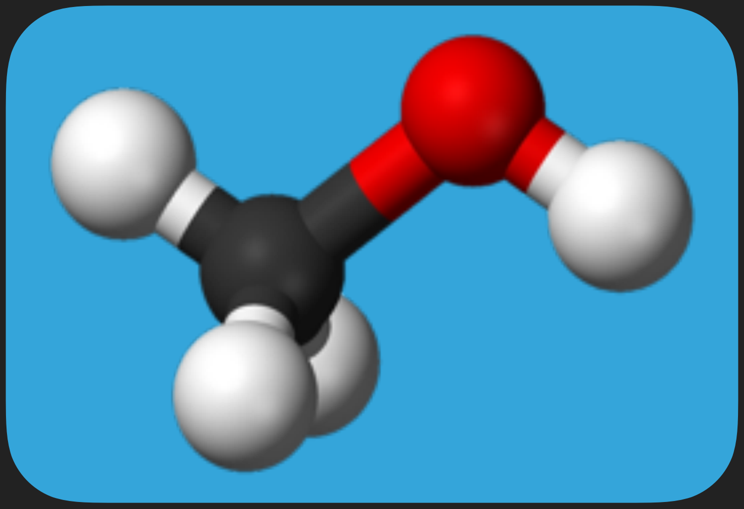
Astrochemistry: from Space to Earth 2016
Grenoble, France



IPAG
Institut de Planétologie et d'Astrophysique de Grenoble

ANDREA CERNUTO, JOAN ENRIQUE, ÁGNES KÓSPÁL, MARKO MITIĆ, ANTONIO OCAÑA, ANNA PUNANOVA, VICTOR DE S. MAGALHAES, URSZULA SZCZEPANIAK, FANNY VAZART

THE MYSTERY OF METHANOL IN THE ISM

Tutor: Cecilia Ceccarelli

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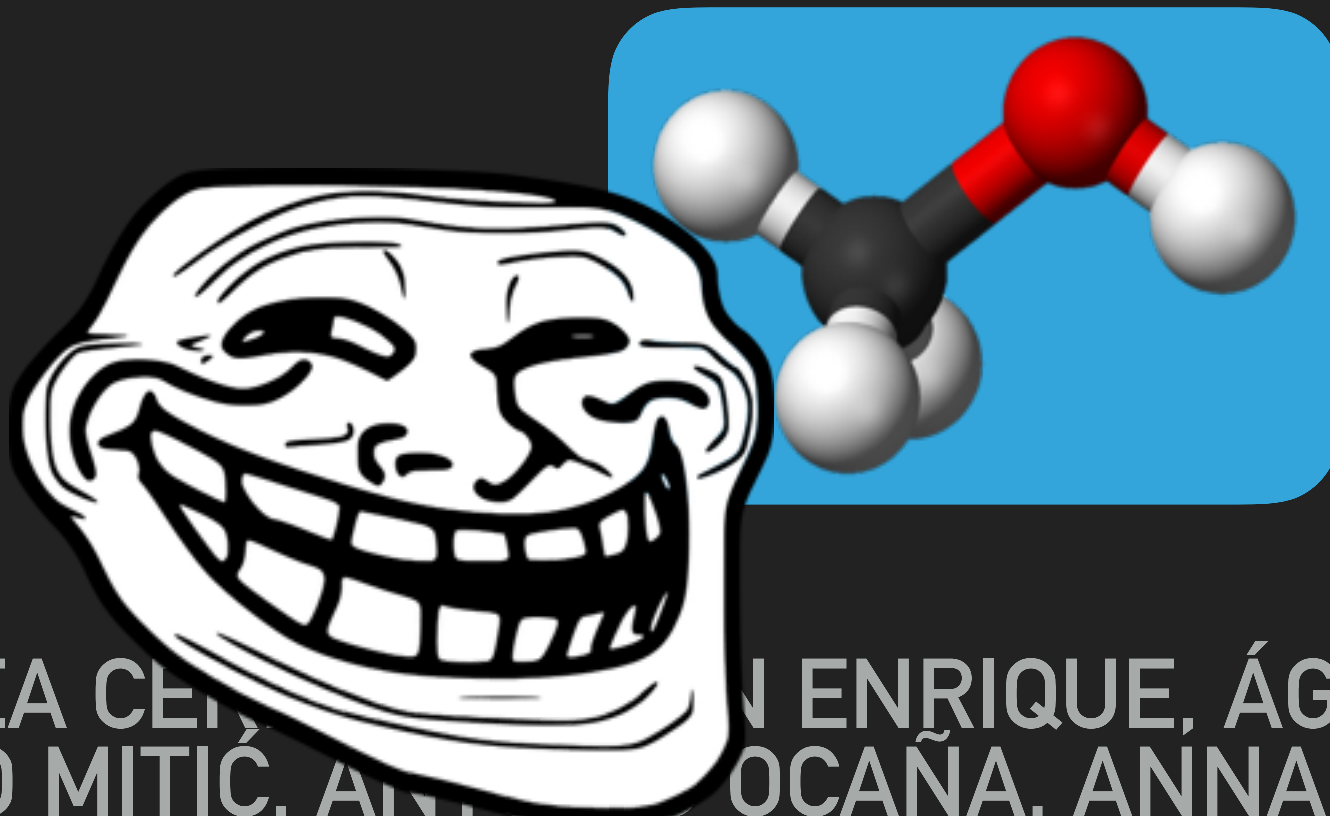


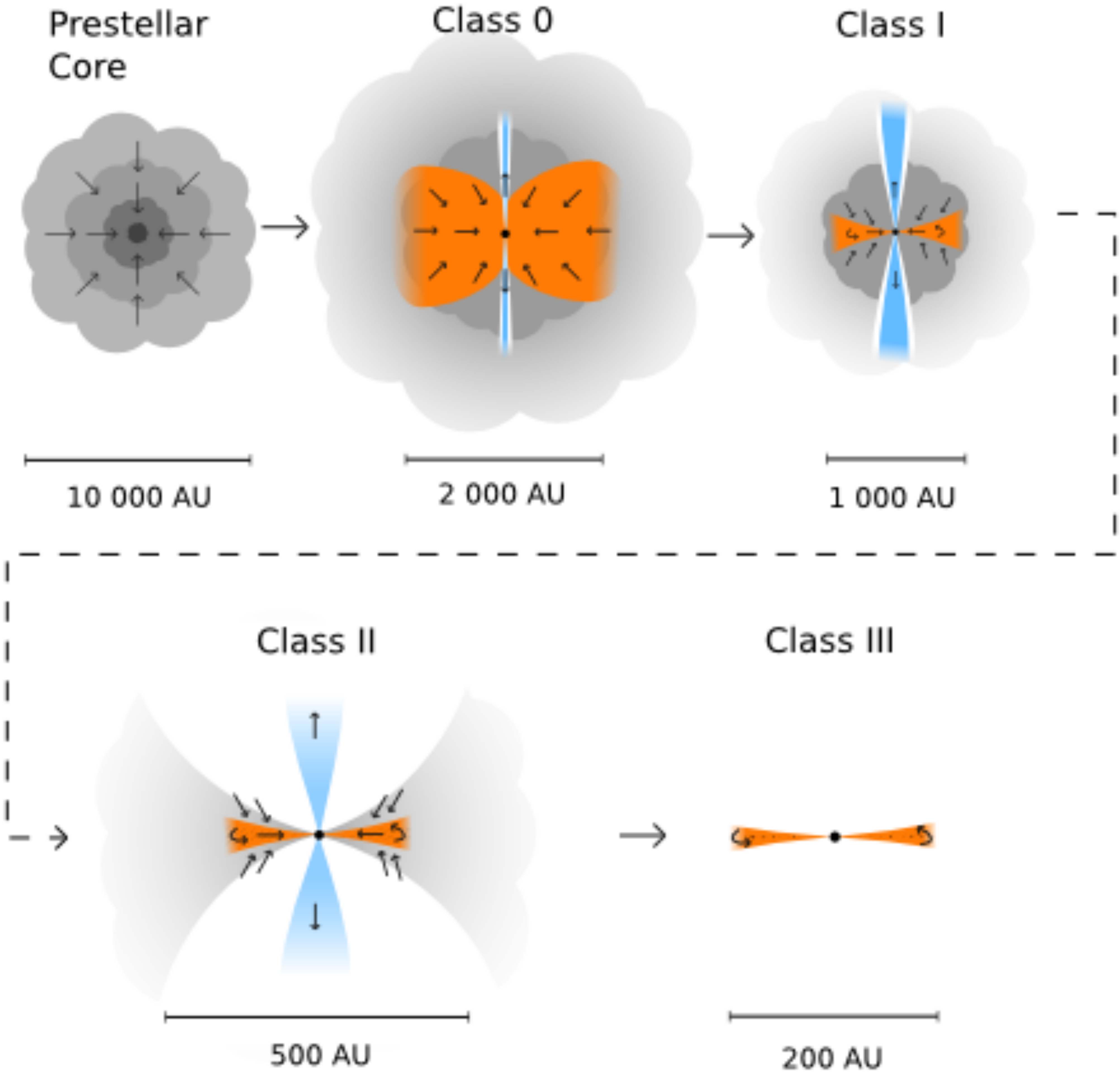
ANDREA CE[illegible]N ENRIQUE, ÁGNES KÓSPÁL, MARKO MITIĆ, AN[illegible] OCAÑA, ANNA PUNANOVA, VICTOR DE S. MAGALHAES, URSZULA SZCZEPANIAK, FANNY VAZART

THE MYSTERY OF METHATROLL IN THE ISM

Tutor: Cecilia Ceccarelli

SCIENTIFIC CONTEXT

- Methanol has been observed in large quantities in the ISM.
    - Up to about 10% of elemental carbon in the solid phase.
- From molecular clouds and prestellar cores to protostars.
- Methanol is the precursor molecule for many astronomic complex organic molecules.
- Even though it was first detected decades ago, its routes of formation and destruction in the ISM are still a mystery!



