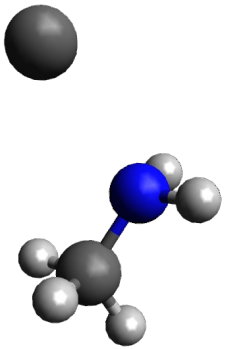

# Rate constants and product yields of astrochemically relevant reactions

**Kevin M. Hickson**
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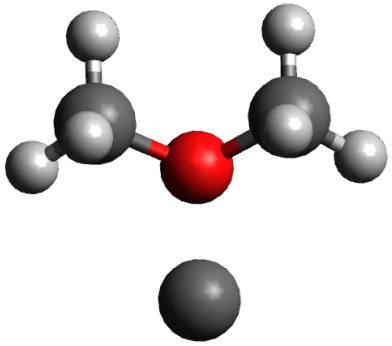
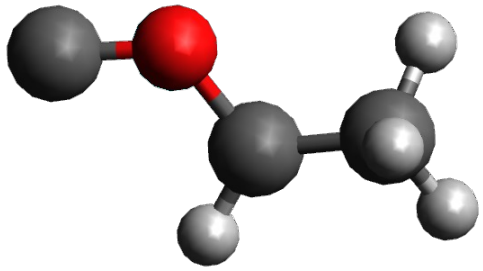
**Université de Bordeaux**

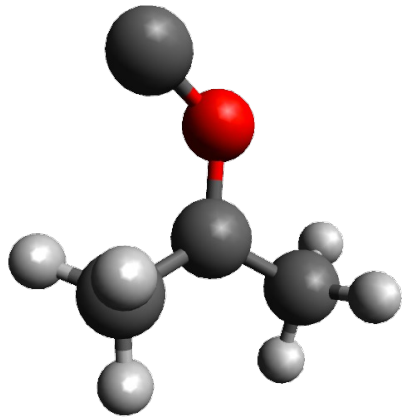


**PCMI2024-Bordeaux : Colloque du Programme Physique Chimie du Milieu Interstellaire 2024**
**28-31 October 2024**

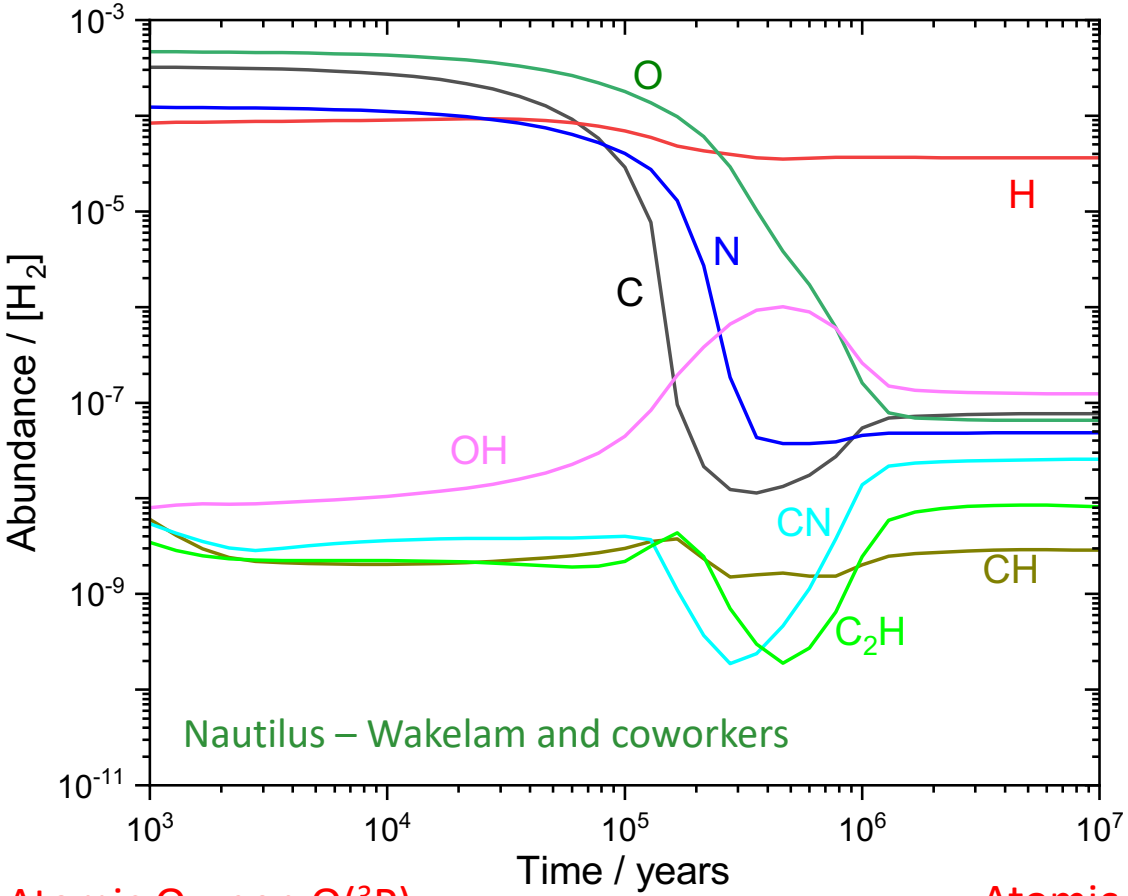
# Outline

- Why study C-atom reactions ?
- How do we measure rate constants and product yields ?
- How can theory help to interpret the results ?
- Example systems - C + O-bearing COMs, C + N-bearing COMs
- Experiments on $C_2N$ reactions





# Reactive atoms in the interstellar medium




High abundances of C, N, O and H ($10^{-3}$ – $10^{-5}$ / $H_2$)

Reactions of atomic radicals likely to have an important influence on interstellar chemistry

## Atomic Oxygen O($^3$P)

$O + C_3H_6 \rightarrow CH_3 + CH_2CHO$

$\rightarrow H_2CO + C_2H_4$ Leonori et al. 2015

$O + C_2H \rightarrow CH + CO$ Devriendt et al. 1996

O-atom reactions lead to C-C bond fission – lower complexity

## Atomic Nitrogen N($^4$S) and Hydrogen H($^2$S)

$N + C_2N \rightarrow CN + CN$ Stubbing et al. 2015

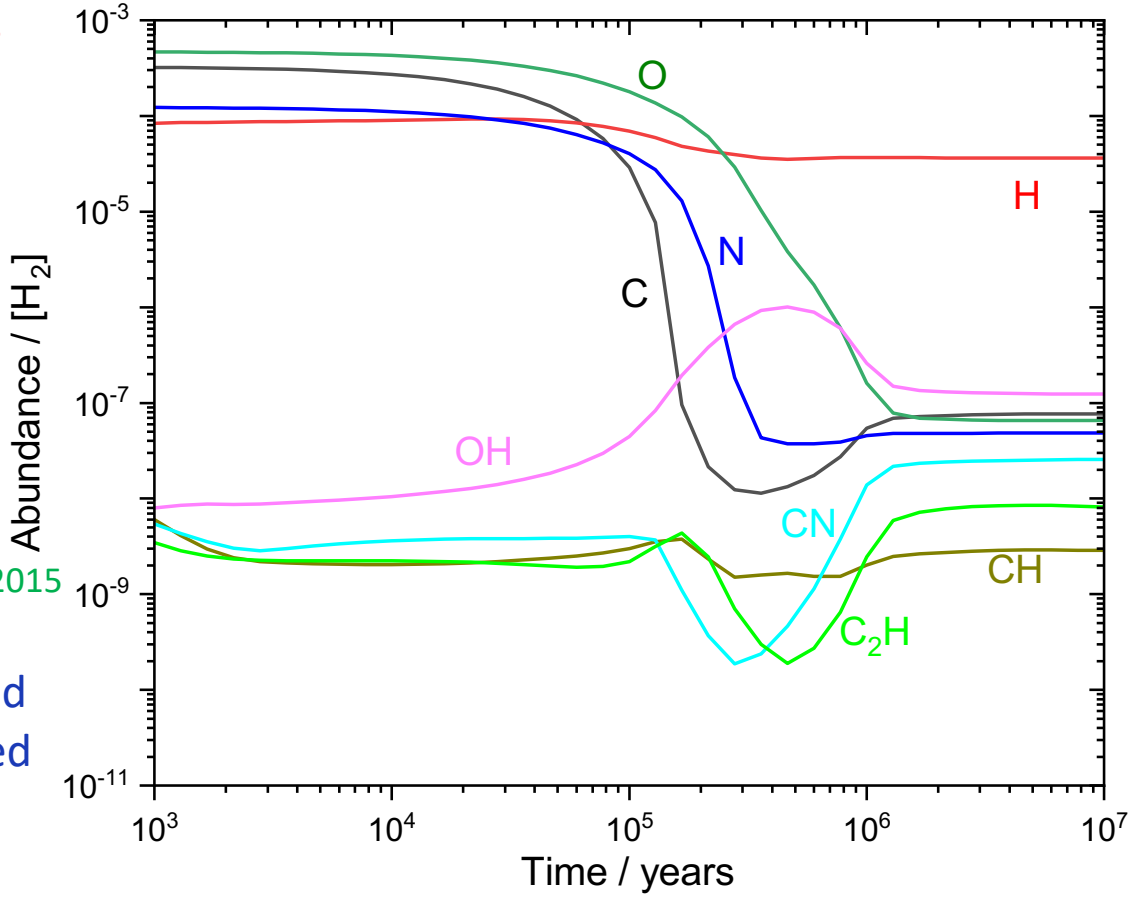
$N + CH_3 \rightarrow H + H_2CN$ Marston et al. 1989

$H + CH \rightarrow C + H_2$

N-, H-atoms only react with radicals

F. Leonori et al., *J. Phys. Chem. C* **2015**, *119*, 14632-14652.
K. Devriendt et al., *Chem. Phys. Lett.* **1996**, *261*, 450-456.
J. Stubbing et al., *J. Phys. Chem. A* **2015**, *119*, 3194-3199.
G. Marston et al., *J. Chem. Phys.* **1989**, *91*, 3483-3491.

# What about atomic carbon ?




## Atomic Carbon

$C + C_2H_2 \rightarrow$ *l*-,*c*-$C_3H + H$ Leonori et al. 2008

$\rightarrow C_3 + H_2$

$C + C_2H_4 \rightarrow C_3H_3 + H$ Capron et al. 2015

$C + NH_3 \rightarrow H_2CN/HCNH + H$ Hickson et al. 2015

C-atoms react with stable molecules and radicals. Reactions with HCs → increased C-chain lengths.

Generally

$C + HX \rightarrow CX + H$ H-atom production could indicate an increase in complexity.

But what happens with other interstellar species such as COMs ?


