rightarrow$ products $k \approx 10^{-10}$ cm^3 s^{-1} at 300 K (NIST)

Chemistry of HCCO revisited by Wakelam et al. (2015)

HCCO formed by OH + C_2H at late times

Grain-surface chemistry seems to play a big role for HCCO survivability



Formation:

OH + C_2H → HCCO + H	~~*k* ≈ 3×10^{-11} cm^3 s^{-1} (Frenklach et al. 1992)~~
	k ≈ 2×10^{-10} cm^3 s^{-1} (estimation based on O + C_2H, OH + radicals)
~~O + C_2H_2 → HCCO + H~~	~~*important activation barrier* (Balucani et al. 2012)~~
~~OH + H_2CCO → HCCO + H_2O~~	~~*rapid but low yield of HCCO* (Brown et al. 1989; Grußdorf et al. 1994)~~
H(s) + CCO(s) → HCCO	*grain-surface reaction*

Destruction:

HCCO + H → products	*k* ≈ 10^{-10} cm^3 s^{-1} at 300 K (NIST)
HCCO + O → products	*k* ≈ 10^{-10} cm^3 s^{-1} at 300 K (NIST)
HCCO + N → products	*k* ≈ 10^{-10} cm^3 s^{-1} at 300 K (NIST)

The HCO radical in cold dark clouds

Radical typically observed in PDRs but not in cold dark clouds (until a few years ago)

First detection of HCO in a dark cloud (L1448) reported by Jiménez-Serra et al. (2004)

HCO detection in TMC-1 and B1 reported by Cernicharo et al. (2012)

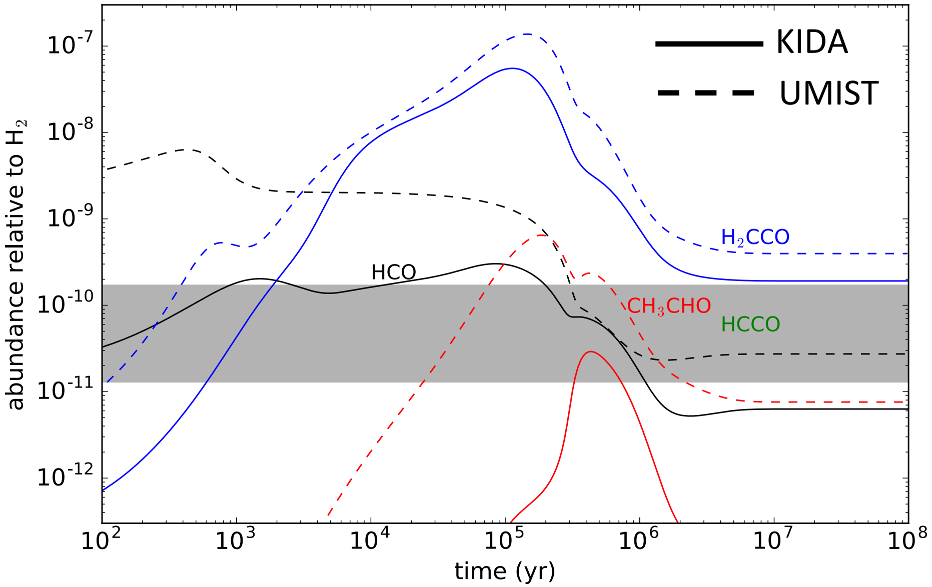
Agúndez et al. (2015) reported the detection of HCO in their 9 targeted dark clouds, confirming the widespread occurrence of HCO in these environments

Later on, Bacmann & Faure (2016) reported additional detections of HCO in dark clouds

