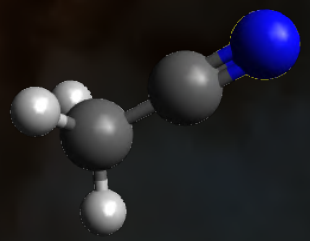
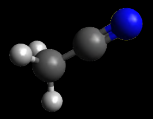


Gas-phase formation of interstellar methyl cyanide: review and new theoretical calculations

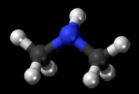
Lisa Giani
Université Grenoble Alpes, 1st year PhD student

Supervisors:
Cecilia Ceccarelli (Université Grenoble Alpes) and Nadia Balucani (Università di Perugia)

interstellar Complex Organic Molecules (iCOMs: C-bearing molecules with ≥ 6 atoms)



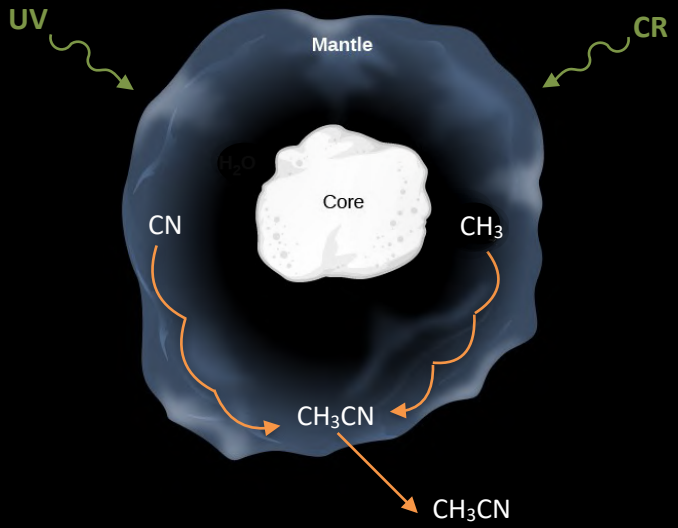

HOW DO iCOMs FORM?
(Example of CH_3CN)



Two paradigms:

1. **Gas-phase**: freeze-out and hydrogenation, mantle desorption (thermal or non thermal) and then gas-phase reactions.

2. **Grain surface (diffusive or non diffusive)**: radical formation on mantles, diffusion (at least 20-30 K) and surface reactions.



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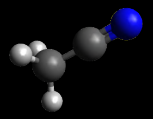


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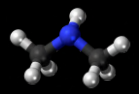

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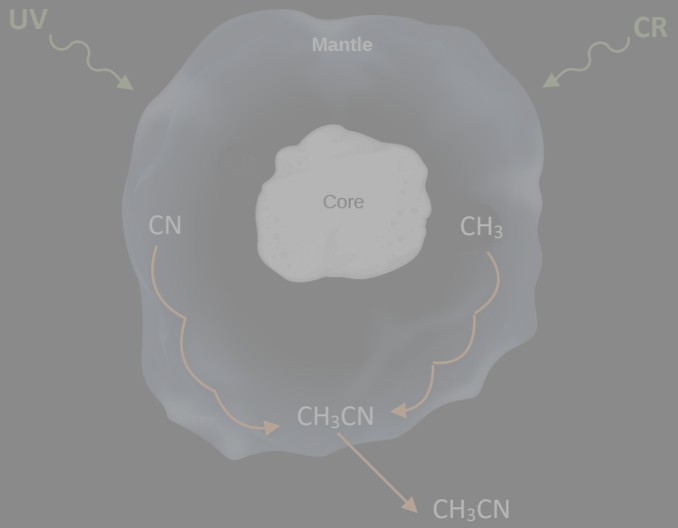
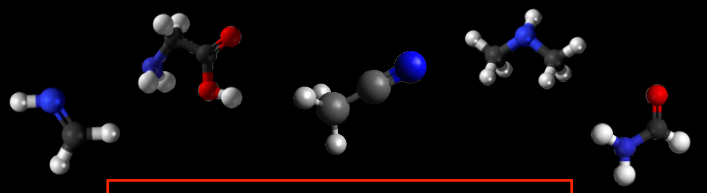