F. Leonori et al., *J. Phys. Chem. A* **2008**, *112*, 1363-1379.

M. Capron et al., *Phys. Chem. Chem. Phys.* **2015**, *17*, 23833-23846.

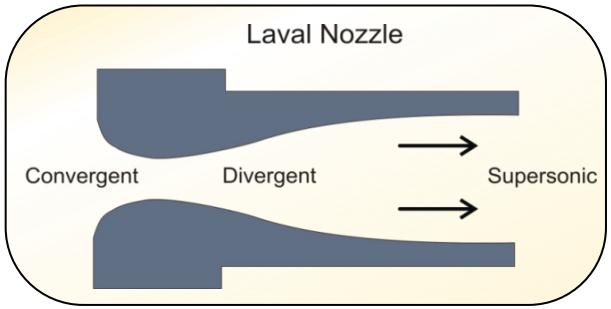
# How to study gas-phase reactivity at low temperature

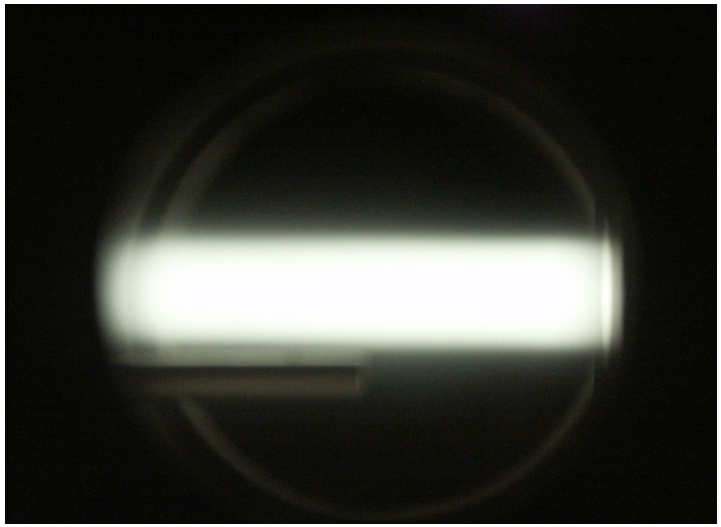
How can we obtain low temperatures whilst keeping reagents in the gas phase?

Cryogenic cooling methods → condensation of species on the reactor walls

## CRESU : Cinétique de Réaction en Ecoulement Supersonique Uniforme

– Cold supersonic flow produced by isentropic expansion of gas through a Laval Nozzle
➔ constant density, velocity and temperature



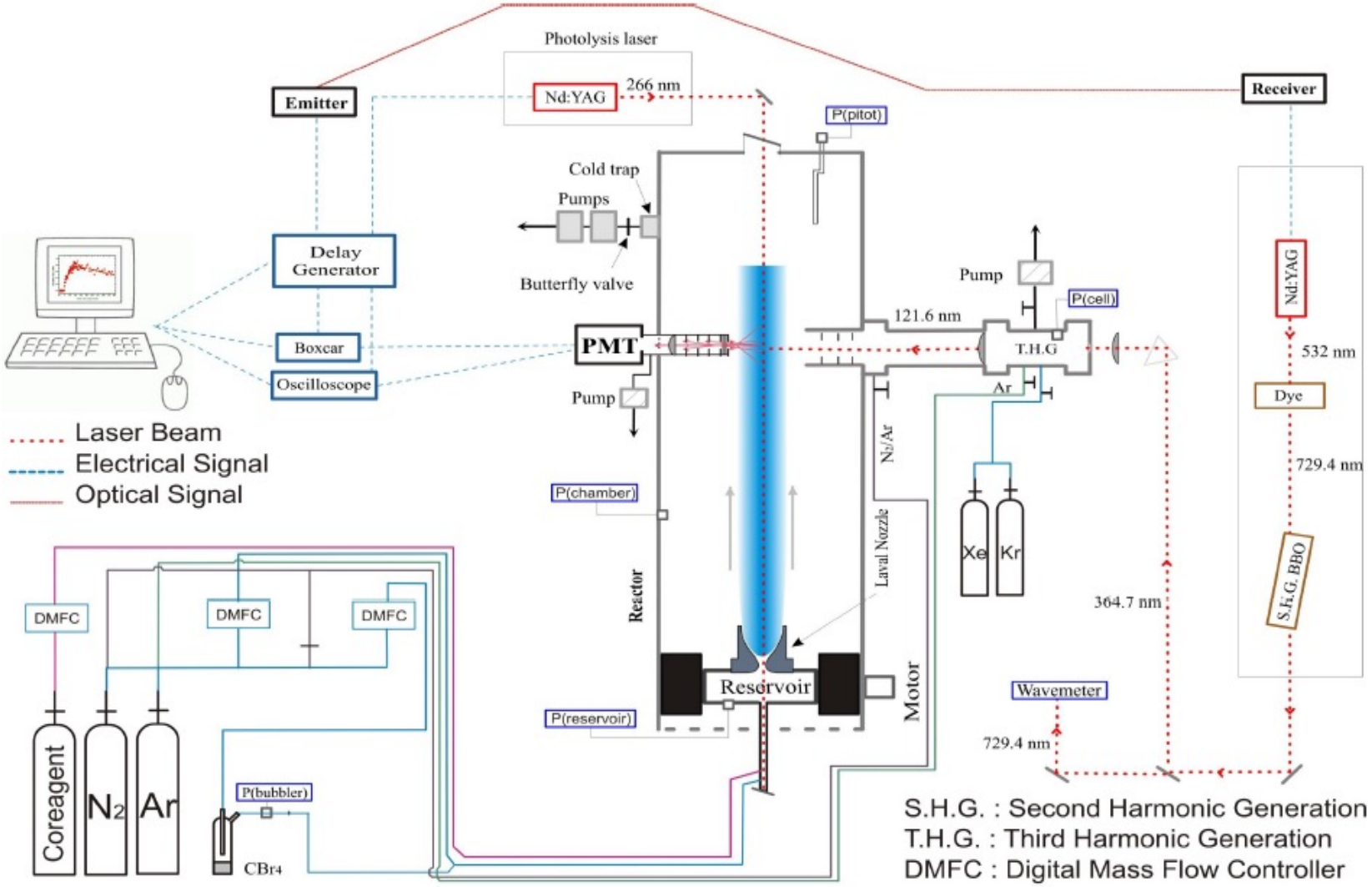
Isolated flow ➔ no condensation

**Continuous supersonic flow characteristics**

| Laval nozzle | Mach2 Ar | Mach3 Ar | Mach3 Ar | Mach3 N2 | Mach4 Ar | Mach4 Ar |
|---|---|---|---|---|---|---|
| Mach Number | 2.0 ± 0.03 | 3.0 ± 0.1 | 3.0 ± 0.1 | 3.0 ± 0.02 | 3.9 ± 0.1 | 3.9 ± 0.1 |
| Temperature (K) | 127 ± 2 | 75 ± 2 | 77 ± 2 | 106 ± 1 | 50 ± 1 | 52 ± 1 |
| Carrier gas | Ar | Ar | Ar (7% $N_2$) | $N_2$ | Ar | Ar (7% $N_2$) |
| Density (x$10^{16}$ $cm^{-3}$) | 12.6 | 14.7 | 14.7 | 10.3 | 25.9 | 25.9 |
| Impact Pressure (Torr) | 10.5 | 15.3 | 15.3 | 15.3 | 29.6 | 29.6 |
| Stagnation Pressure (Torr) | 13.9 | 34.9 | 34.9 | 34.9 | 113 | 113 |
| Mean flow velocity ($ms^{-1}$) | 419 ± 3 | 479 ± 3 | 479 ± 3 | 626 ± 2 | 505 ± 1 | 505 ± 1 |

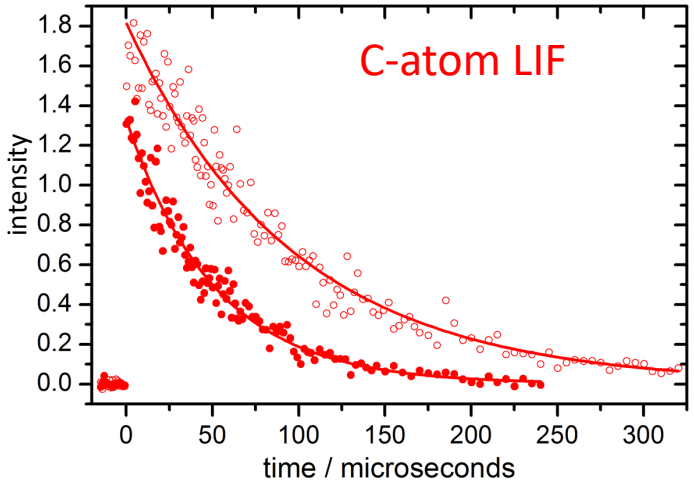
# Experimental Method – CRESU PLP VUV-LIF

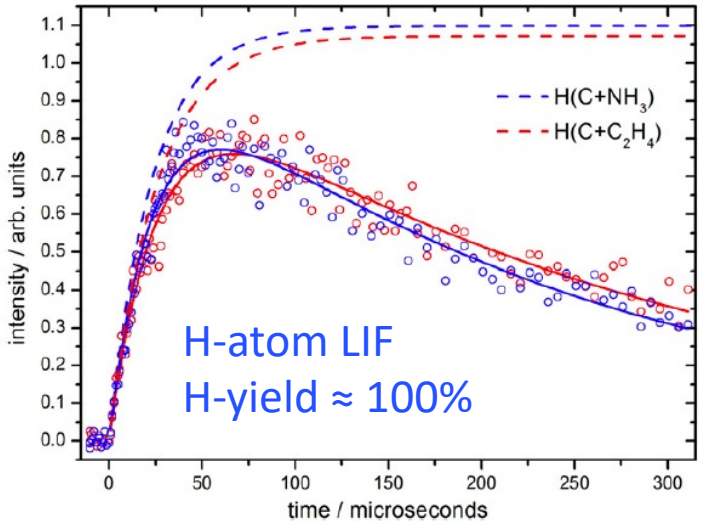
C($^3$P) from $CBr_4$ photolysis (266 nm)
C($^3$P) detection by VUV LIF (115.802 or 127.755 nm)
product H($^2$S) detection (121.567 nm)