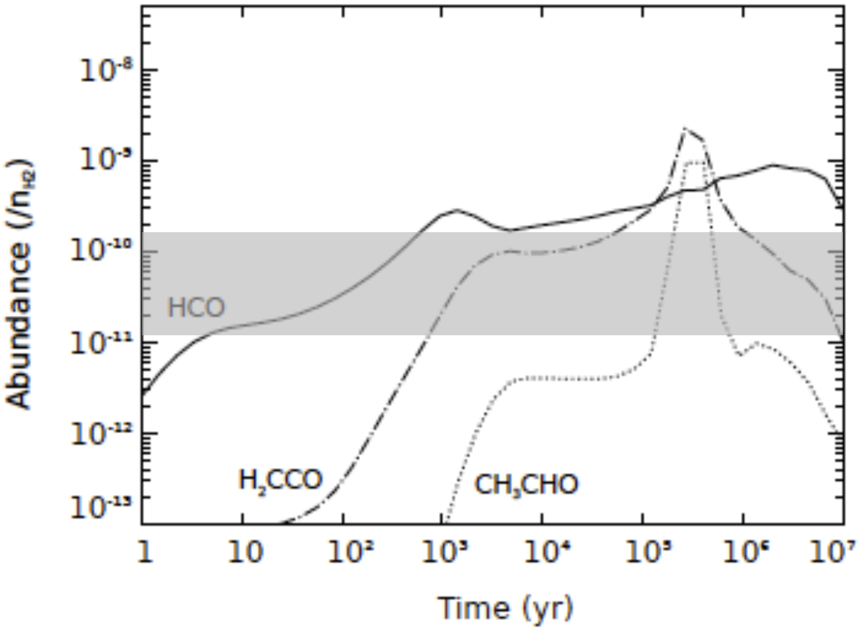
$N(HCO)/N(H_2) = (1.3\text{-}17) \times 10^{-11}$	$10^{-11}\text{-}10^{-10}$
$N(H_2CO)/N(HCO) = 7\text{-}22$	≈ 10

The HCO radical in cold dark clouds

Agúndez et al. (2015)
gas-phase model



Wakelam et al. (2015)
gas-grain model



Gas-phase models form HCO with abundances close to the observed values.

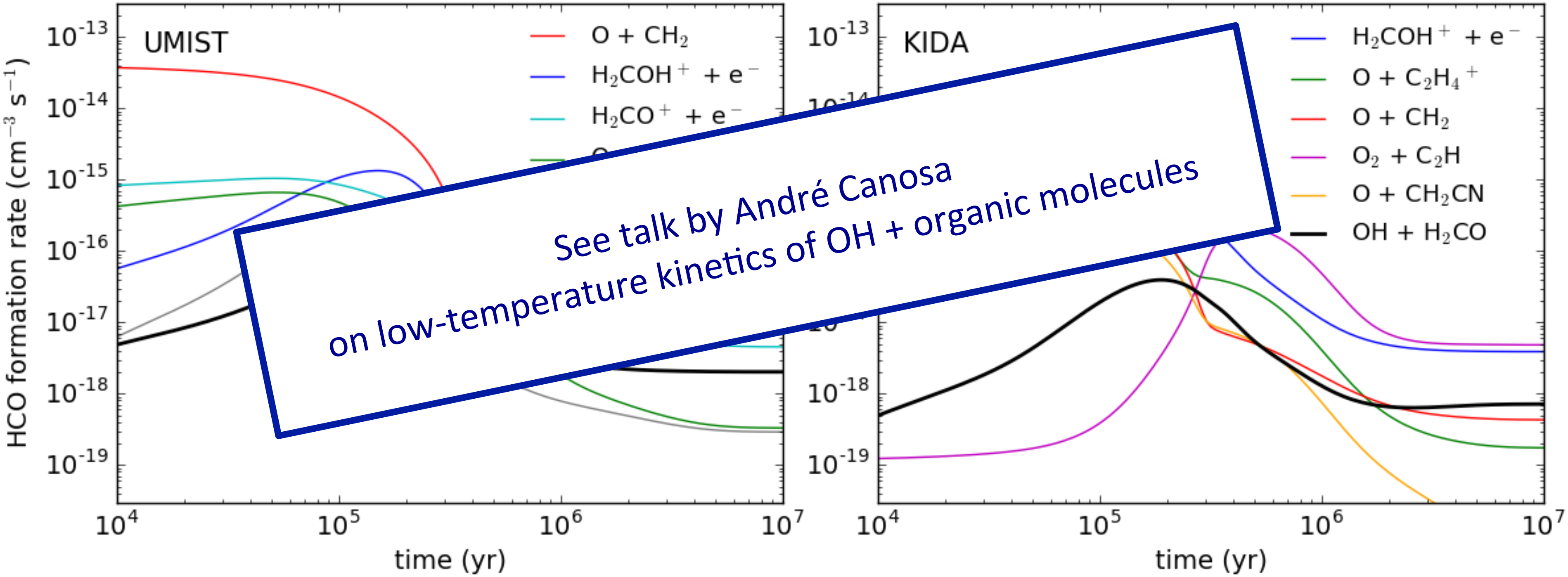
Including grain-surface chemistry increases the HCO abundance at late times (>10^5-10^6 yr).