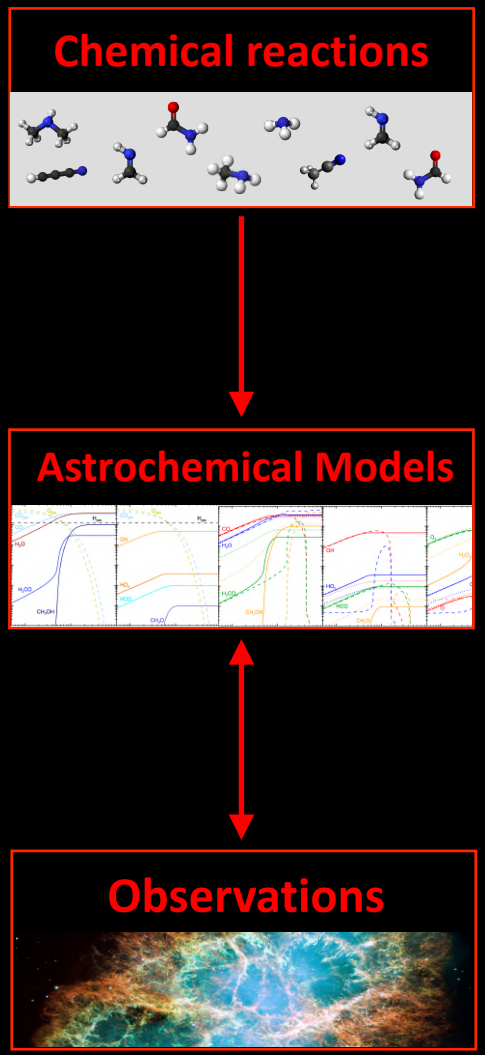
ASTROCHEMICAL GAS-PHASE REACTION NETWORKS



- **More than 8000 gas-phase reactions in the databases.**

- Only **10-20% studied, often not even in the appropriate temperature** (10-100 K) **and pressure** (10^2 -10^6 particles cm^{-3}) **conditions.**

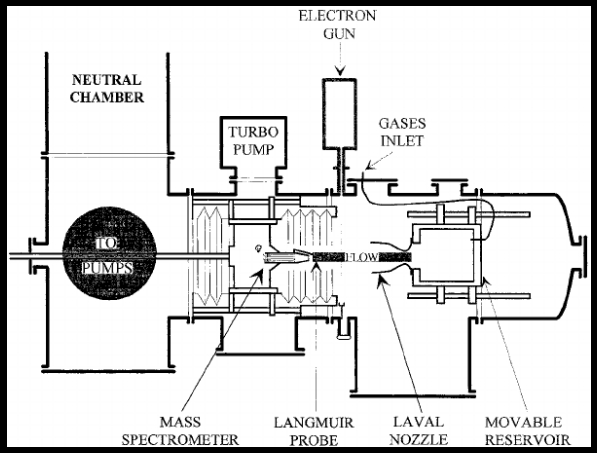
- Need to determine:
  - **Thermodynamic Feasibility → Exothermicity**
  - **Kinetics → Rate Constants**
  - **Products and Branching Fractions (BF)**

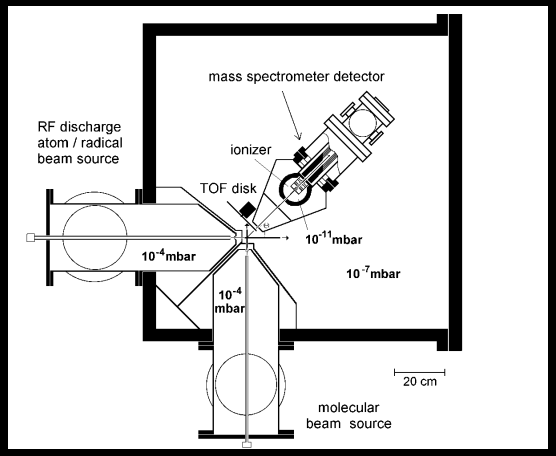


GAS-PHASE REACTIONS: WHY THEORETICAL CALCULATIONS?