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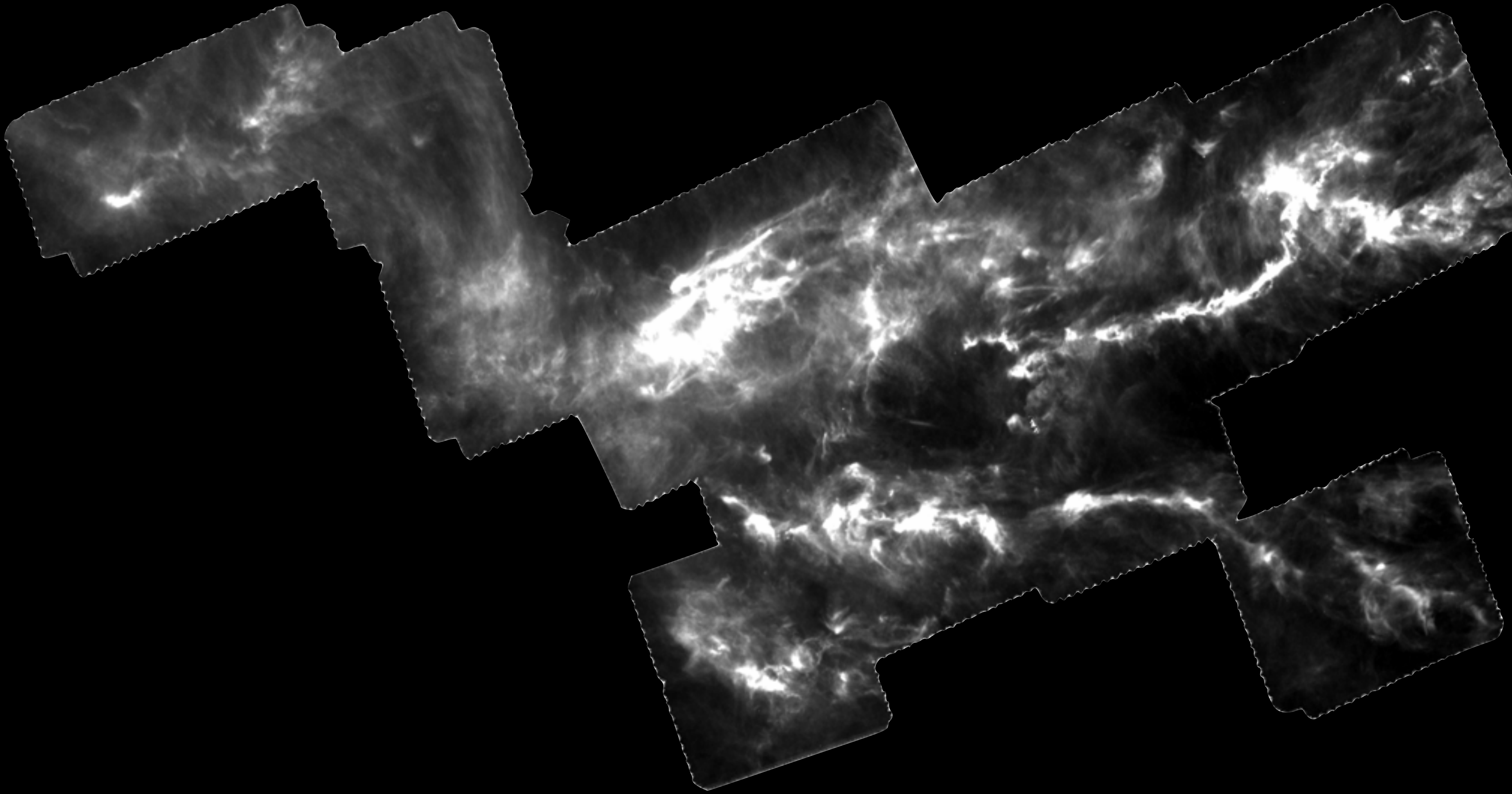
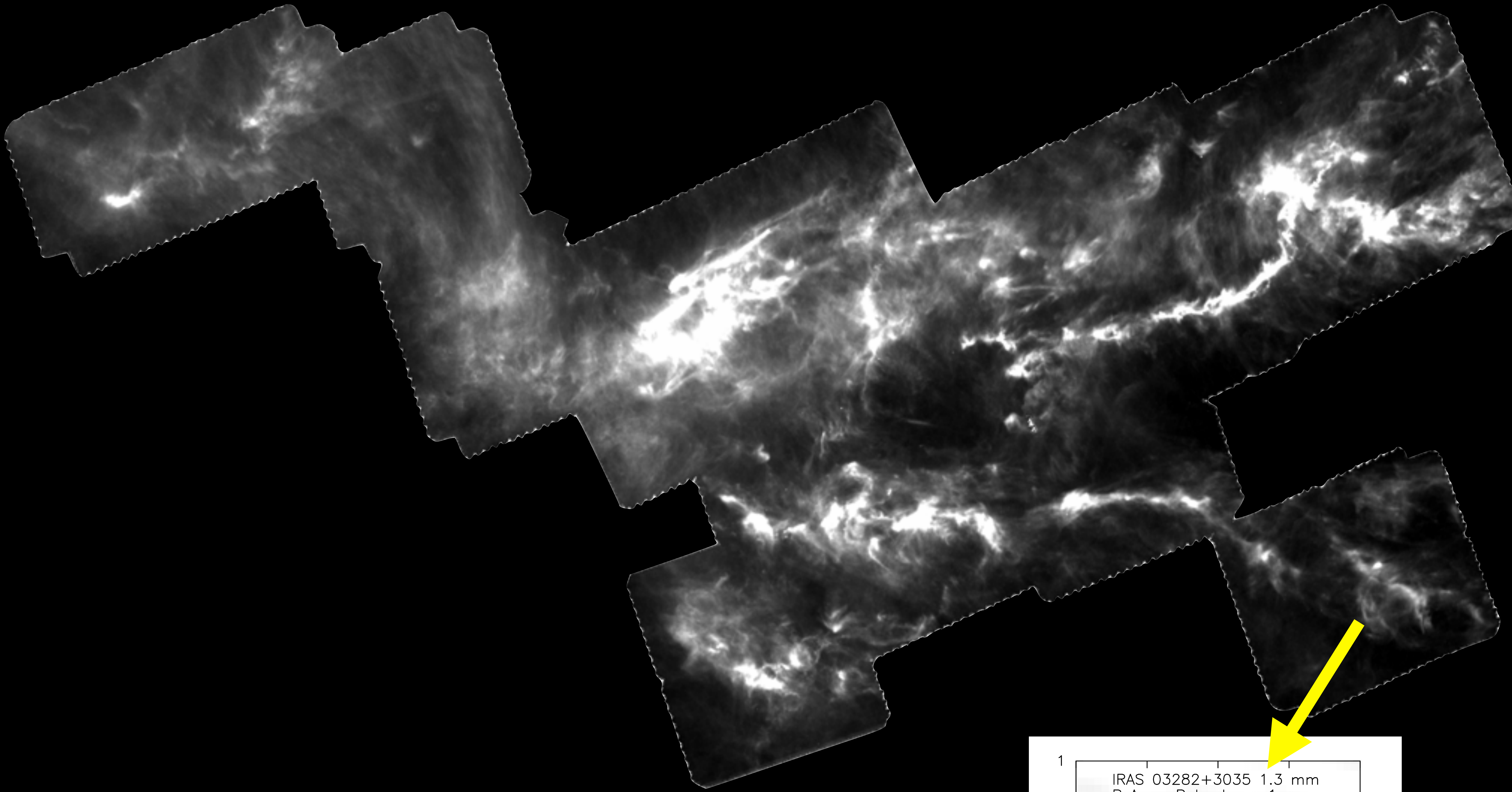
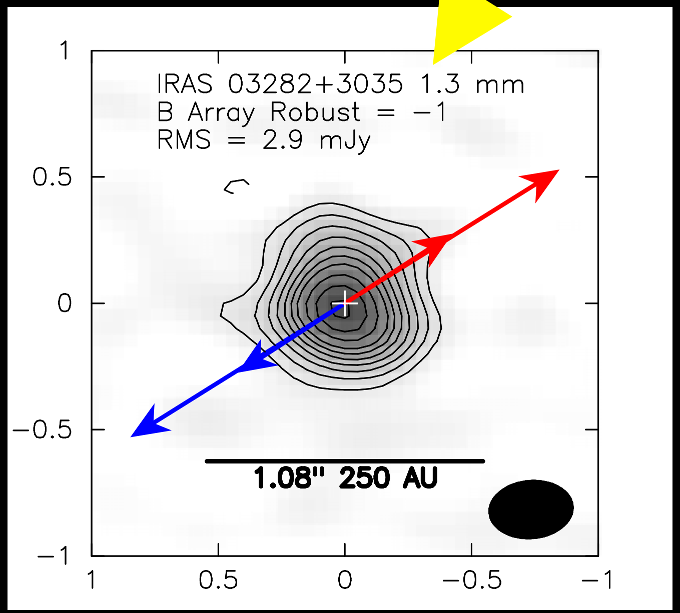
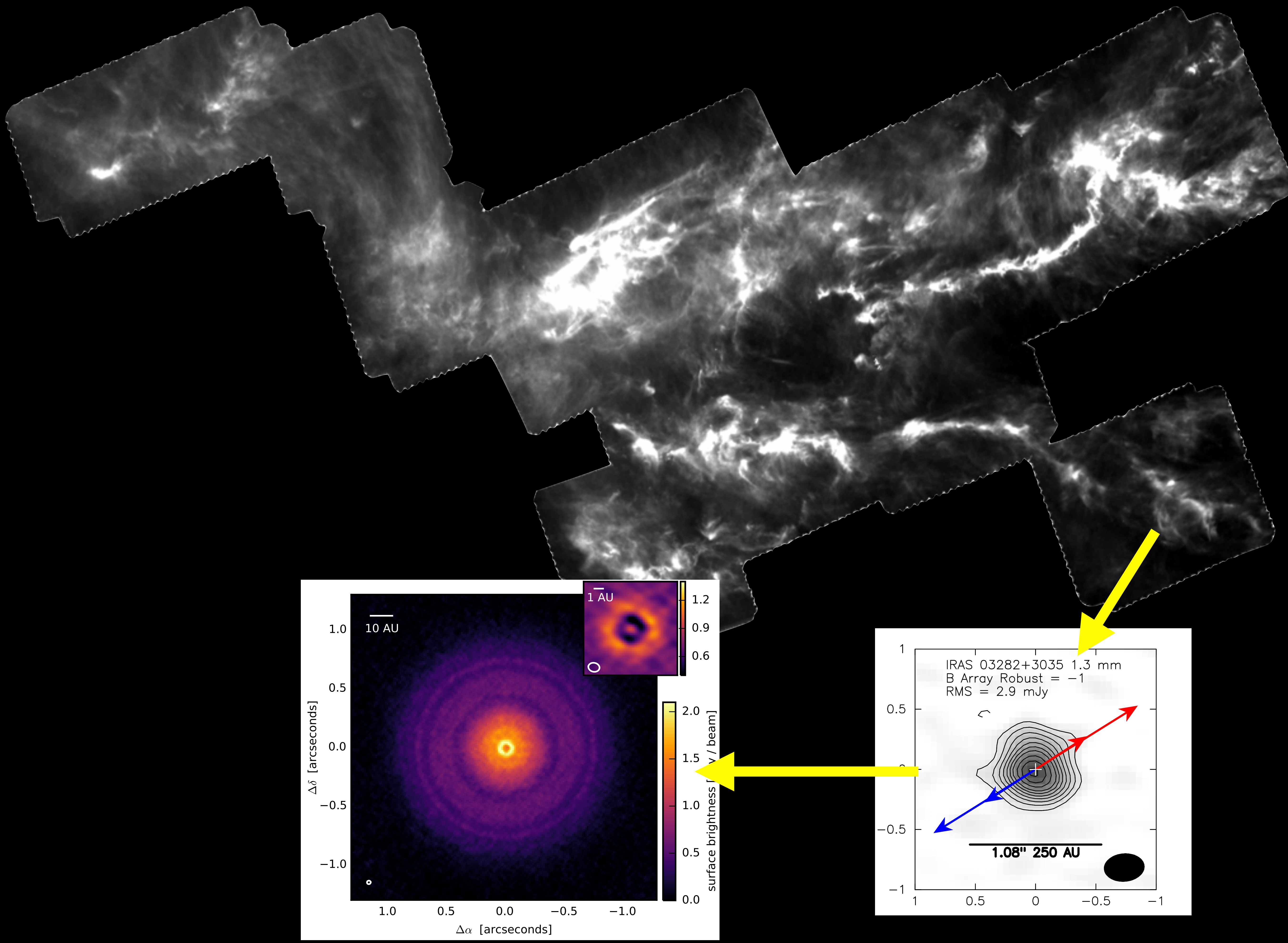