Gas-phase formation of HCO in cold dark clouds

HCO chemistry discussed by Bacmann & Faure (2016) based on simple steady-state chemical schemes

Neutral-neutral route	$H_2CO + OH \rightarrow HCO + H_2O$	fast but not the main HCO-forming reaction
	$O + CH_2 \rightarrow HCO + H$	✓
Ion-molecule route	$H_2COH^+ + e^- \rightarrow HCO + H + H$	✓
	$O + C_2H_4^+ \rightarrow HCO + CH_3^+$	✓

Rate constant of reaction $H_2CO + OH$ measured down to 22 K at CRESU, Ciudad Real (Ocaña et al. 2017)



See talk by André Canosa
on low-temperature kinetics of OH + organic molecules

Propylene (CH_2CHCH_3) in cold dark clouds

Partially saturated hydrocarbon first detected in TMC-1 by Marcelino et al. (2007)

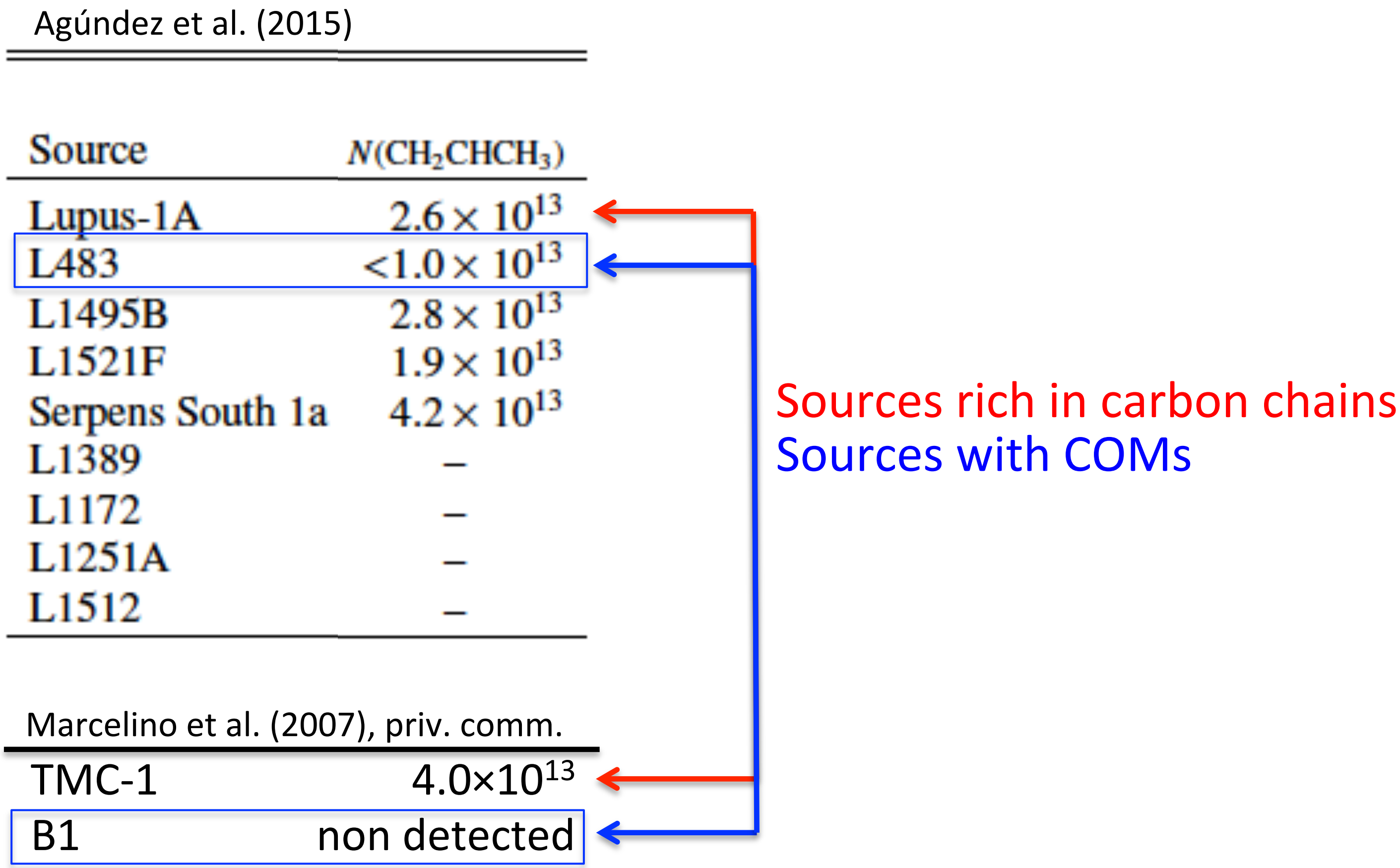
Herbst et al. (2010) proposed $C_3H_3^+ \xrightarrow{H_2} C_3H_5^+ \xrightarrow{H_2} C_3H_7^+ \xrightarrow{e-} C_3H_6$