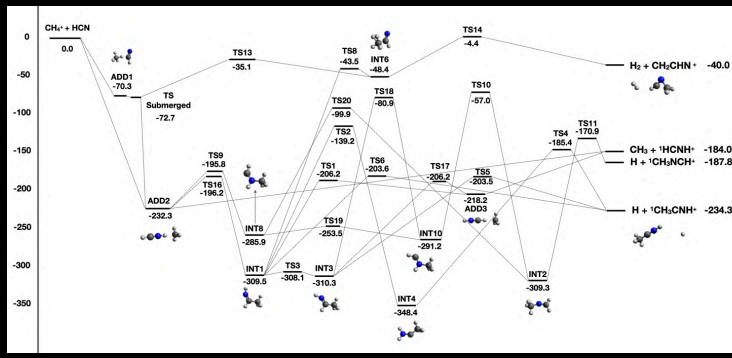
1) Laboratory experiments

CRESU, CMB, … but not always feasible





2) Theoretical Calculations



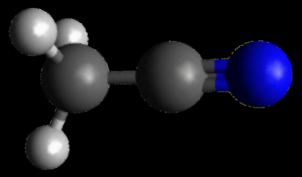
Potential Energy Surface (PES) → **Reaction Paths**

+

Kinetic Calculations → **Rate Constants**

$$k(T) = \alpha \left(\frac{T}{300}\right)^{\beta} \exp^{-\frac{\gamma}{T}}$$

TARGET OF THIS WORK: INTERSTELLAR METHYL CYANIDE



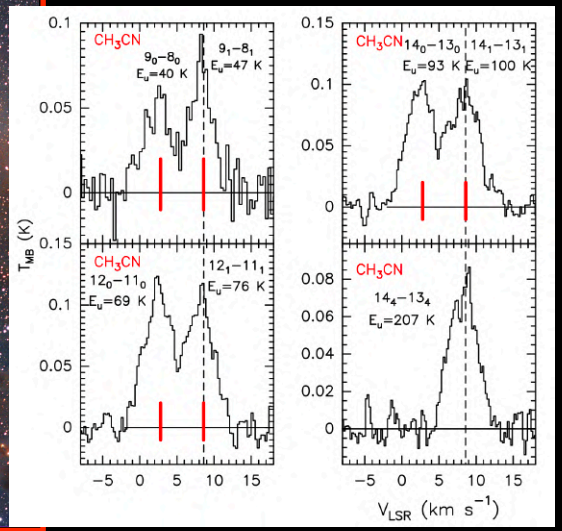
WHY?

UBIQUITOUS IN SPACE

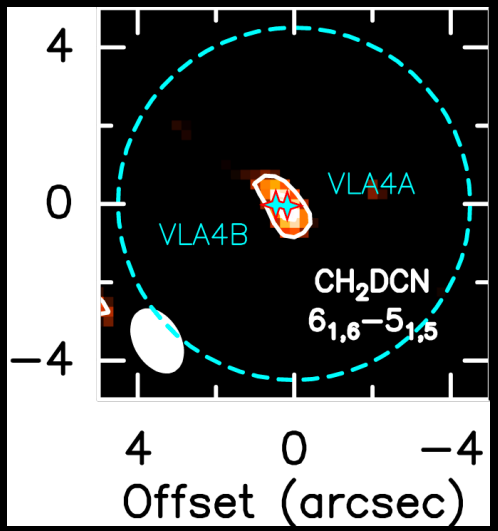
One of the few molecules observed in all star forming regions (molecular clouds, prestellar cores, protostars, protoplanetary disks) and comets.

Example of the hot corino of SVS-13A:

Bianchi et al. 2022



NOEMA



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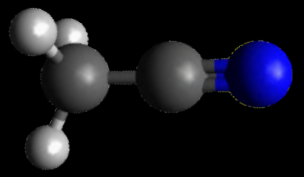