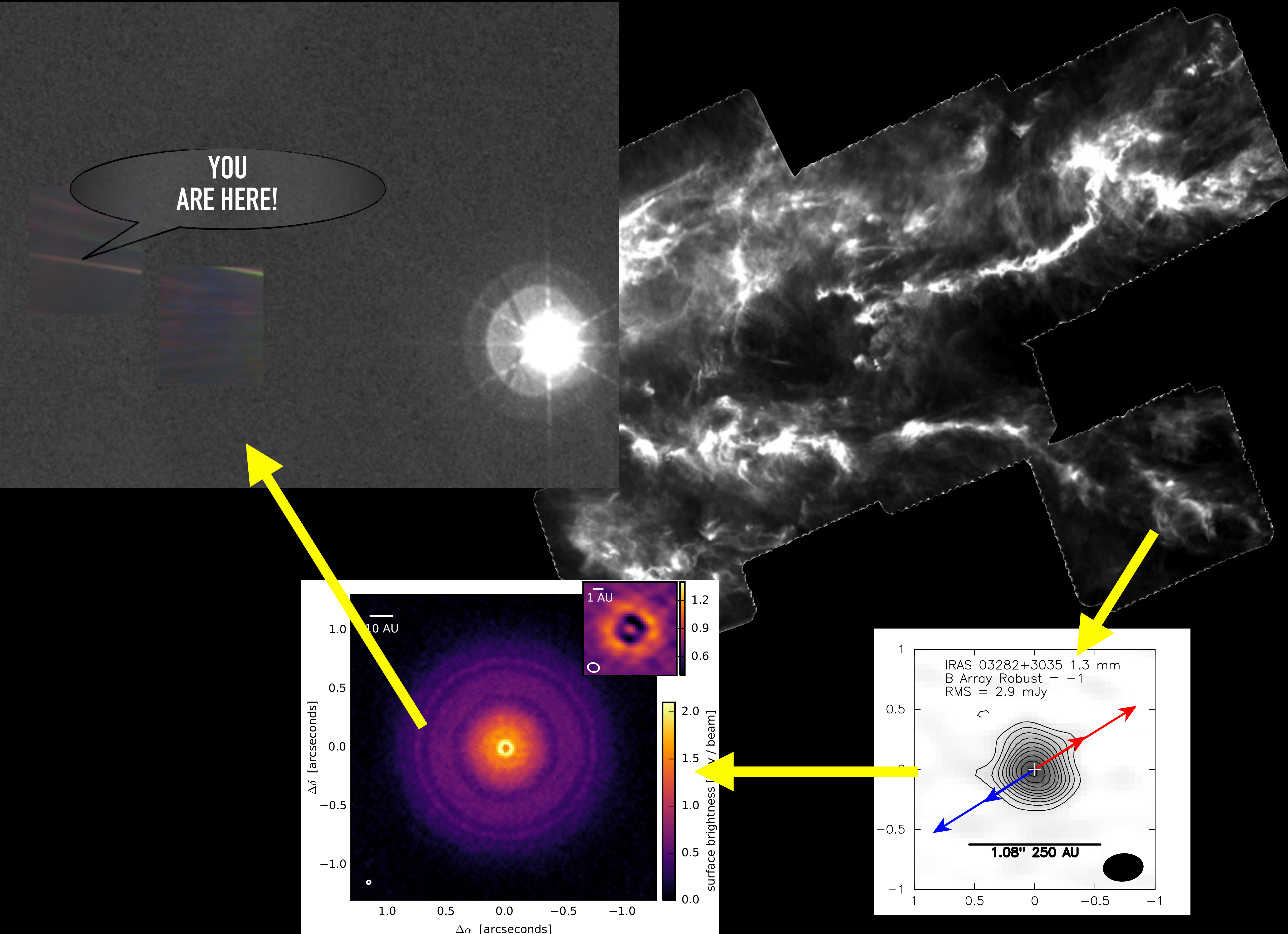


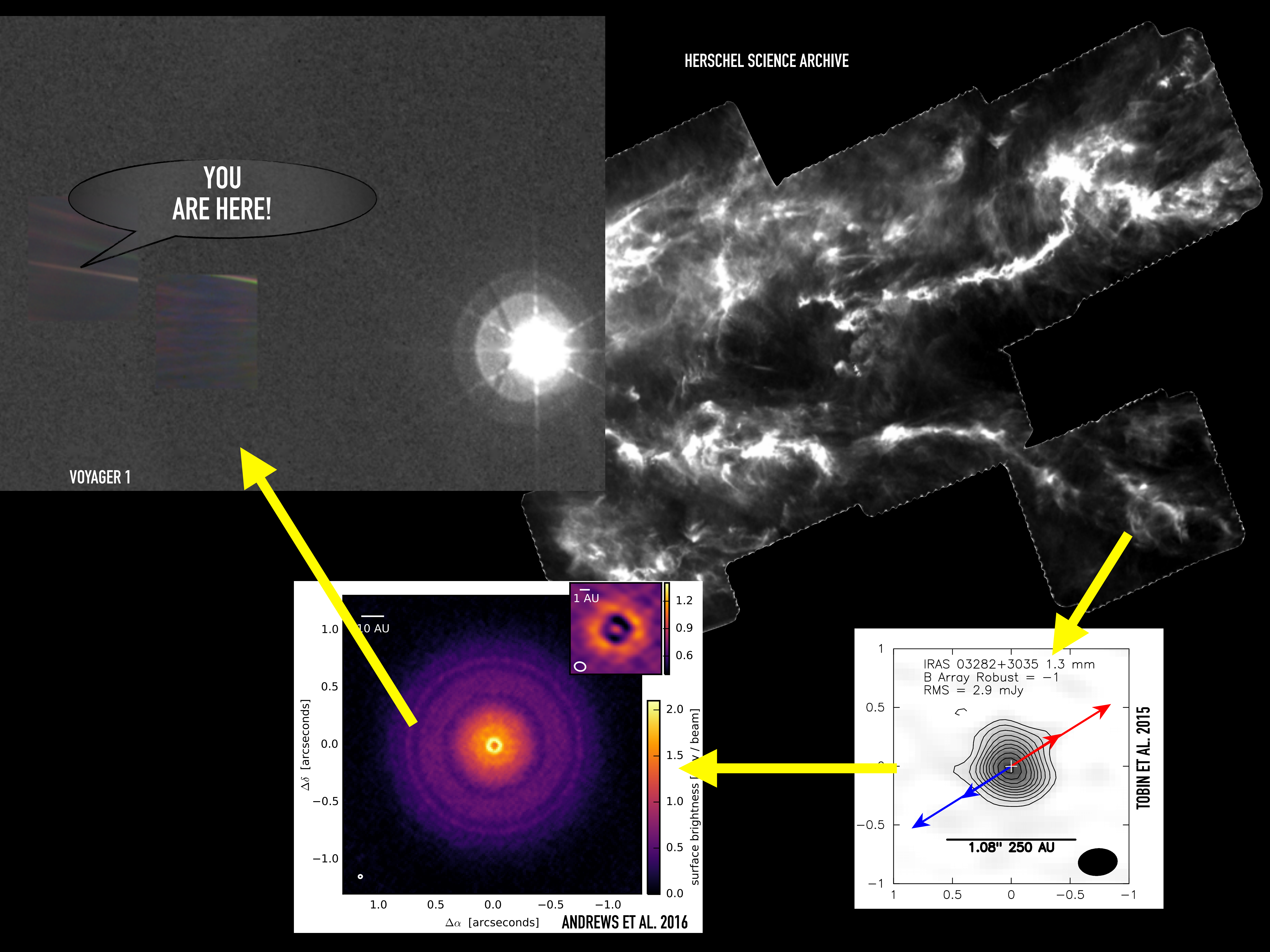


IRAS 03282+3035 1.3 mm
B Array Robust = −1
RMS = 2.9 mJy
1.08" 250 AU



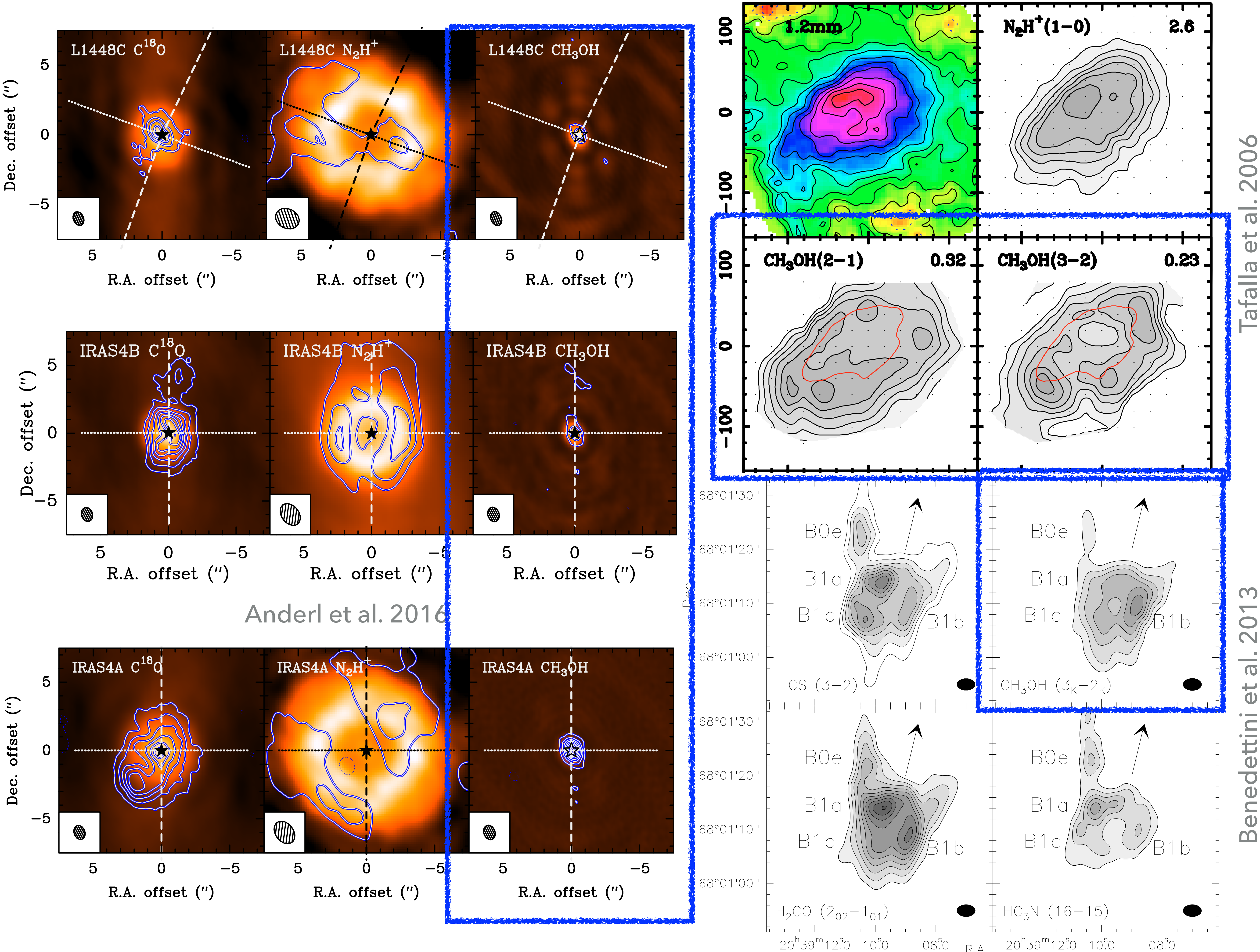
10 AU
1 AU
Δδ [arcseconds]
Δα [arcseconds]
IRAS 03282+3035 1.3 mm
B Array Robust = −1
RMS = 2.9 mJy
1.08" 250 AU


YOU
ARE HERE!
10 AU
1 AU
1.2
0.9
0.6
Δδ [arcseconds]
Δα [arcseconds]
surface brightness
2.0
1.5
1.0
0.5
0.0
IRAS 03282+3035 1.3 mm
B Array Robust = −1
RMS = 2.9 mJy
1.08" 250 AU


YOU
ARE HERE!
VOYAGER 1
HERSCHEL SCIENCE ARCHIVE
10 AU
1 AU
1.2
0.9
0.6
2.0
1.5
1.0
0.5
0.0
surface brightness [mJy / beam]
Δδ [arcseconds]
Δα [arcseconds]
ANDREWS ET AL. 2016
IRAS 03282+3035 1.3 mm
B Array Robust = −1
RMS = 2.9 mJy