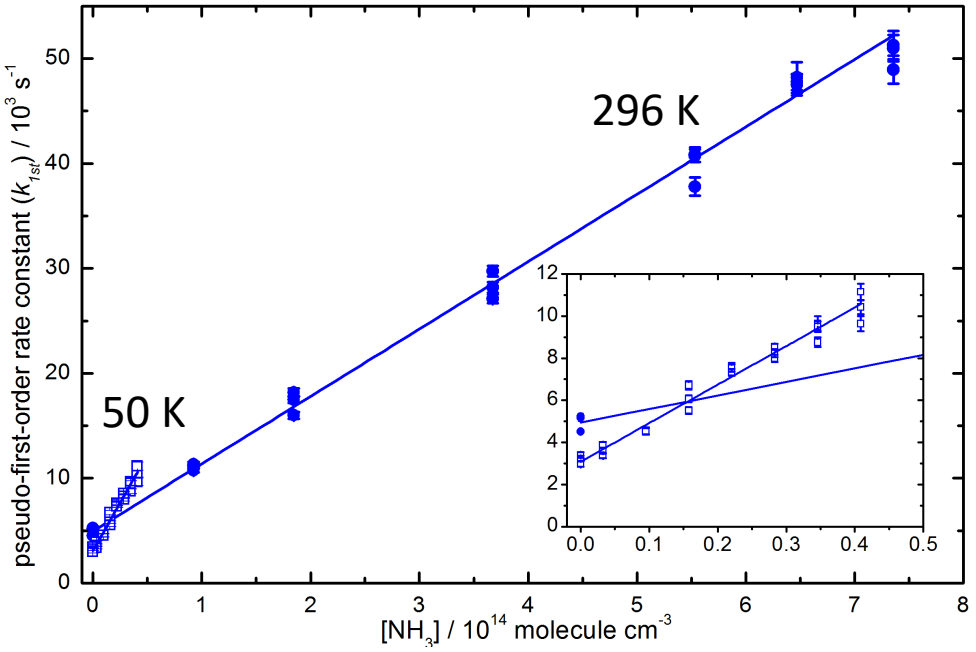
# Experimental Methods

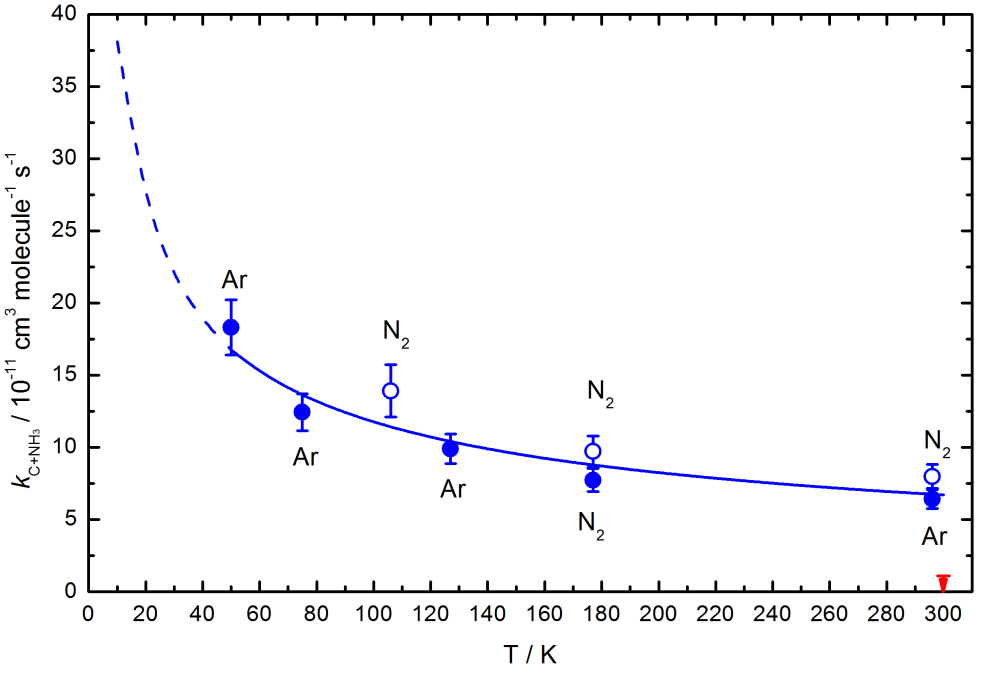
## The C + $NH_3$ reaction




K. M. Hickson et al., *Astrophys. J.*, **812**, 107, **2015**.



# Why detect atomic hydrogen rather than the molecular coproduct ?

<u>Molecular coproduct</u>

Techniques: LIF, Mass spectrometry, Rotational/Vibrational Spectroscopy

$CN + C_2H_2 \rightarrow HC_3N + H$

Advantages:
Direct method

Disadvantages:
Spectroscopy - Complex rovibronic structure
Mass Spectrometry – Product fragmentation

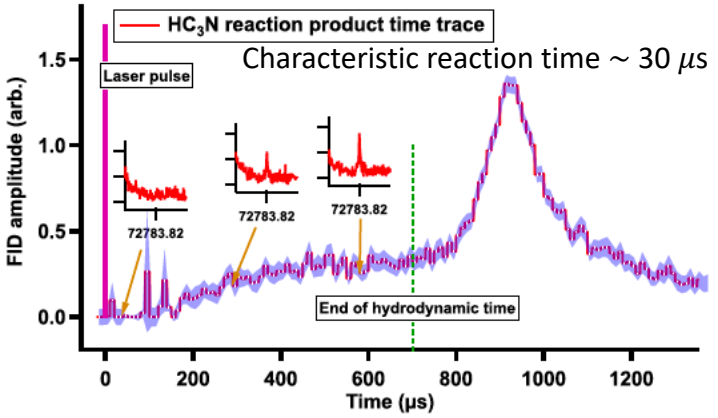



**FIG. 10.** Time evolution of the reaction product $HC_3N$ $J = 8–7$ vibrational ground state transition (time-domain Voigt fit), in the Ar 30 K flow under the conditions displayed in Table I with $1.2 \times 10^5$ averages per point. The shaded zones correspond to 95% confidence limits on the amplitude fits. The insets present the FFTs of the data at different times, with the line center frequency indicated in MHz.

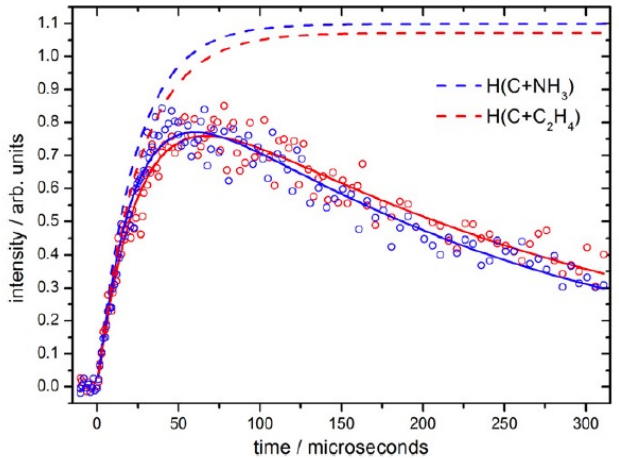
T. Guillaume et al., *J. Chem. Phys.*, **160**, 204201, **2024**.

<u>Atomic coproduct</u>

Techniques: LIF

Advantages:
No rotational/vibrational structure

Disadvantages:
Indirect method - further interpretation required



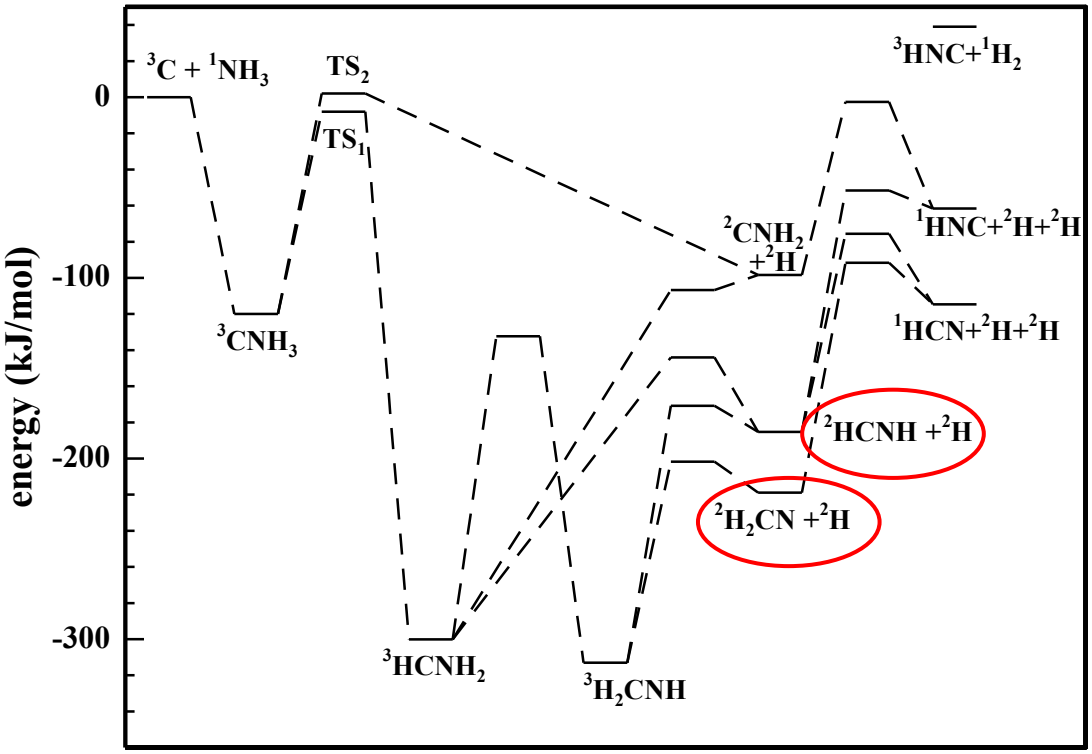

K. M. Hickson et al., *Astrophys. J.*, **812**, 107, **2015**.

# Theoretical Methods

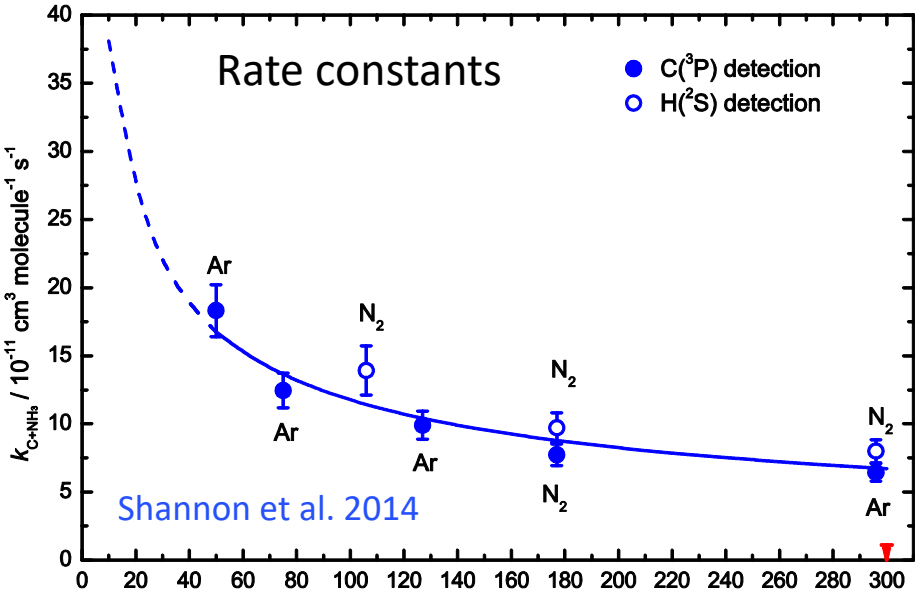
Calculations of the reactive PES → essential to interpret the experimental results.

- Optimized geometries and energies of the reagents, intermediates and transition states (Gaussian, ORCA) using DFT (M06-2X functional coupled with reasonable basis functions (aug-cc-pVTZ)

- Better energies were obtained using CCSD(T) (DLPNO-CCSD(T)) based on the DFT geometries.