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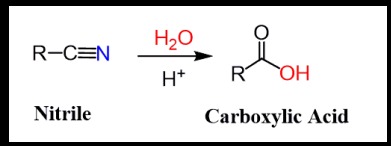
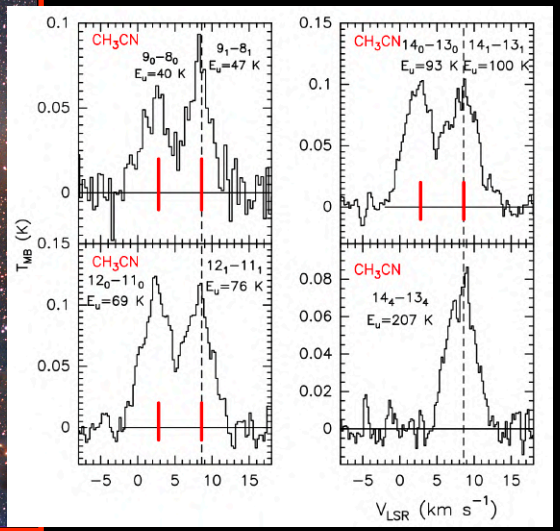
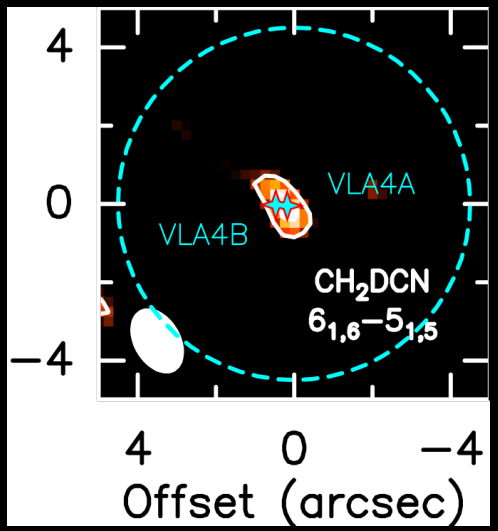
➡ PREBIOTIC MOLECULE: Possible role in the synthesis of RNA and protein precursors.

Nitriles can be hydrolyzed and via multistep synthesis ultimately lead to amino acids