1.08" 250 AU
TOBIN ET AL. 2015

OBSERVATIONS IN THE GAS

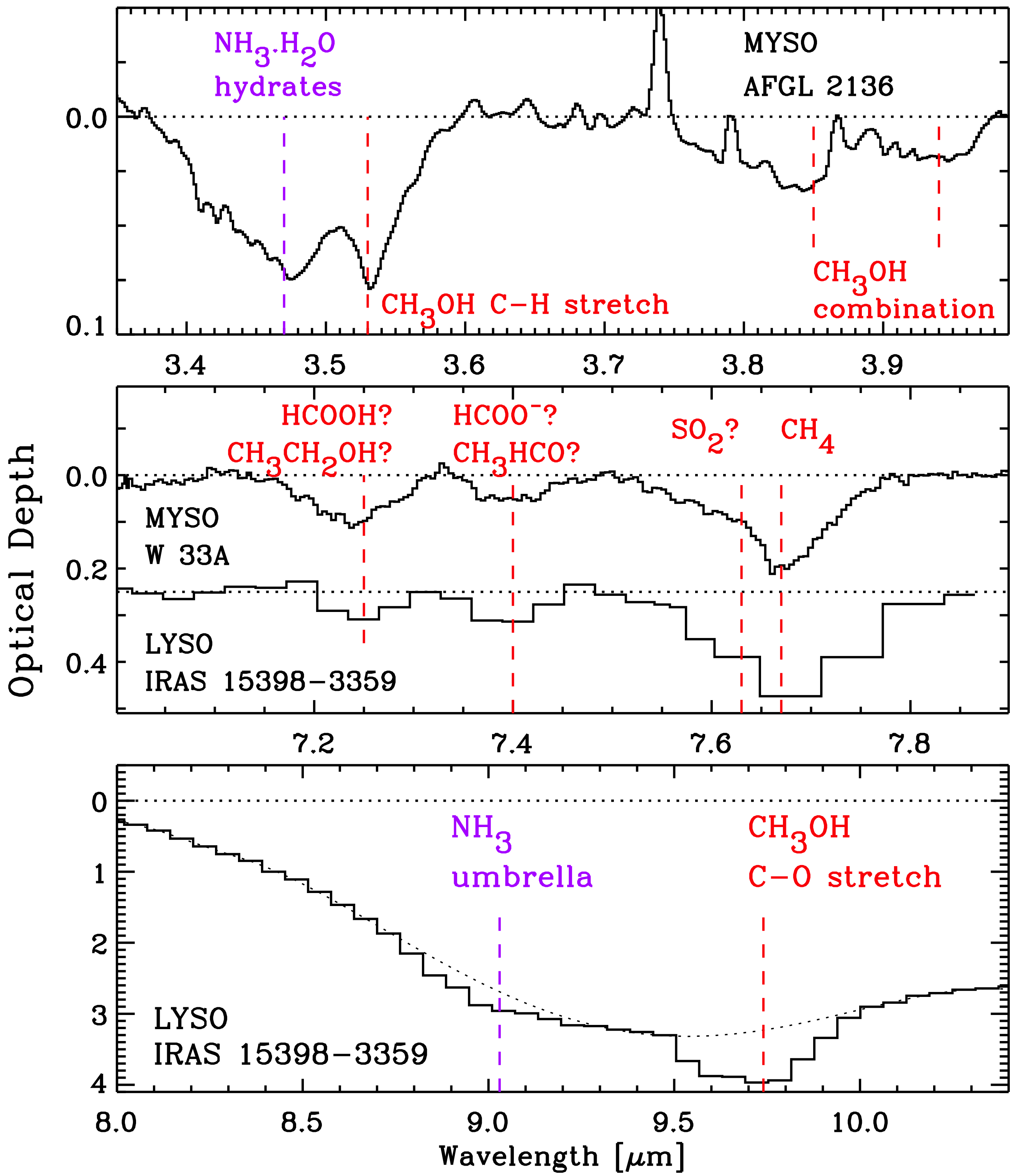
- Methanol was detected for the first time by Ball et al. 1970 in Sagittarius A and B2.
- Since then it has been detected in diffuse molecular clouds; prestellar cores (Bizzocchi et al. 2014, Vastel et al. 2014), hot cores (Blake et al. 1997) and hot corinos (Schöier et al. 2002).
- In the pre-stellar stages its abundance in the gas phase is comparable to other trace species like HCN (X_{CH_3OH}~10^{-9}-10^{-10}/H_2 e.g. Tafalla et al. 2006).
- In regions with protostars its abundance can be as high as 1% of that of CO due to the sublimation of the ice mantles (X_{CH_3OH}~10^{-6}/H_2 e.g. Maret et al. 2005).