# The C($^3$P) + $CH_3OH$ reaction



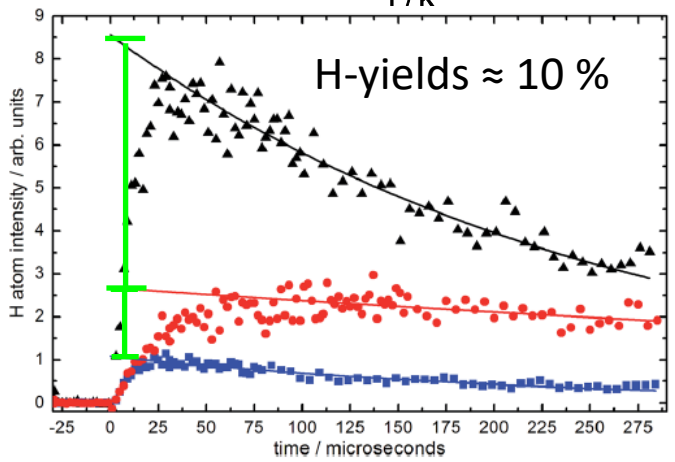
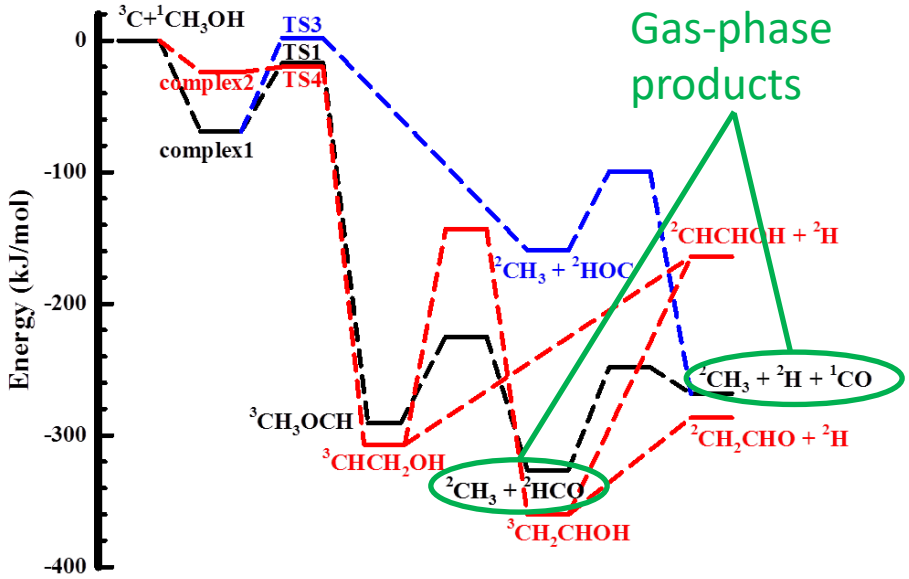
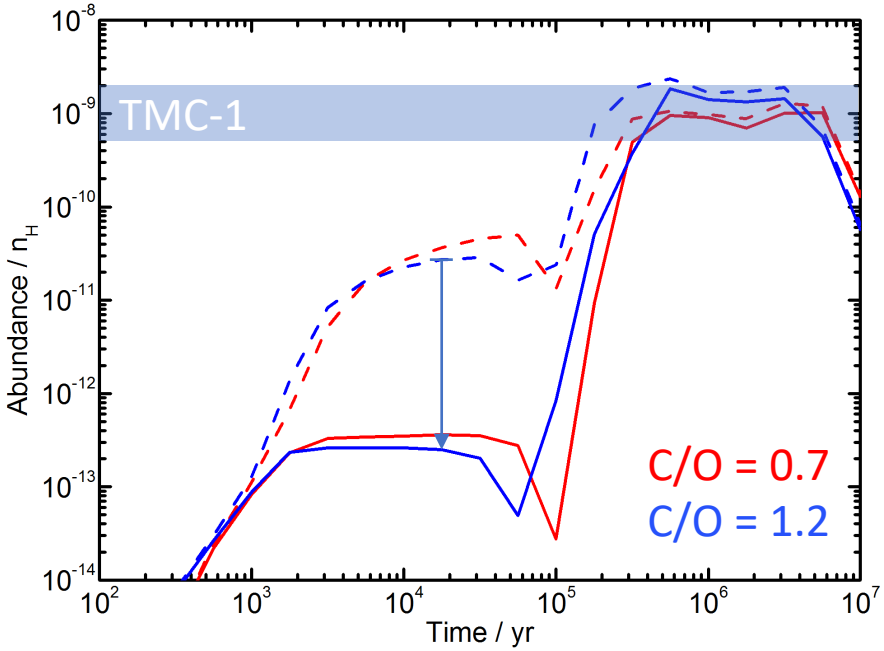




Fig. 2 Variation of the VUV LIF emission from H($^2$S) atoms produced by three different reactions at 127 K. (Black filled triangles) the C($^3$P)/($^1$D) + $C_3H_4$ reaction with [$C_3H_4$] = 2.9 × 10$^{14}$ molecule cm$^{-3}$; (red filled circles) the C($^3$P)/($^1$D) + $CH_3OH$ reaction with [$CH_3OH$] = 1.4 × 10$^{14}$ molecule cm$^{-3}$; (blue filled squares) the C($^1$D) + $H_2$ reaction with [$H_2$] = 3.2 × 10$^{14}$ molecule cm$^{-3}$. The fits to the long-time part of each trace (representing the diffusional loss of H($^2$S)) were extrapolated to time zero to obtain the nascent H atom yields.



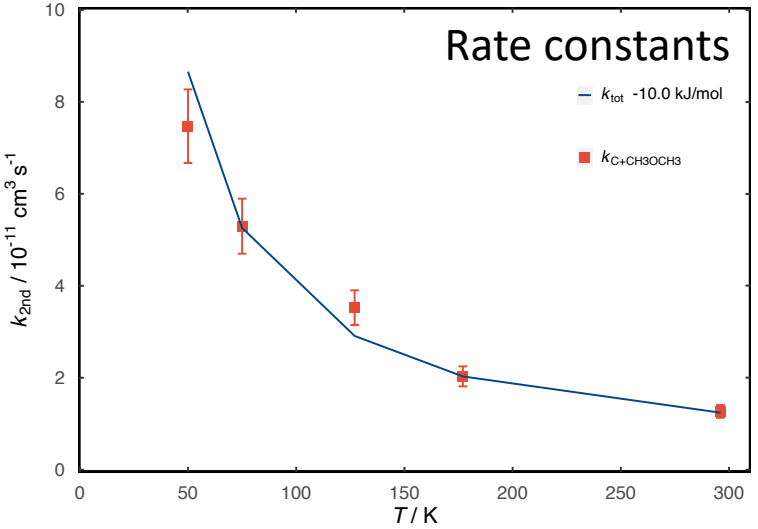



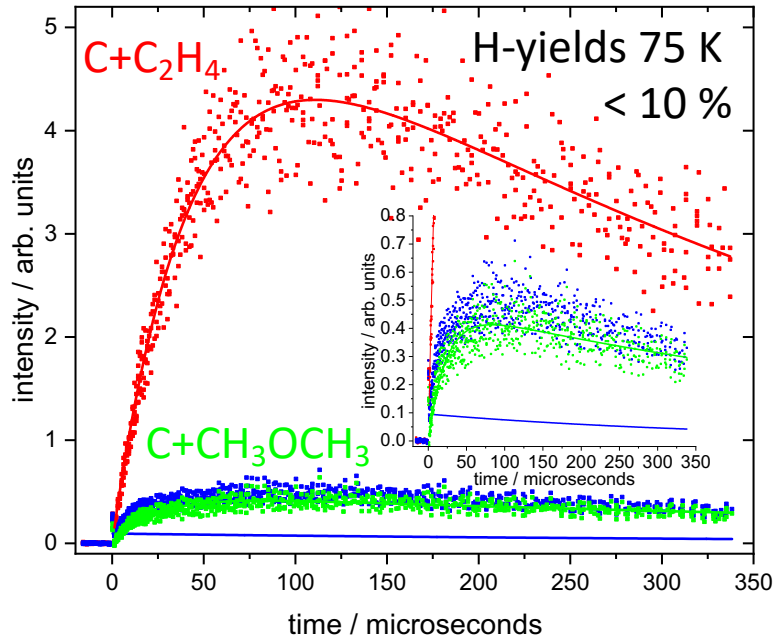


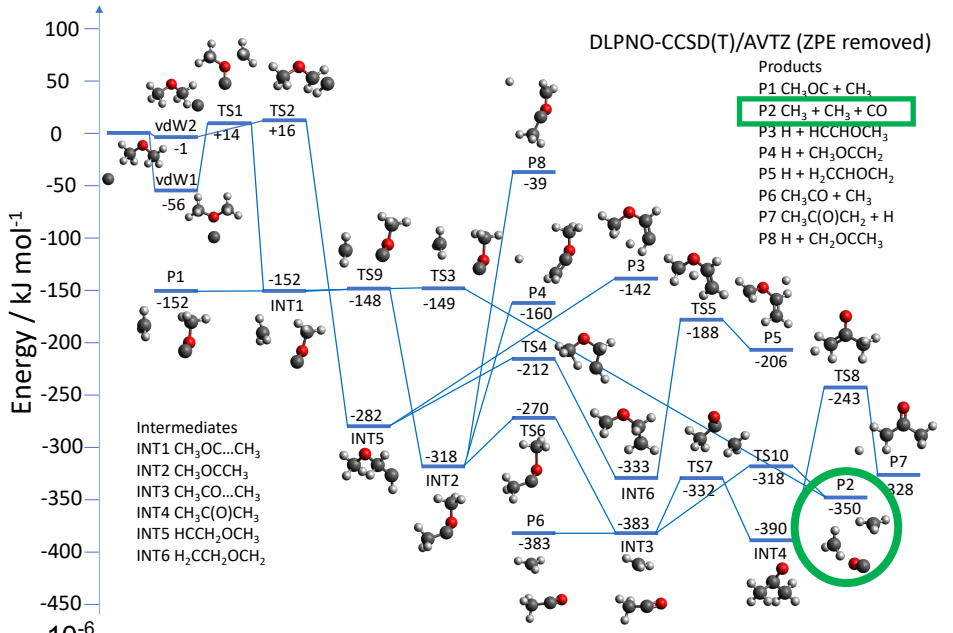
R. J. Shannon et al., *RSC Adv.*, **4**, 26342, **2014**.