Lin et al. (2013) find that the above scheme should not work at low temperature

Agúndez et al. (2015) reported the detection of C_3H_6 in four additional dark clouds, confirming the widespread occurrence of C_3H_6 in these environments

Hickson et al. (2016) explain the formation of C_3H_6 through the hydrogenation of C_3 on grain surfaces plus chemical desorption

Propylene (CH_2CHCH_3) in cold dark clouds



Agúndez et al. (2015)

Source	$N(CH_2CHCH_3)$
Lupus-1A	2.6×10^{13}
L483	$<1.0 \times 10^{13}$
L1495B	2.8×10^{13}
L1521F	1.9×10^{13}
Serpens South 1a	4.2×10^{13}
L1389	–
L1172	–
L1251A	–
L1512	–

Marcelino et al. (2007), priv. comm.

TMC-1	4.0×10^{13}
B1	non detected

Sources rich in carbon chains

Sources with COMs

Propylene is detected in dark clouds rich in carbon chains (TMC-1, Lupus-1A, …)
Propylene is not detected in dark clouds with complex organic molecules (B1, L483, …)

Summary

Detection of $NCCNH^+$ evidences that

NCCN is a nitrile as abundant as HCN, HNC, and HC_3N in dark clouds

NCCN chemistry needs to be revisited

Detection of HCCO and widespread occurrence of HCO

Various related couples of "stable molecule/radical" found in dark clouds

H_xCO
- H_2CO / HCO — HCO: gas-phase, various reactions
- CH_3OH / CH_3O — CH_3O: gas-phase, OH + CH_3OH (Antiñolo et al. 2016, talk by A. Canosa)

H_xCCO
- H_2CCO / HCCO — HCCO: gas-phase OH + C_2H (assisted by grain-surface chemistry ?)
- CH_3CHO / CH_3CO, CH_2CHO
- CH_3CH_2OH / …

Widespread presence of CH_2CHCH_3 in dark clouds

It is the most saturated hydrocarbon detected in these environments

It is detected in sources rich in carbon chains and with no COMs