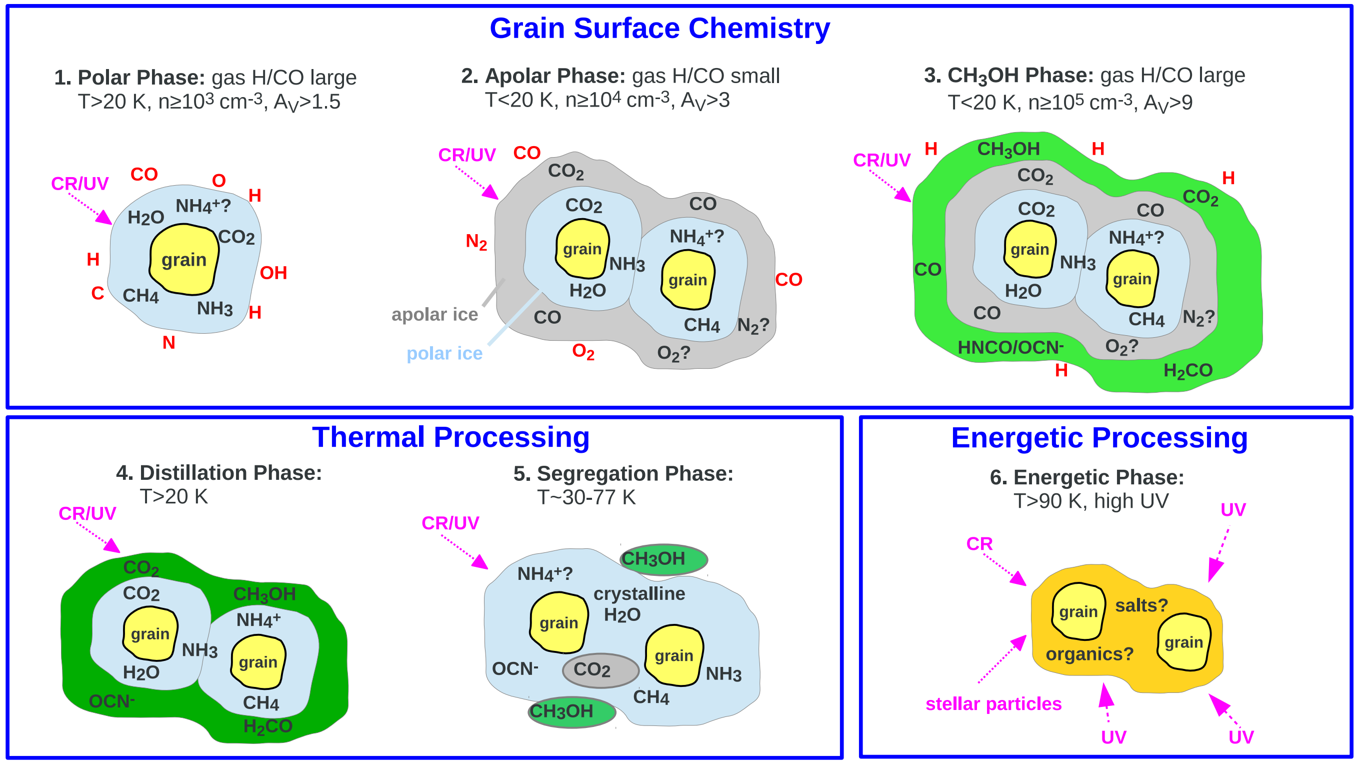


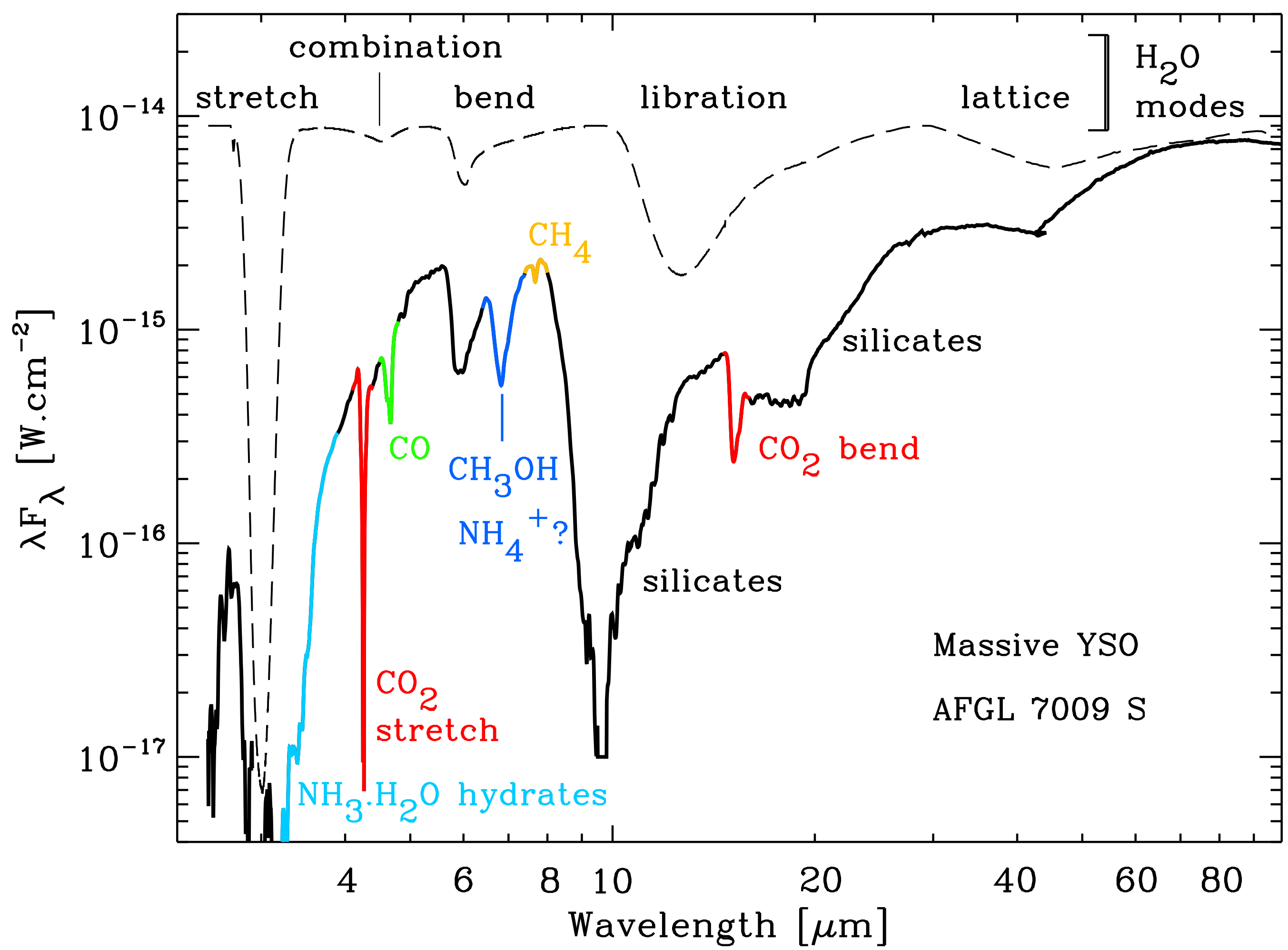
L1448C C18O
L1448C N2H+
L1448C CH3OH
IRAS4B C18O
IRAS4B N2H+
IRAS4B CH3OH
IRAS4A C18O
IRAS4A N2H+
IRAS4A CH3OH
Dec. offset (″)
R.A. offset (″)
Anderl et al. 2016
1.2mm
N2H+(1−0) 2.6
CH3OH(2−1) 0.32
CH3OH(3−2) 0.23
Tafalla et al. 2006
B0e
B1a
B1c
B1b
CS (3−2)
CH3OH (3K−2K)
H2CO (202−101)
HC3N (16−15)
68°01′30″
68°01′20″
68°01′10″
68°01′00″
20h39m12.s0 10.s0 08.s0
R.A.
Benedettini et al. 2013

OBSERVATIONS IN THE ICE

- Methanol was first detected in the ices by Tielens et al. 1991.
- Since then it has been observed towards protostars and pre-stellar phase material in absorption in front of strong continuum sources.
- From these observations it was inferred that the abundance of methanol in the ices can vary from 1% to 30% of the abundance of water ice (Pontoppidan et al. 2003; Gibb et al. 2004).
- This very high abundance corresponds to ~10% of the total carbon abundance.







Boogert et al. 2015

FORMATION MECHANISMS

- GAS-PHASE CHEMISTRY
- GRAIN SURFACE CHEMISTRY

FORMATION MECHANISMS

- GAS-PHASE CHEMISTRY
- GRAIN SURFACE CHEMISTRY

DESTRUCTION MECHANISMS

- UV PHOTONS (6.9 - 13.6 eV)
- COSMIC RAYS (keV - MeV)
- IONS (H_3^+ - He^+ - HCO^+ - H_3O^+)

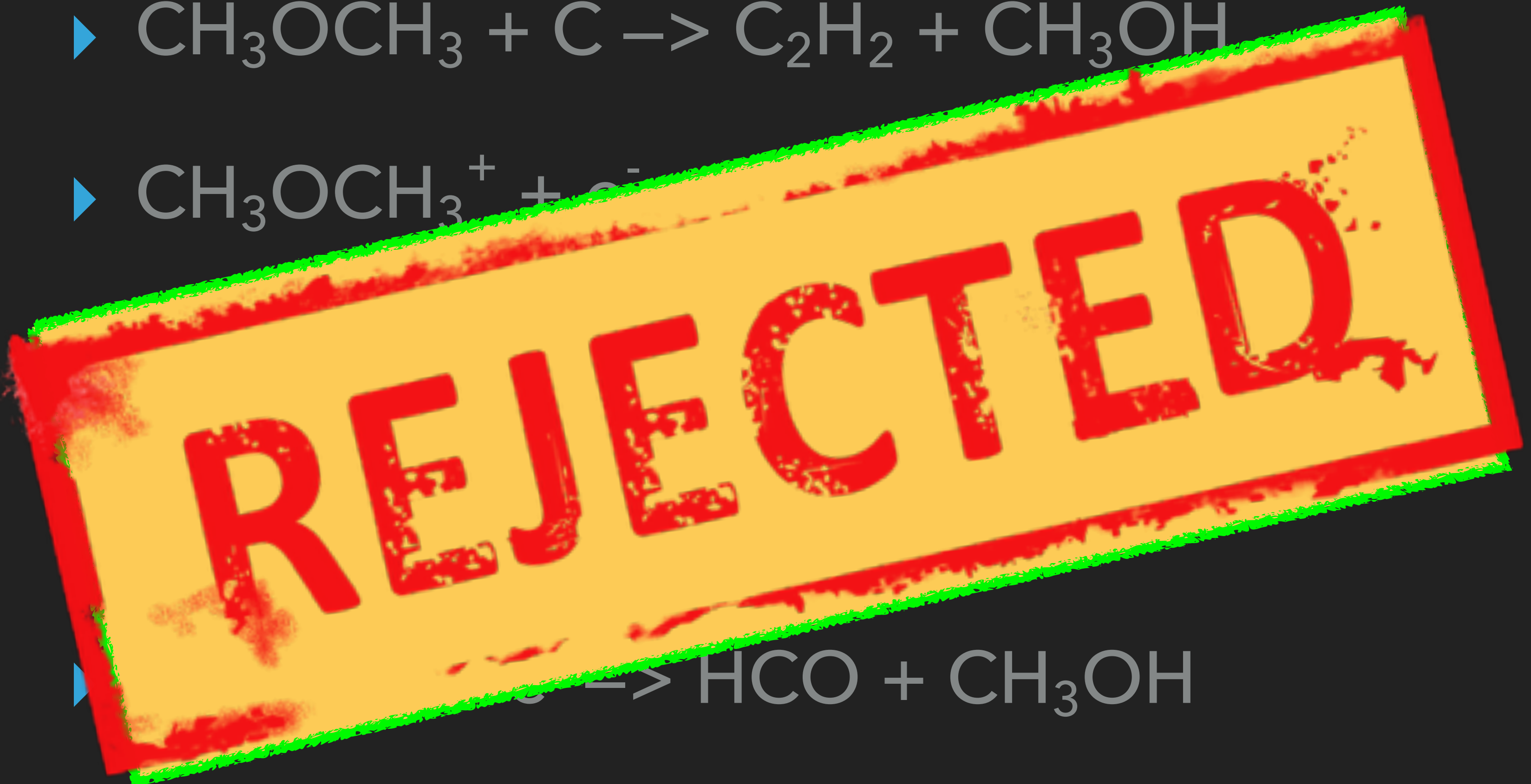
GAS-PHASE PROCESS

- $CH_3^+ + H_2O \rightarrow CH_3OH_2^+$
  - $CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$
- $CH_3OCH_3 + C \rightarrow C_2H_2 + CH_3OH$
- $CH_3OCH_3^+ + e^- \rightarrow CH_2 + CH_3OH$
- $CH_3 + OH^- \rightarrow CH_3OH + e^-$
- $COOCH_4^+ + e^- \rightarrow CO + CH_3OH$
- $H_5C_2O_2^+ + e^- \rightarrow HCO + CH_3OH$
- $CH_3OCH_4^+ + e^- \rightarrow CH_3 + CH_3OH$