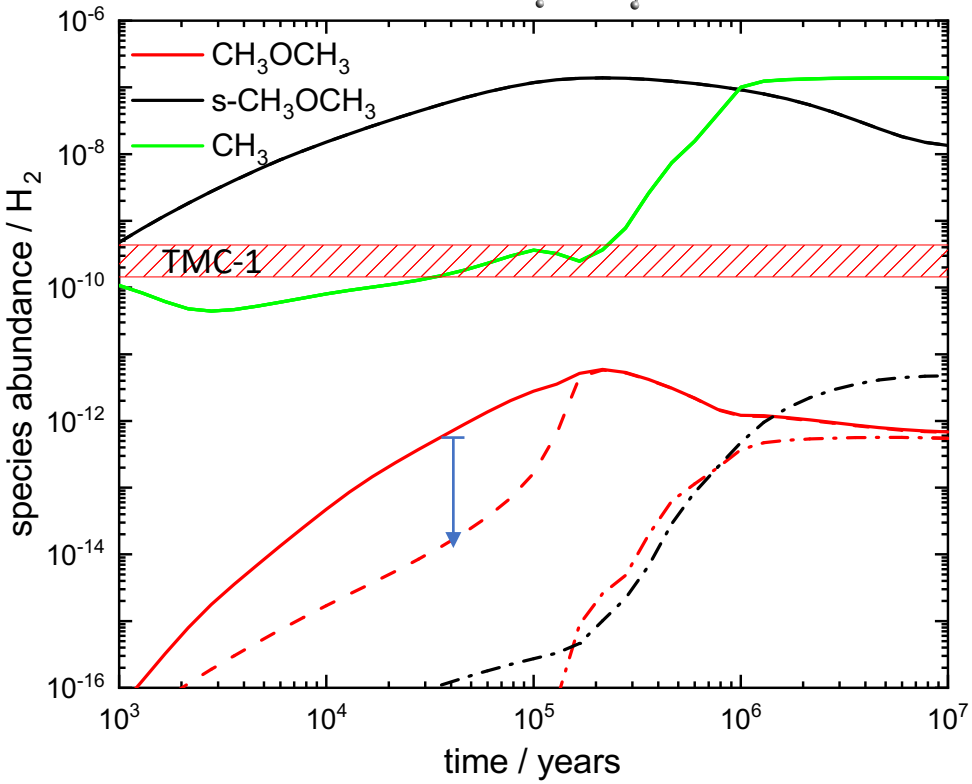
P. Gratier et al., *Astrophys. J. Supp. Ser.*, **225**, 25, **2016**.

# The C($^3$P) + $CH_3OCH_3$ reaction



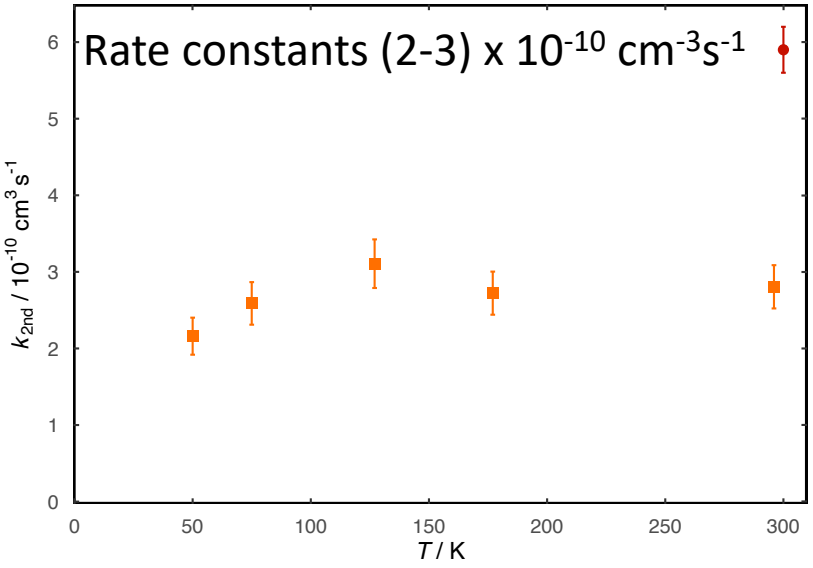



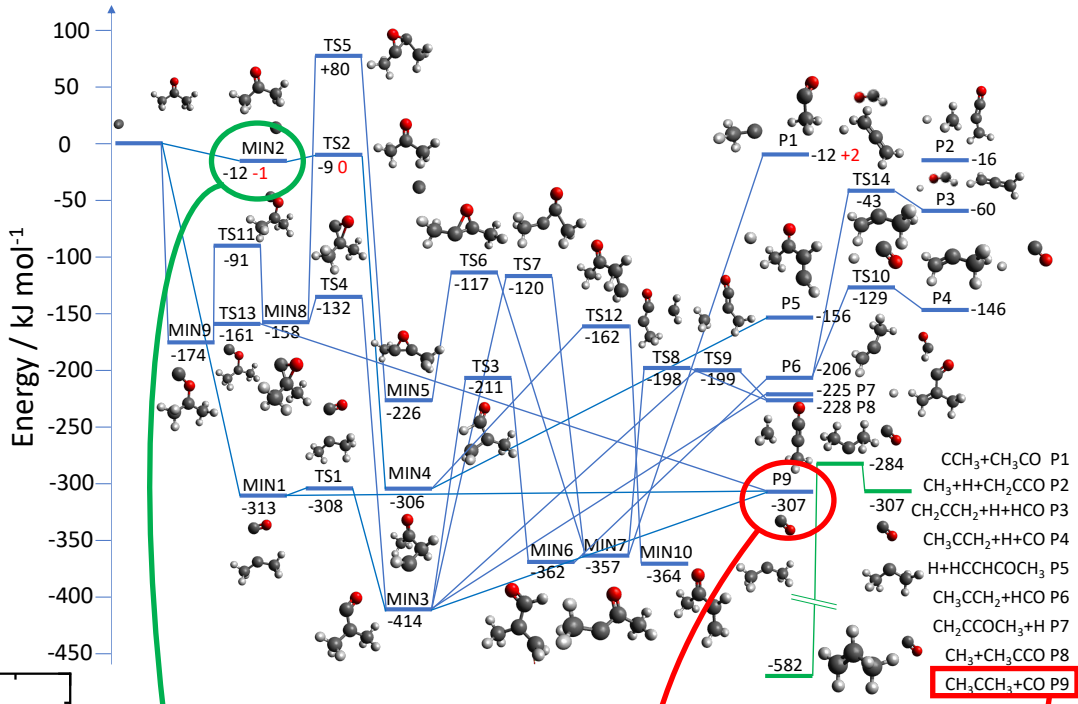



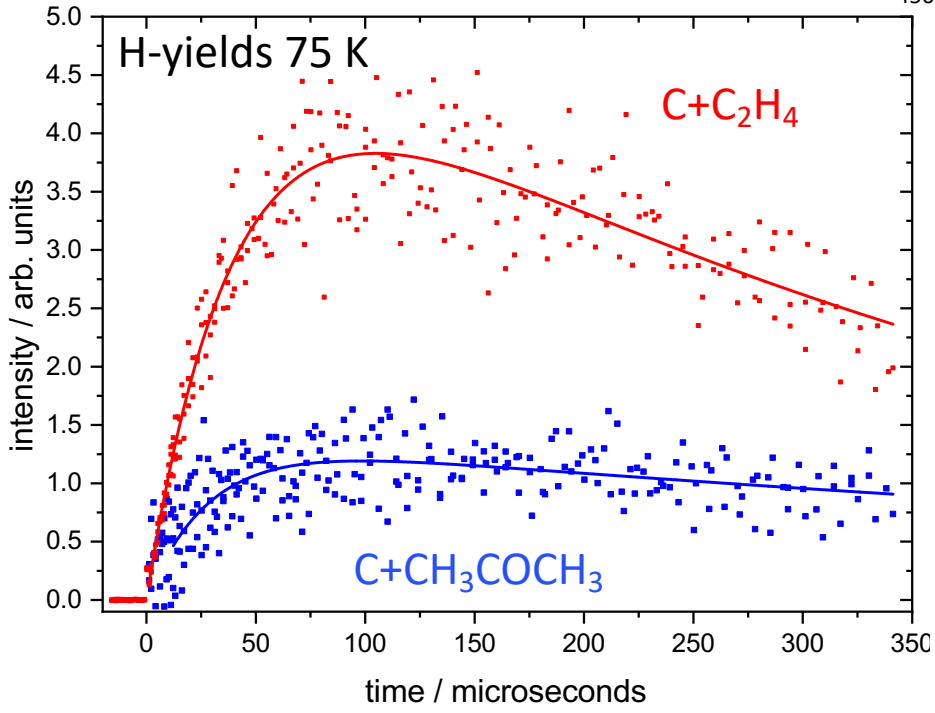


K. M. Hickson et al. *ACS Earth Space Chem.*, **8**, 1087-1100, **2024**.
M. Agúndez et al. *Astron. Astrophys.*, **649**, L4, **2021**.

# The C($^3$P) + $CH_3COCH_3$ reaction




van der Waals complex between C and $CH_3COCH_3$ leading to an increased production of H + $HCCHCOCH_3$ as the temperature falls.

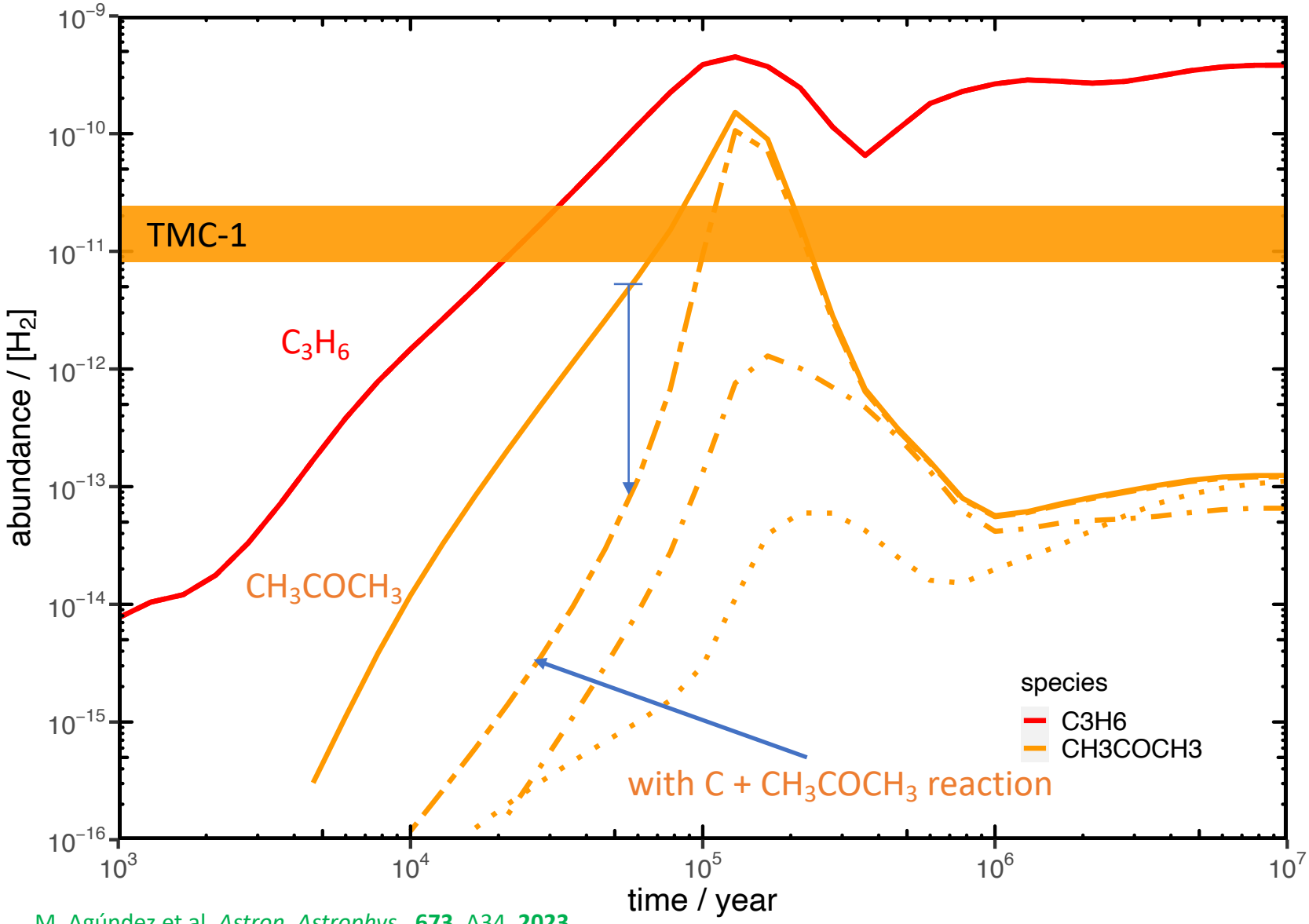
Several minor channels
$CH_2CCOCH_3$ + H,
$CH_3CCH_2$ + H + CO
$C_3H_4$ + HCO + H