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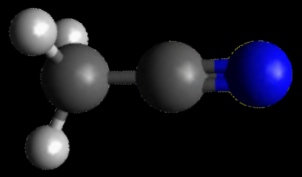

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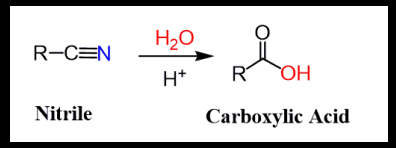
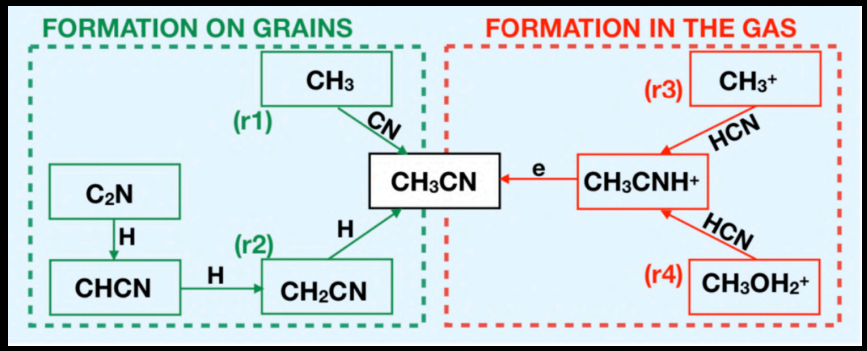
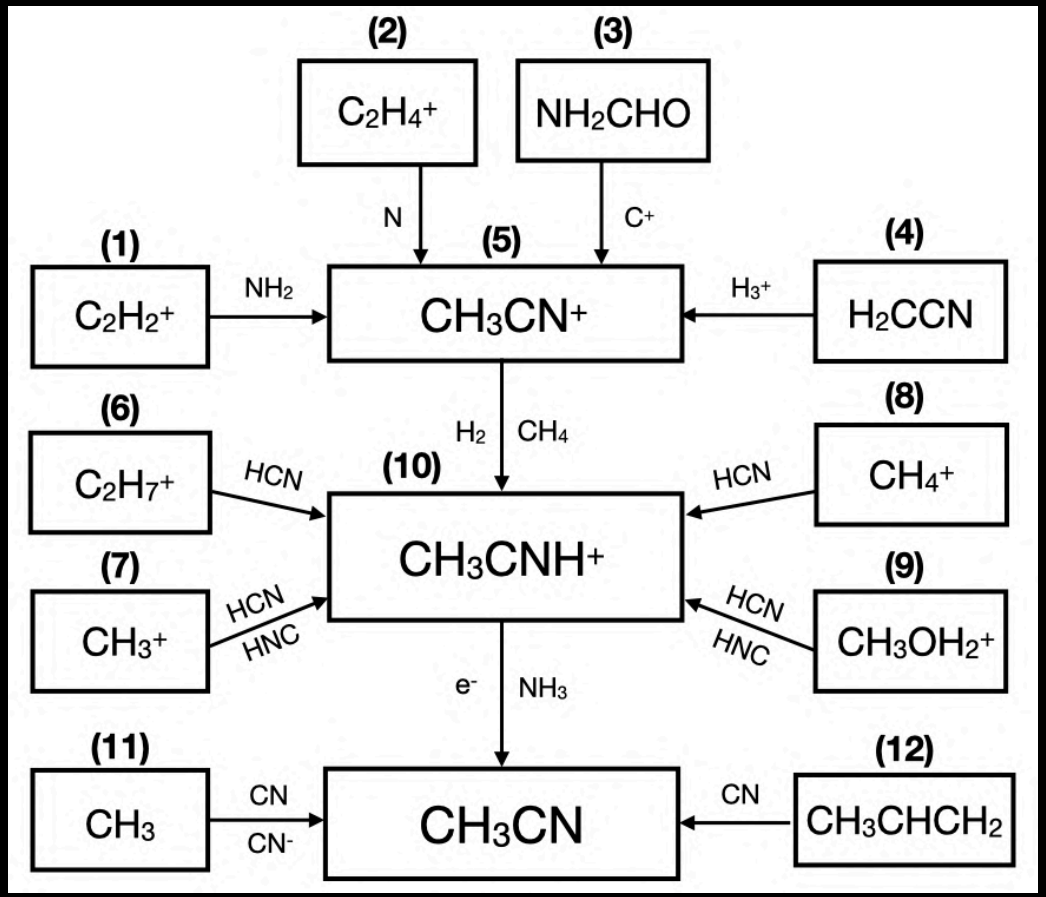