KIDA database 09/2016

GAS-PHASE PROCESS

- $CH_3^+ + H_2O \rightarrow CH_3OH_2^+$
  - $CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$
- $CH_3OCH_3 + C \rightarrow C_2H_2 + CH_3OH$
- $CH_3OCH_3^+ + e^-$ …
- … $\rightarrow HCO + CH_3OH$
- $CH_3OCH_4^+ + e^- \rightarrow CH_3 + CH_3OH$



KIDA database 09/2016

ONE PLAUSIBLE MECHANISM

- $CH_3^+ + H_2O \rightarrow CH_3OH_2^+$
  - $CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$
- Modelled abundance around 10^{-13}:
  - Below the observed values in dark clouds
  - Below the detection limits for existing telescopes

Geppert W. D. et al., 2006, Faraday Discuss., 133, 177

ONE PLAUSIBLE MECHANISM

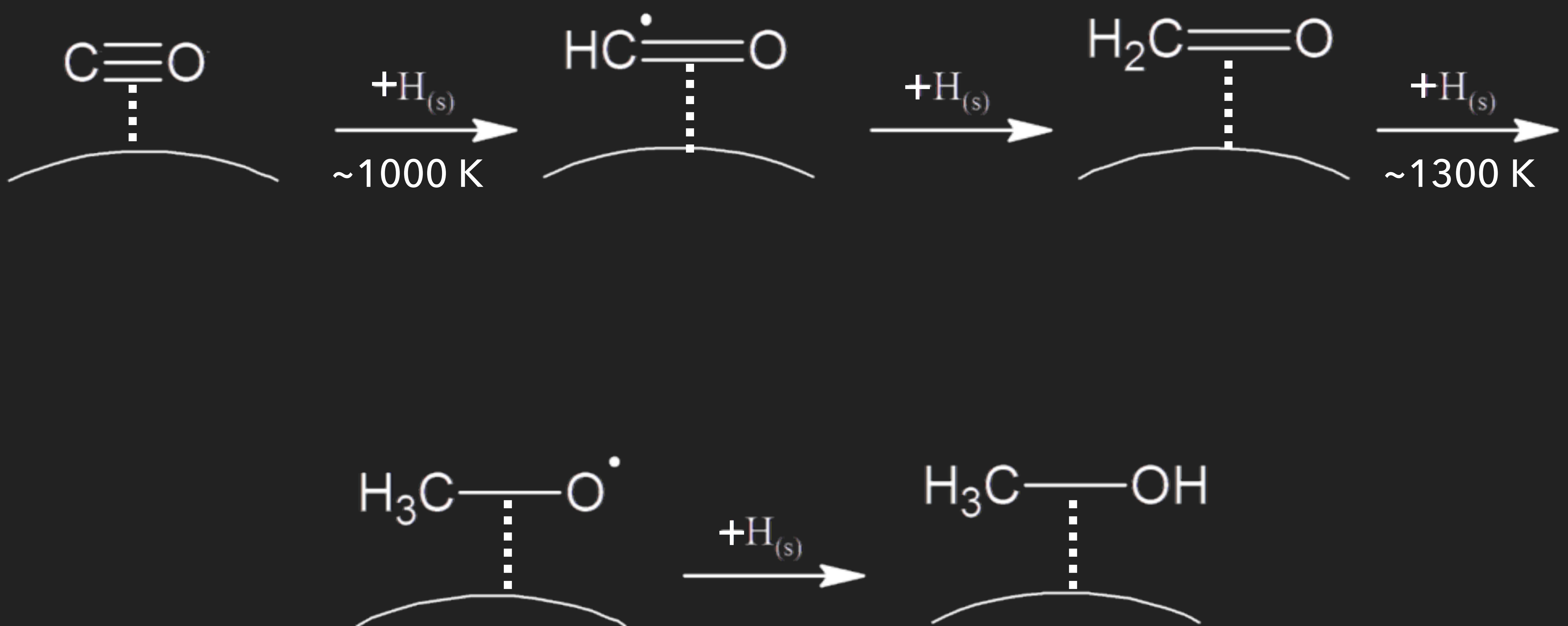
- $CH_3^+ + H_2O \rightarrow CH_3OH_2^+$
  - $CH_3OH_2^+$ + …

- …
  - …ues in dark clouds
  - …low the detection limits for existing telescopes