Major products $C_3H_6$ + CO

| T / K | Number of experiments | H atom yield |
|---|---|---|
| 296 | 12 | 0.13 ± 0.02 |
| 177 | 7 | 0.25 ± 0.04 |
| 75 | 8 | 0.29 ± 0.03 |

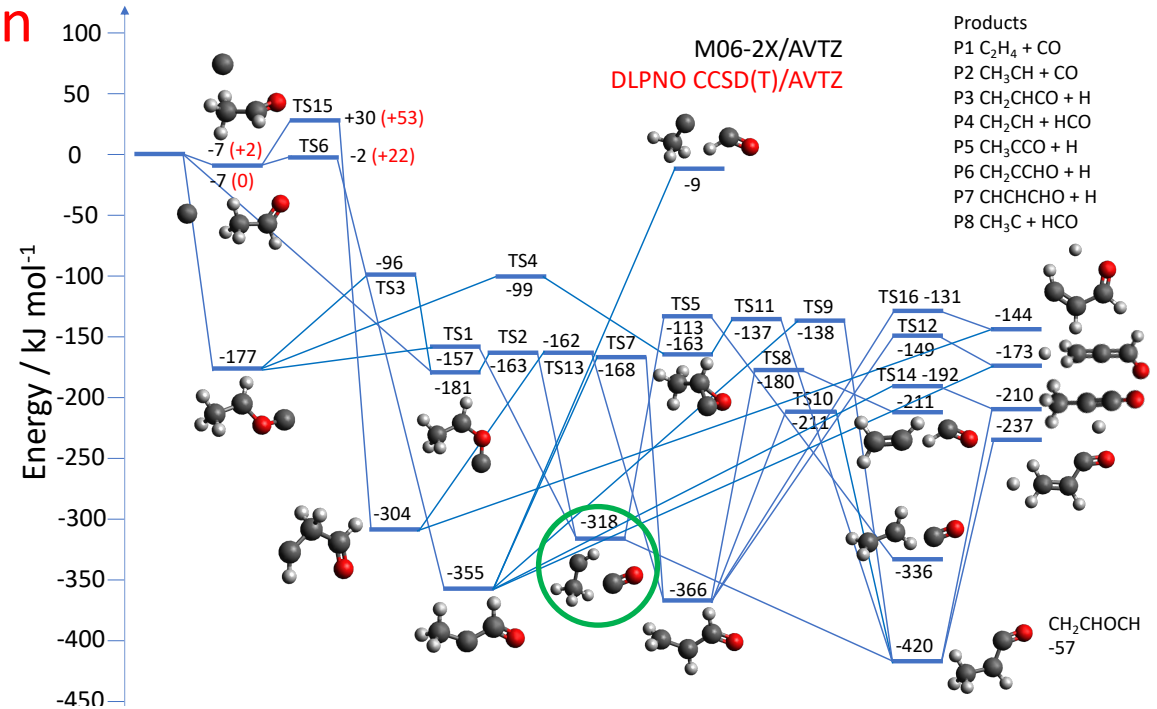
K. M. Hickson et al. *ACS Earth Space Chem.*, **7**, 2091-2104, **2023**.

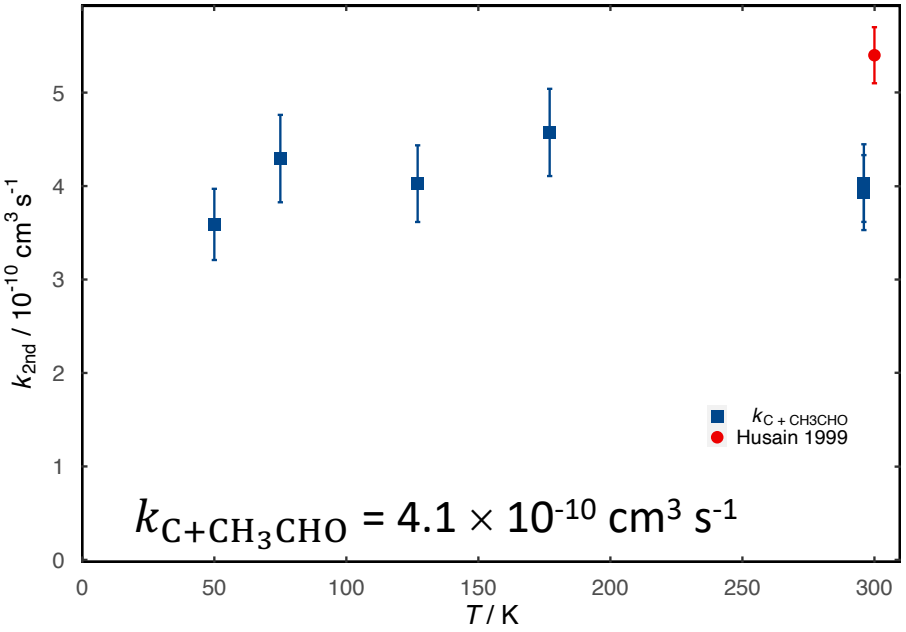
# $C(^3P) + CH_3COCH_3$

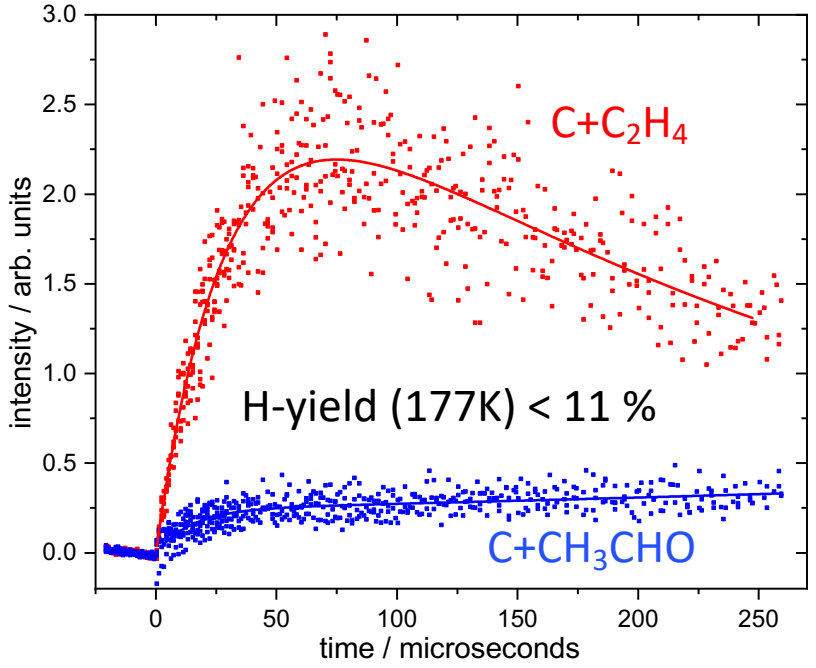



M. Agúndez et al. *Astron. Astrophys.*, **673**, A34, **2023**.

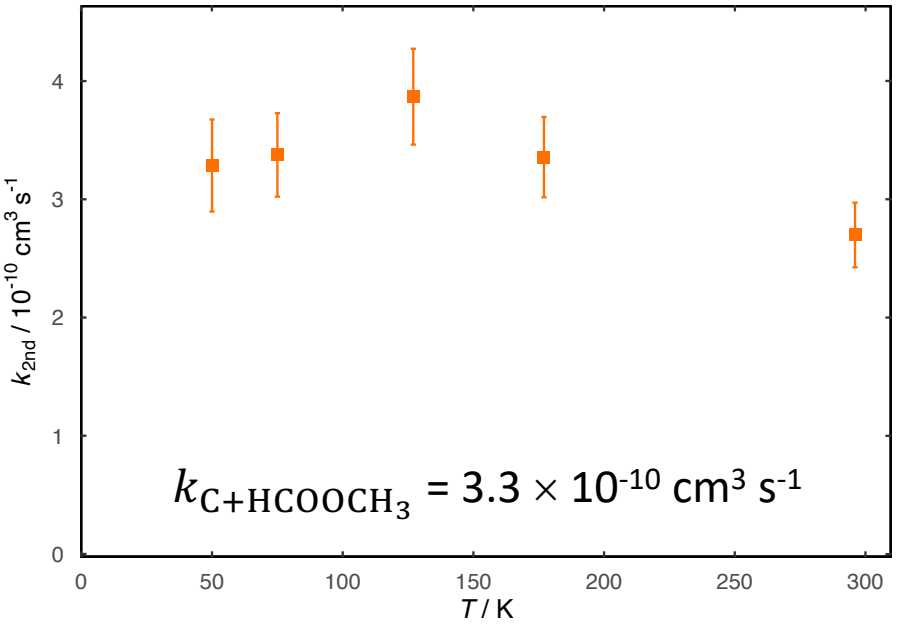
# The C($^3$P) + $CH_3CHO$ reaction

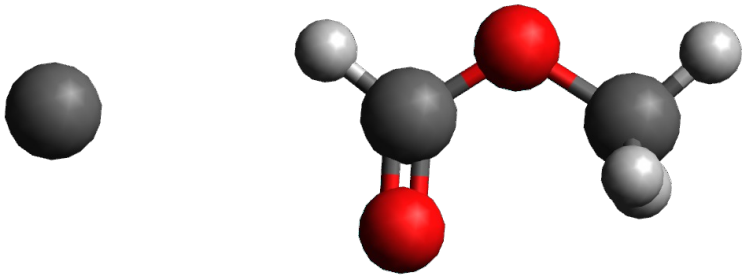


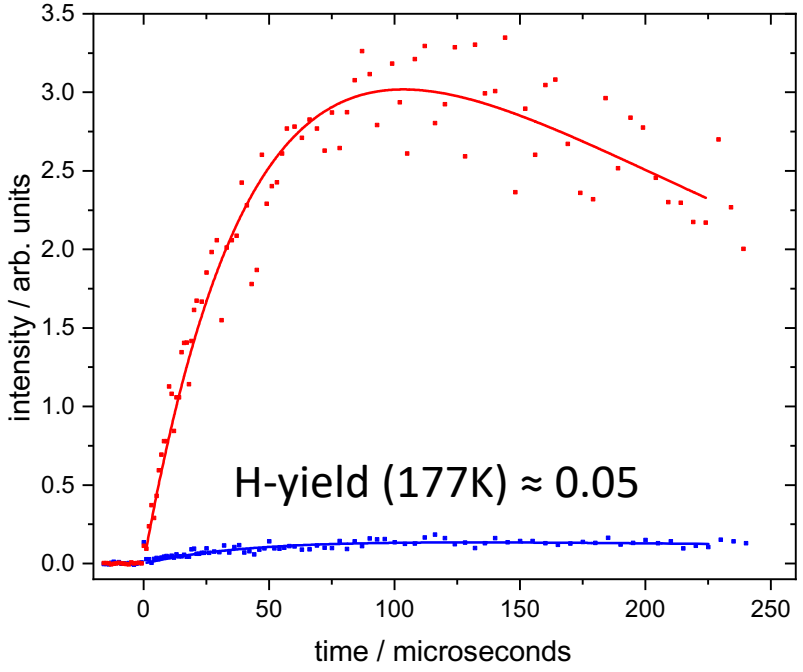



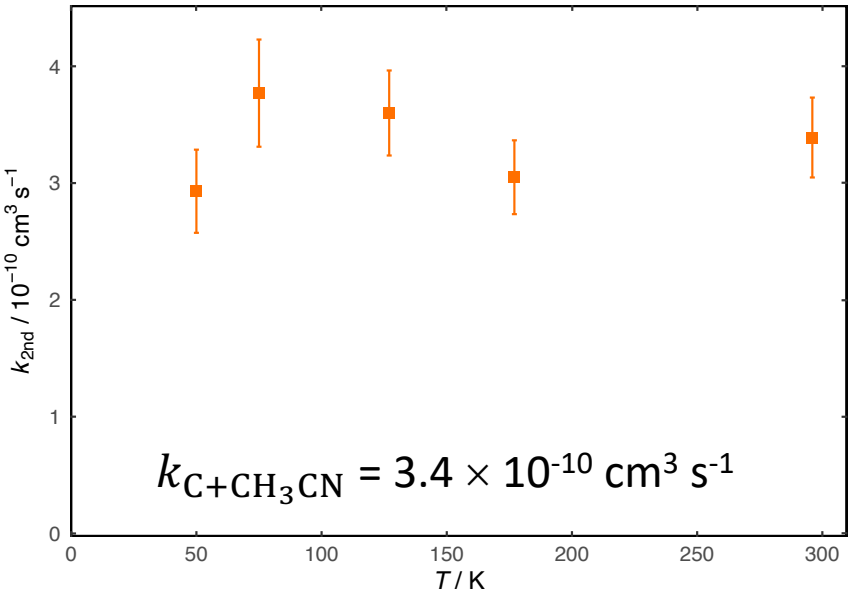
# The C($^3$P) + $HCOOCH_3$ reaction

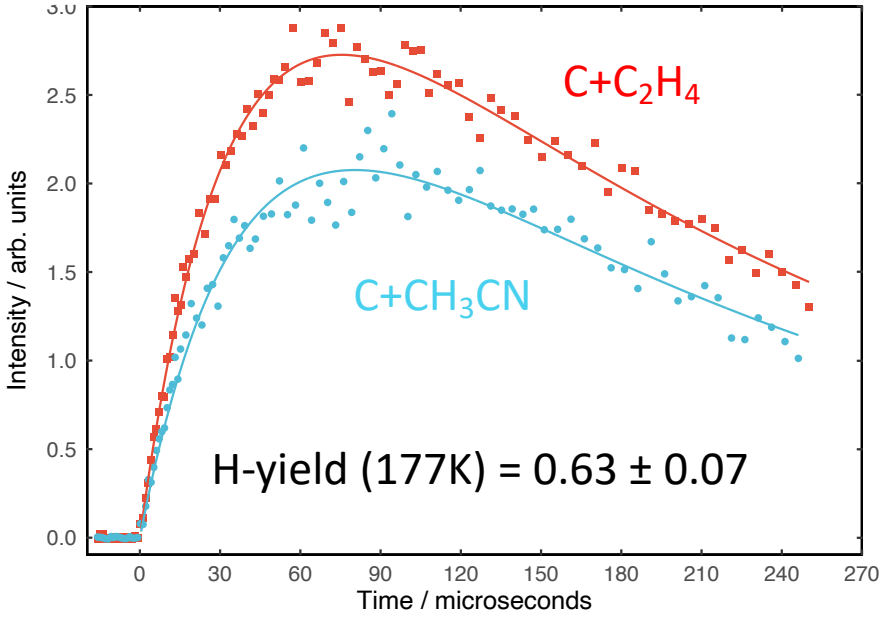


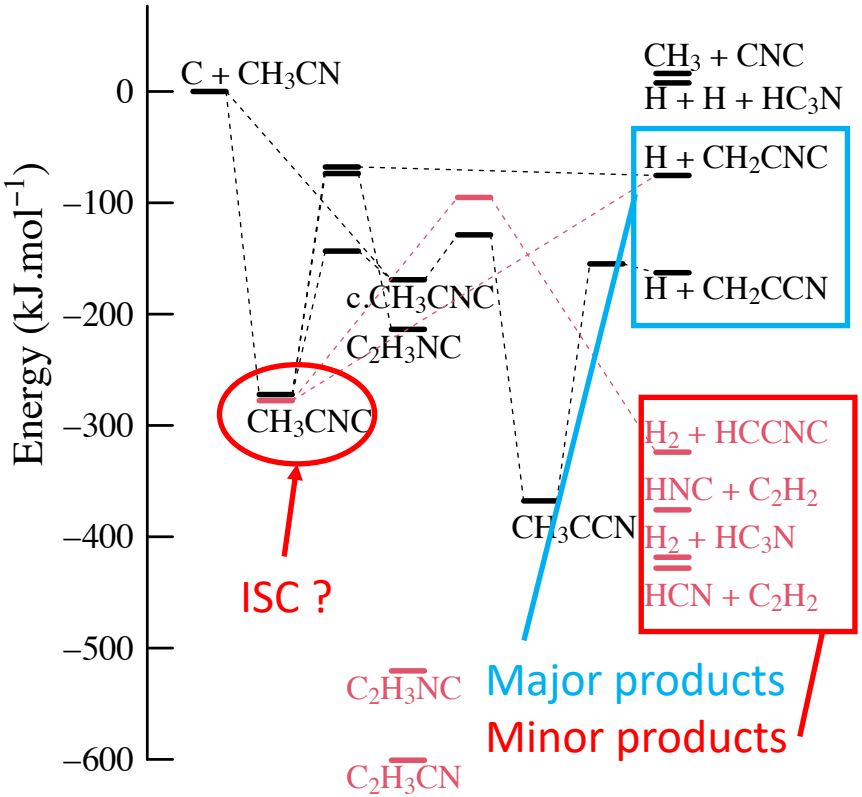



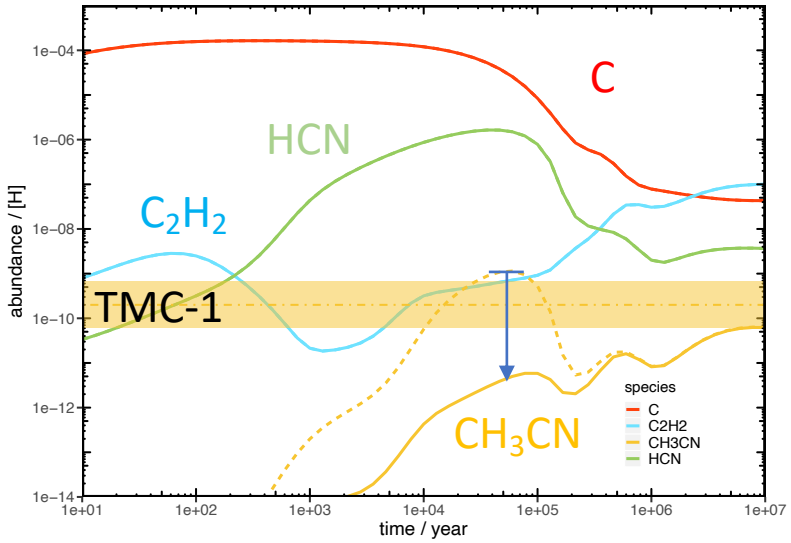


# The C($^3$P) + $CH_3CN$ reaction



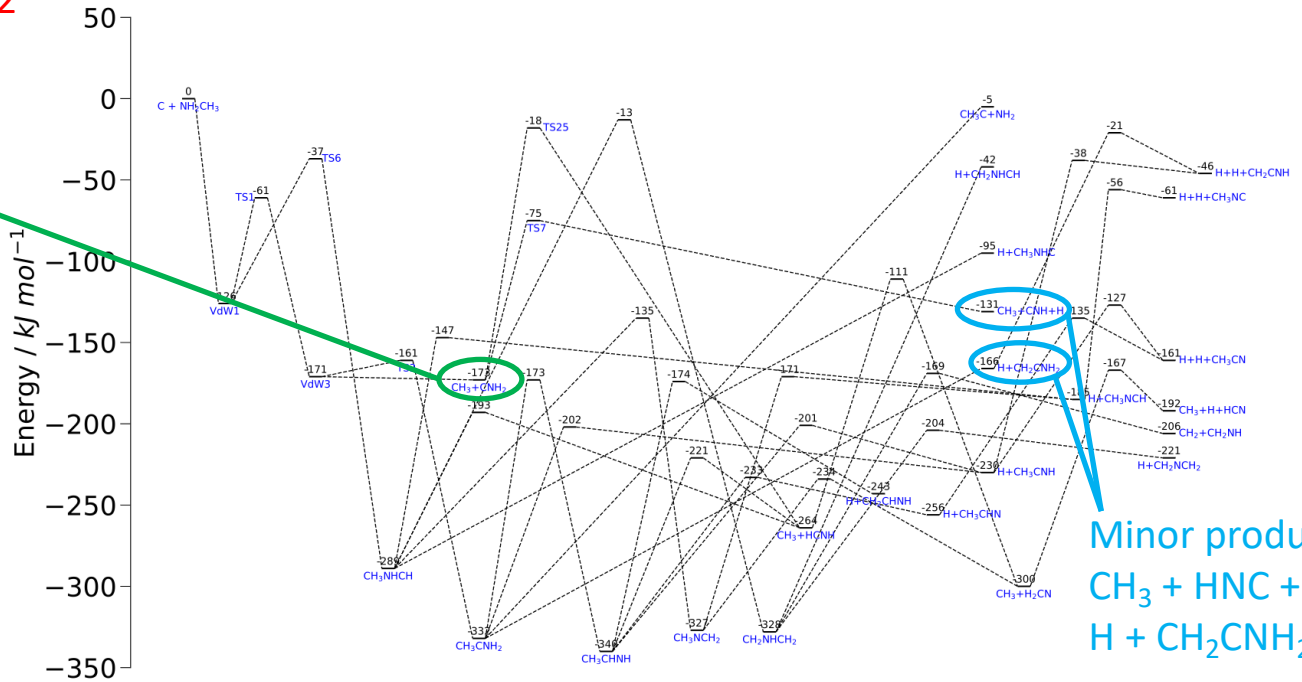


K. M. Hickson et al. *ACS Earth Space Chem.*, **5**, 824-833, **2021**.

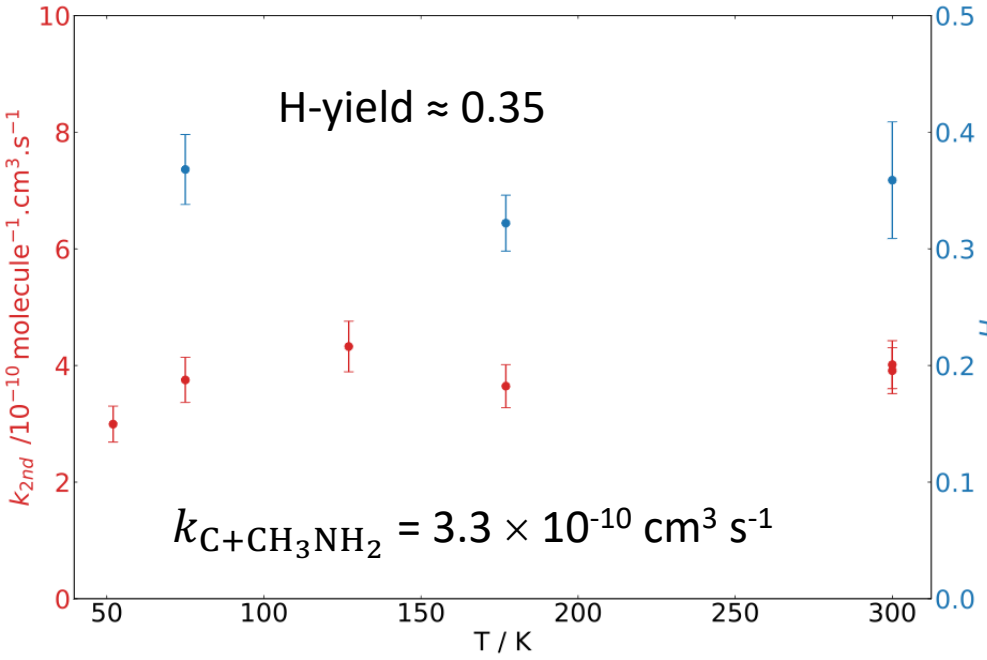
P. Gratier et al., *Astrophys. J. Supp. Ser.*, **225**, 25, **2016**.

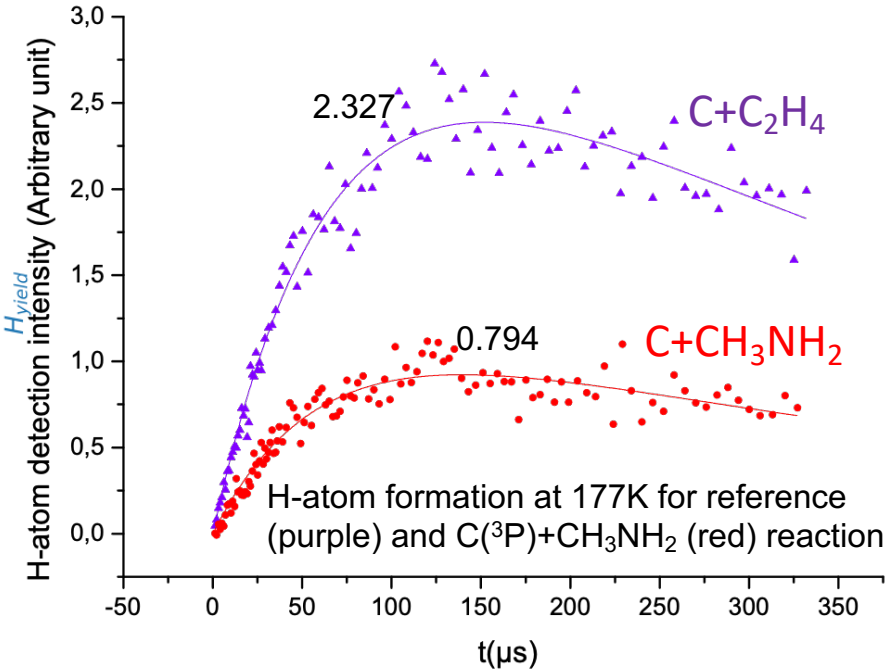
# The $C(^3P) + CH_3NH_2$ reaction

Major products:
$CH_3 + CNH_2$

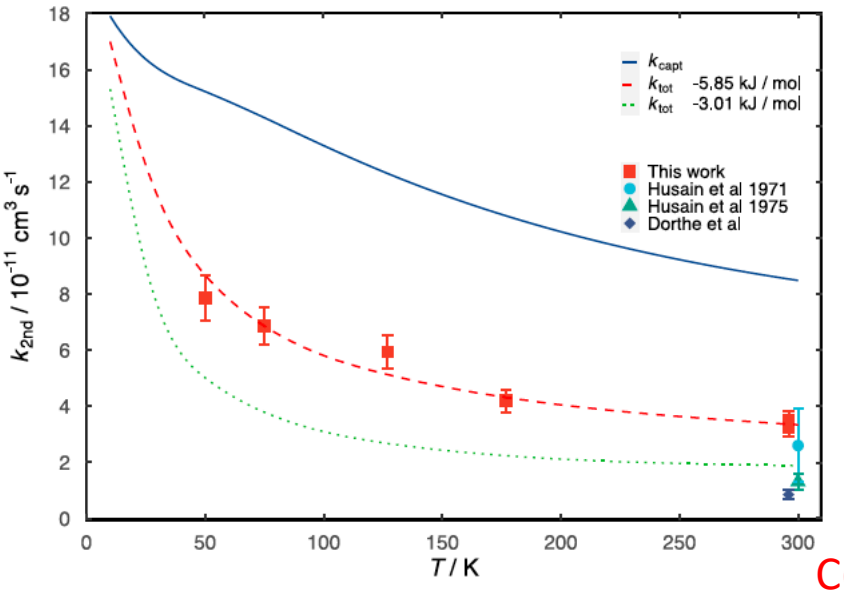


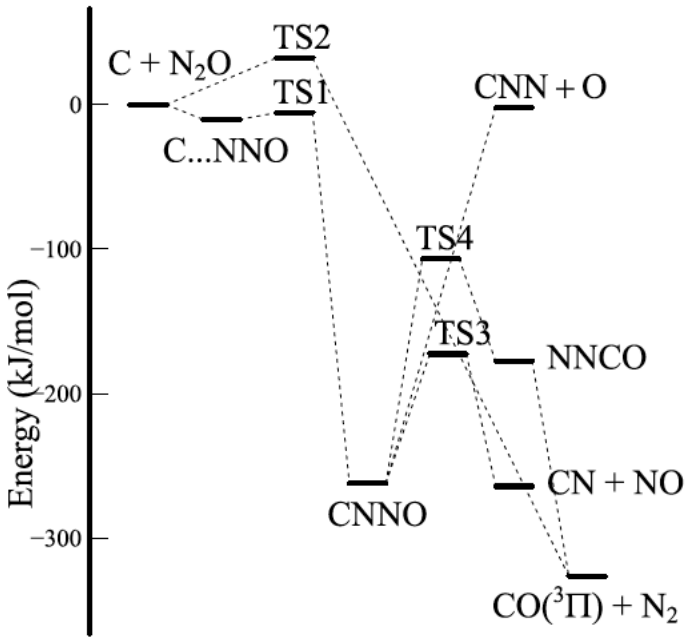