Geppert W. D. et al., 2006, Faraday Discuss., 133, 177

SOLID-STATE PROCESS

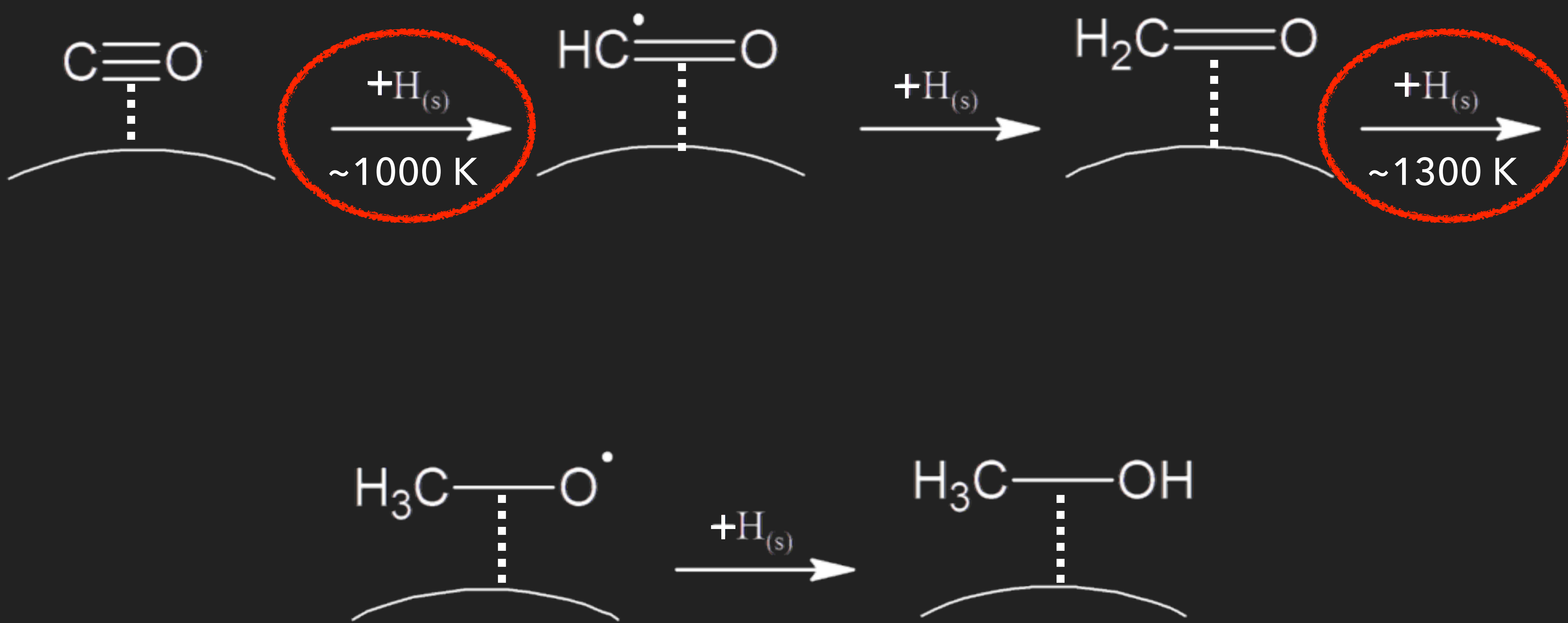
- HYDROGENATION OF CO



Rimola et al., 2014, A&A, 572, A70

SOLID-STATE PROCESS

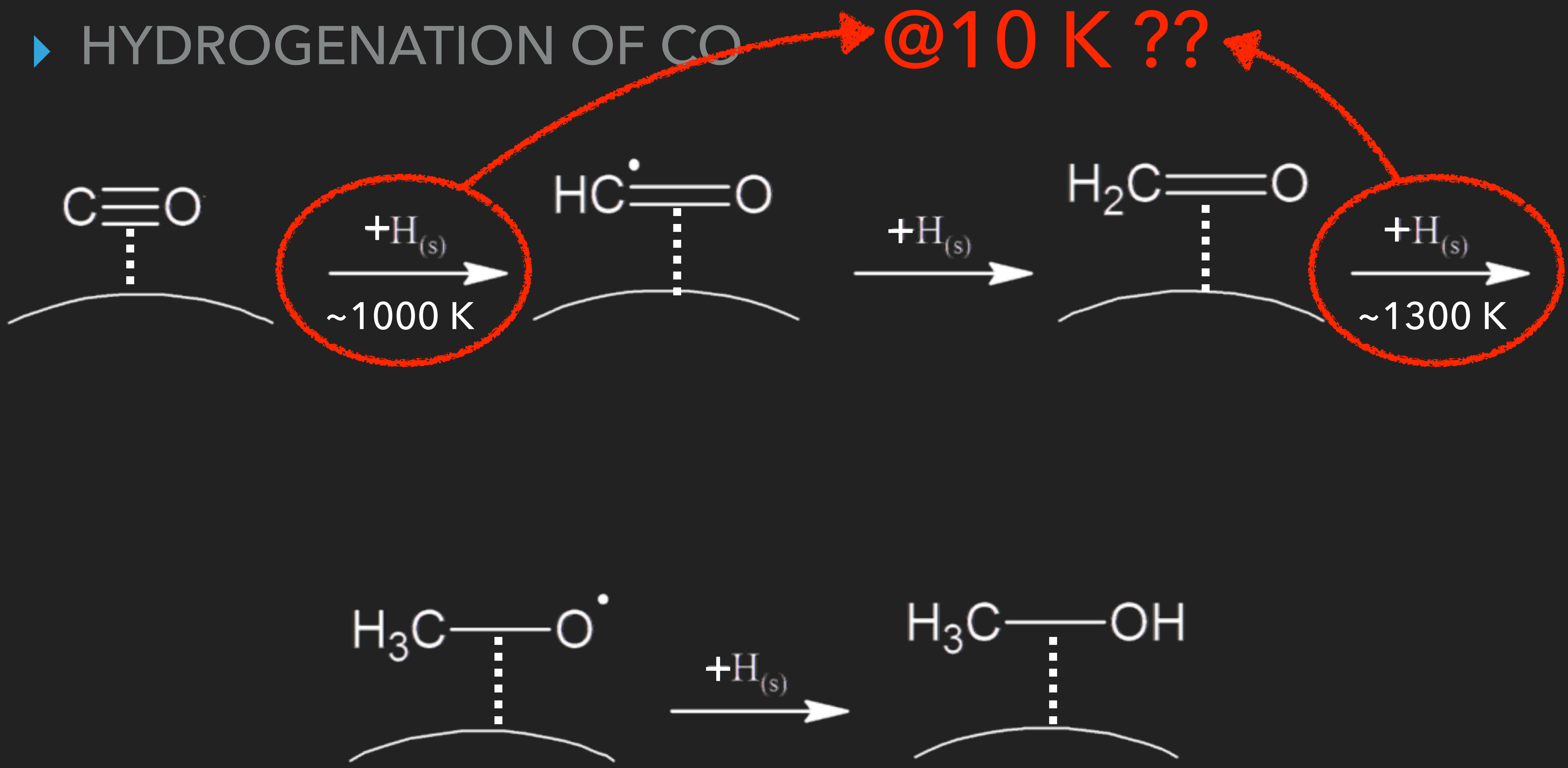
- HYDROGENATION OF CO



Rimola et al., 2014, A&A, 572, A70

SOLID-STATE PROCESS

- HYDROGENATION OF CO

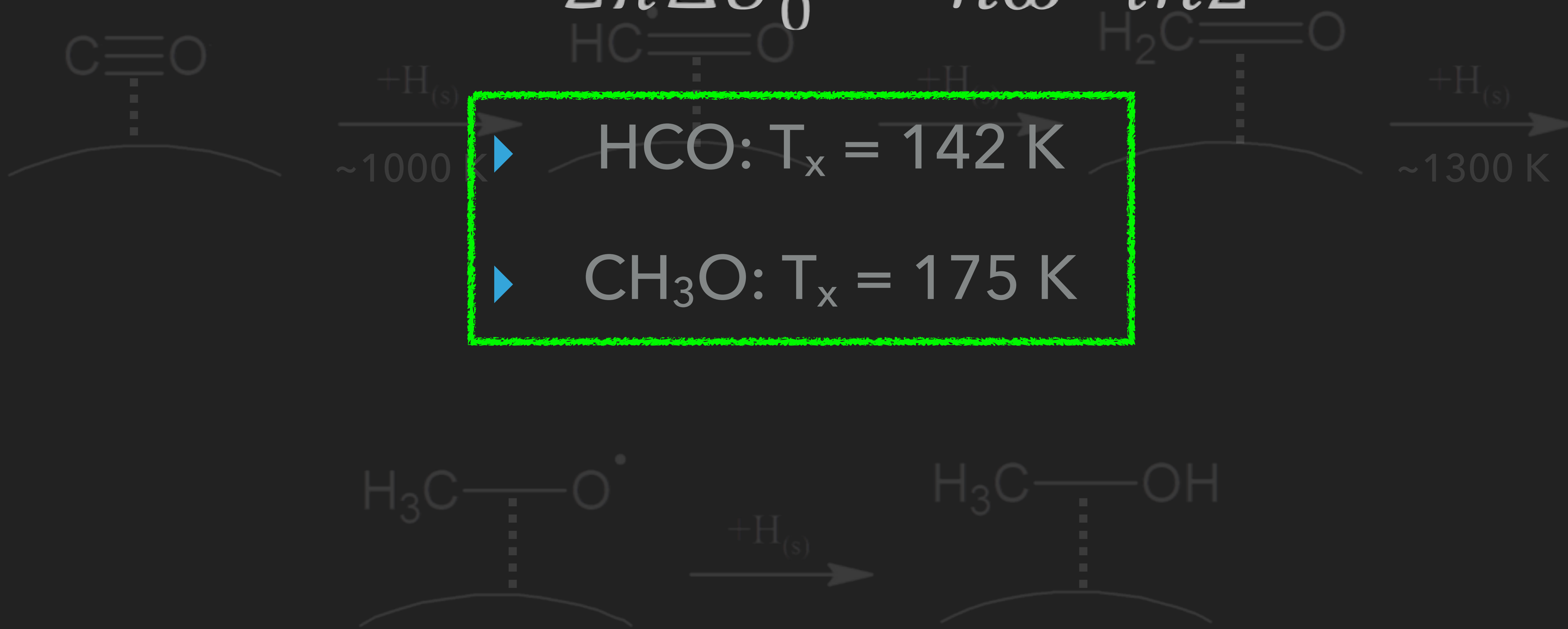


Rimola et al., 2014, A&A, 572, A70

TUNNELLING EFFECT

$$T_x = \frac{\hbar\omega^{\neq}\Delta U_0^{\neq}/k_B}{2\pi\Delta U_0^{\neq} - \hbar\omega^{\neq} ln2}$$

- HCO: T_x = 142 K
- CH_3O: T_x = 175 K



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TUNNELLING EFFECT

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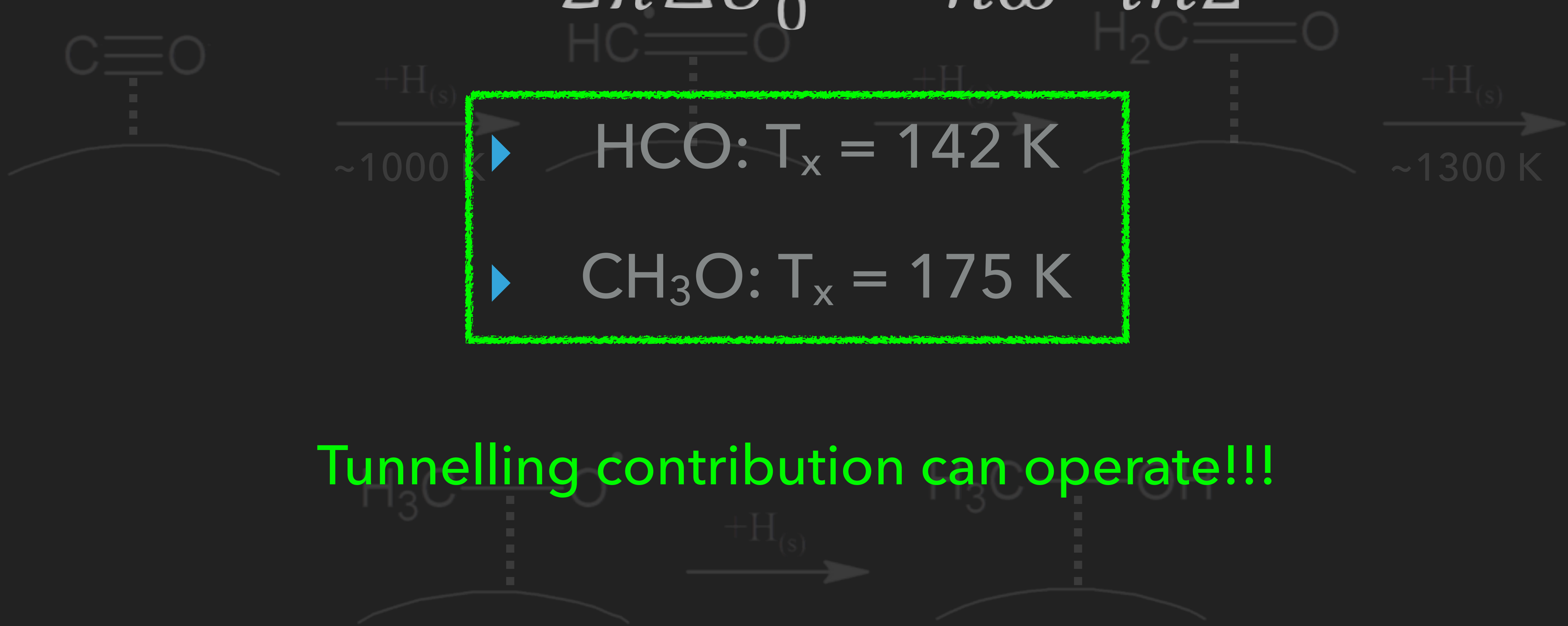


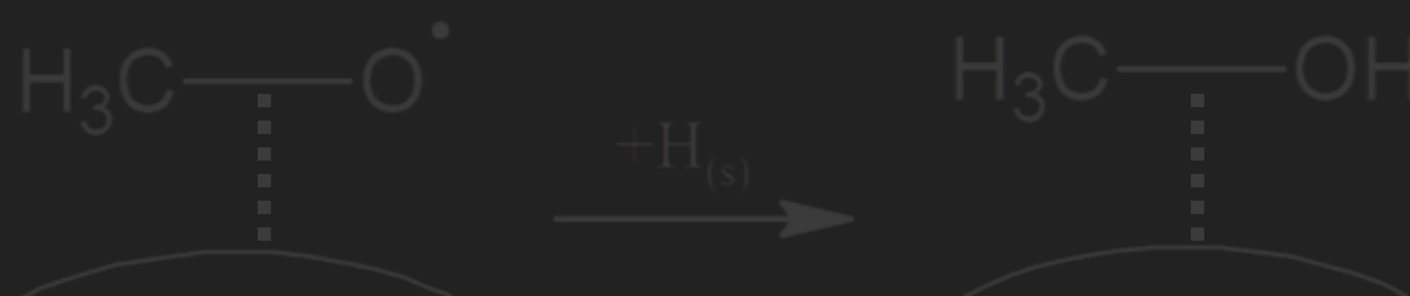
- HCO: T_x = 142 K
- CH_3O: T_x = 175 K

Tunnelling contribution can operate!!!