Minor products:
$CH_3 + HNC + H$ ?
$H + CH_2CNH_2$ ?



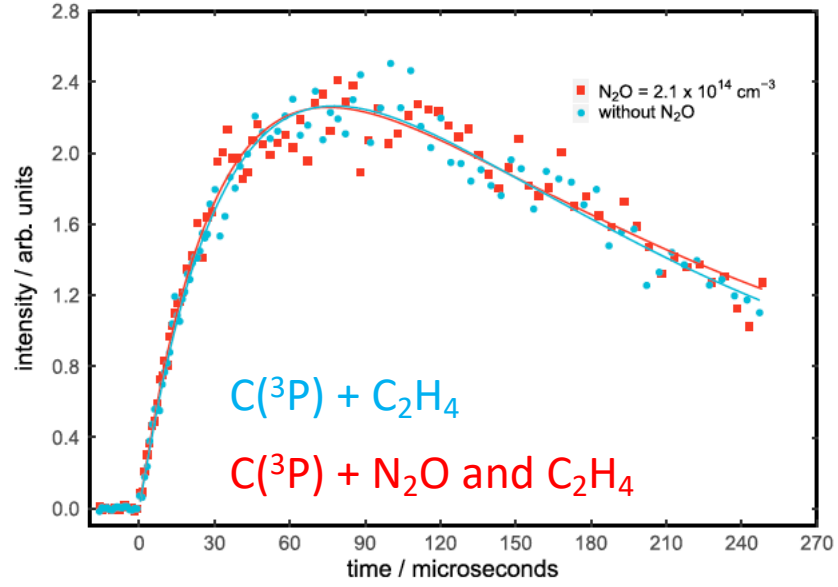



# The C($^3$P) + $N_2O$ reaction

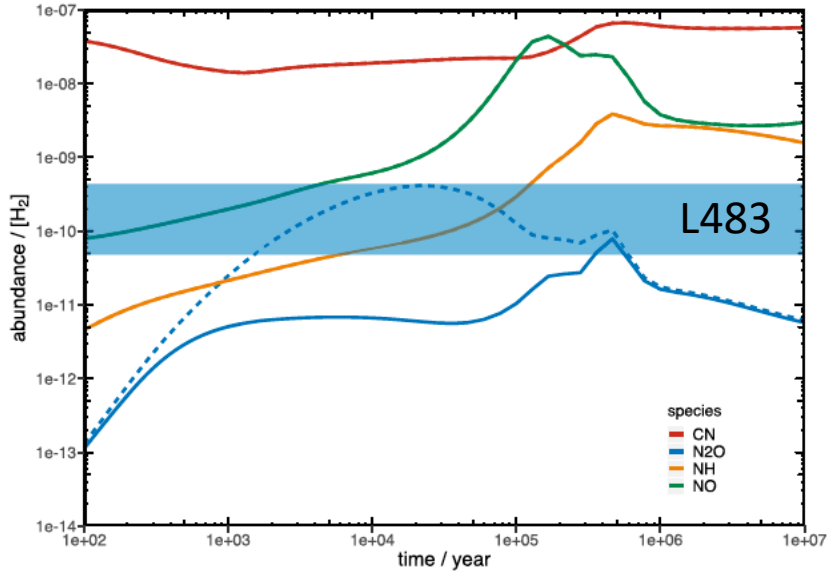



C($^3$P) + $N_2O$ → CN + NO then CN + $C_2H_4$ → $C_2H_3CN$ + H
→ $^1$CO + $^1N_2$




K. M. Hickson et al. *J. Phys. Chem. A*, **126**, 940-950, **2022**.




M. Agúndez et al. *Astron. Astrophys.*, **625**, A147, **2019**.

# Summary C + COMs

C + oxygen bearing COMs ($CH_3OH$, $CH_3OCH_3$, $CH_3CHO$, $HCOOCH_3$, $CH_3COCH_3$)

All these reactions are very fast at low T.

The major products are CO + fragment(s), so these reactions lead to a loss of complexity.

C + nitrogen bearing COMs ($CH_3CN$, $CH_3NH_2$)

These reactions are very fast at low T.

High H-atom yields indicate that products of increased molecular complexity could be formed.

Need to investigate other systems of this type

Modeled gas-phase COM abundances decrease → Less good agreement with observations.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