Rimola et al., 2014, A&A, 572, A70

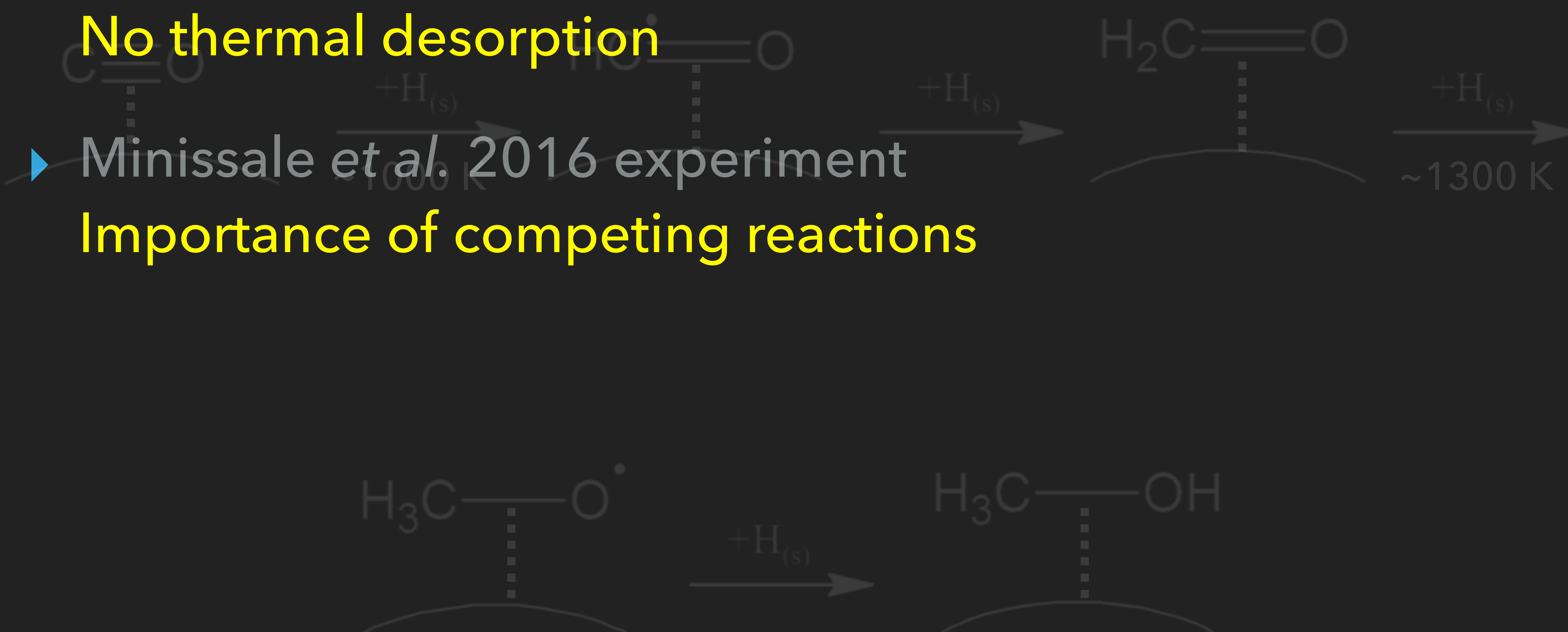
HYDROGENATION OF CO: PROS

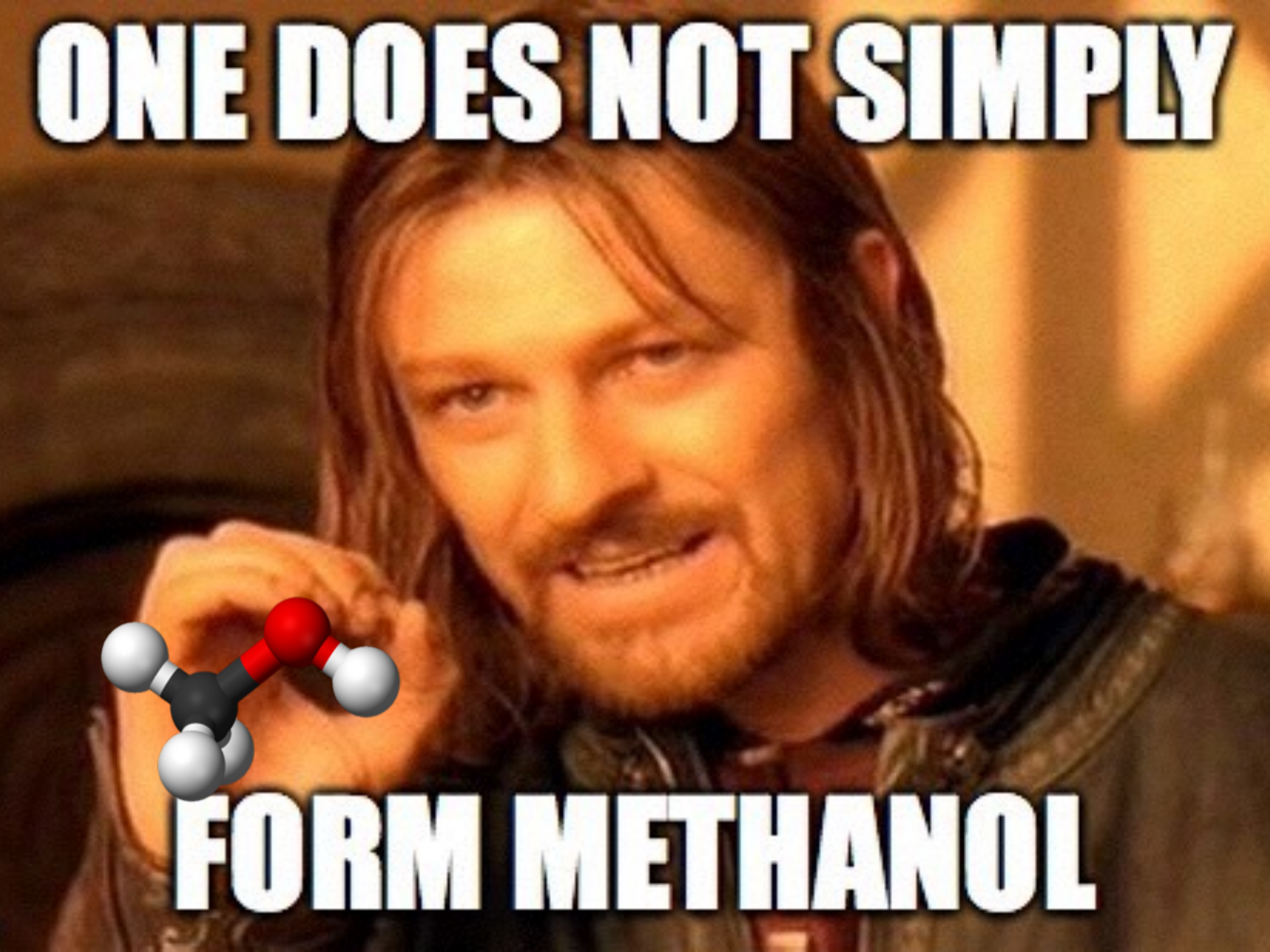
- Easy mechanism.
- Explains relative abundances of CO, H_2CO, CH_3OH observed in ices.
- Experimental evidence (Watanabe *et al.* 2003, Fuchs *et al.* 2009)
- Tunnelling effect can dominate the process.



HYDROGENATION OF CO: CONS

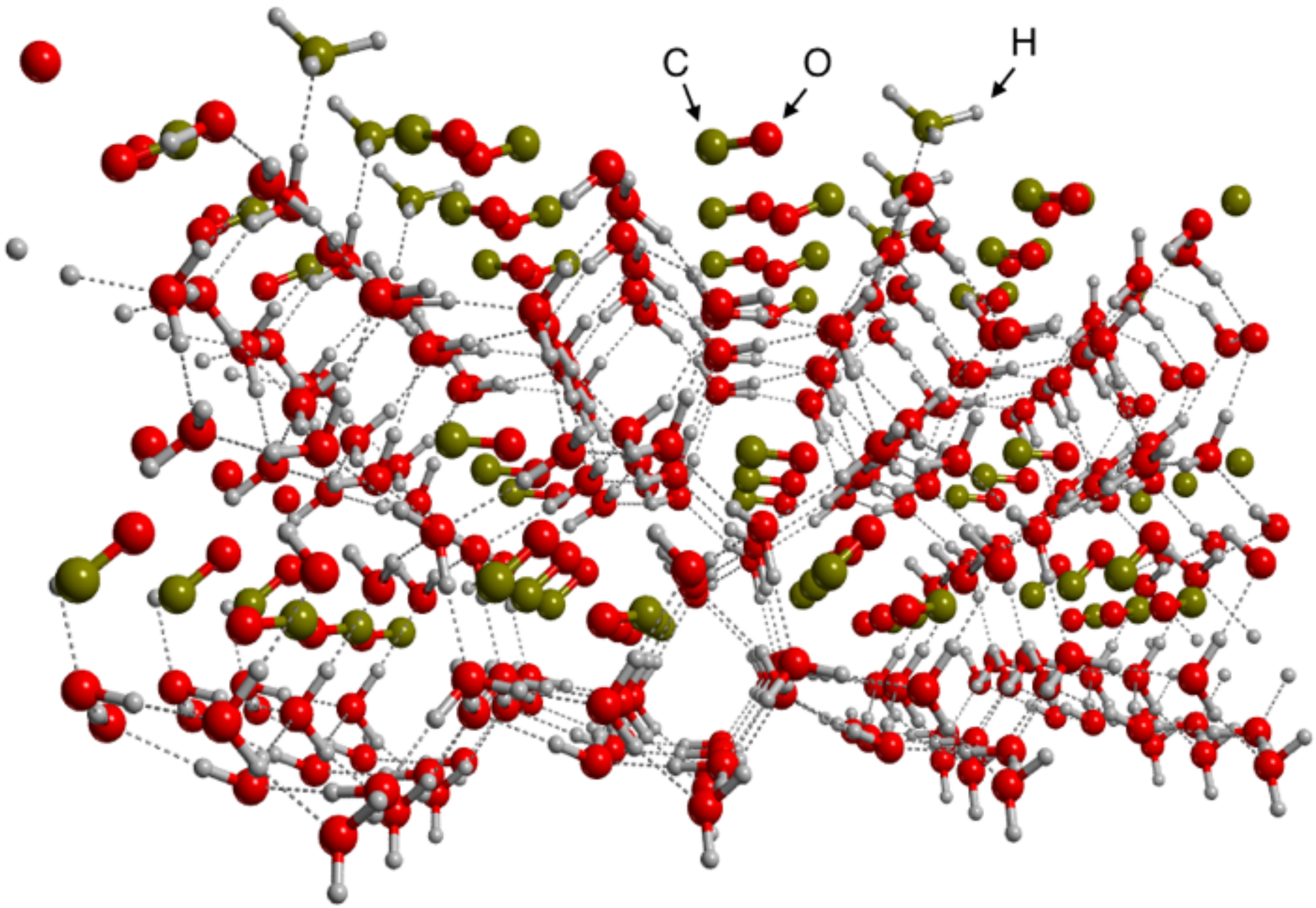
- Gas-phase observations in the cold ISM
  No thermal desorption
- Minissale *et al.* 2016 experiment
  Importance of competing reactions




ONE DOES NOT SIMPLY
FORM METHANOL

FUTURE DIRECTIONS

- Comprehensive experiments on the "methanol cycle".
  - Solid phase + UV irradiation + Energetic ions + gas phase.
- Control over gas phase products in solid state experiments.
- Quantum chemistry calculations of tunnelling mechanisms for surface reactions.
- Desorption experiments (with H_2O, CO and mixed ices).
- Coupled gas-phase + solid phase mechanisms.



- Quantum level calculation with periodic boundary conditions with amorphous H_2O-CO ice.


THE TEAM
THANK YOU!!!