CH_3CN SYNTHESIS (in the literature)



Bianchi et al. 2022

CH_3CN GAS-PHASE NETWORK: CRITICAL REVIEW OF THE LITERATURE



CH_3CN^+ formation

↓

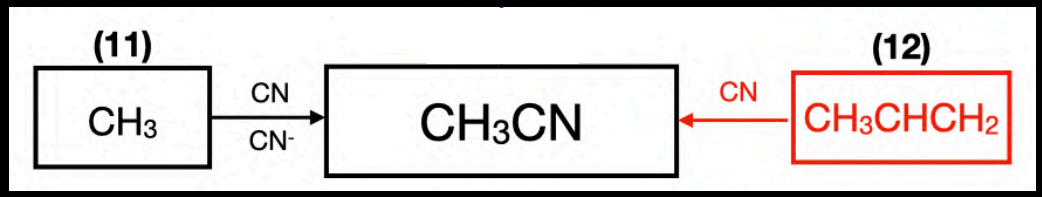
CH_3CNH^+ formation

↓

CH_3CN formation

CH_3CN GAS-PHASE NETWORK: CRITICAL REVIEW OF THE LITERATURE

- The **red** reaction is removed



CH_3CN formation

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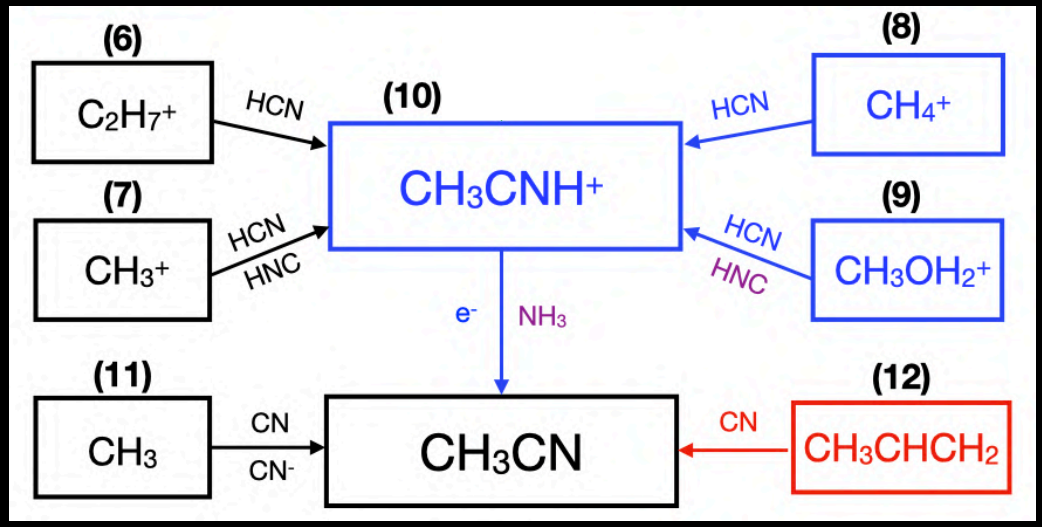
- Theoretical study of the reactions in **blue**: some are new (plum) others need to be revised



CH_3CNH^+ formation

↓

CH_3CN formation

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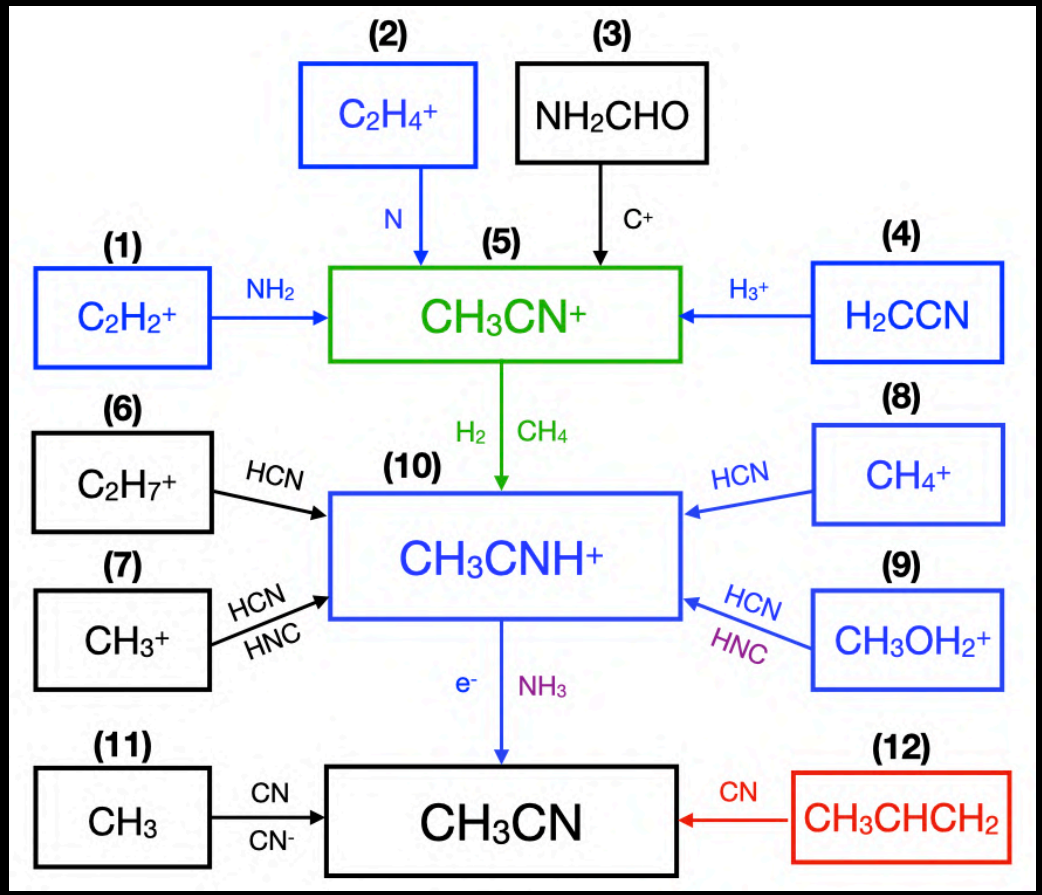

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CH_3CNH^+ formation

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CH_3CN formation

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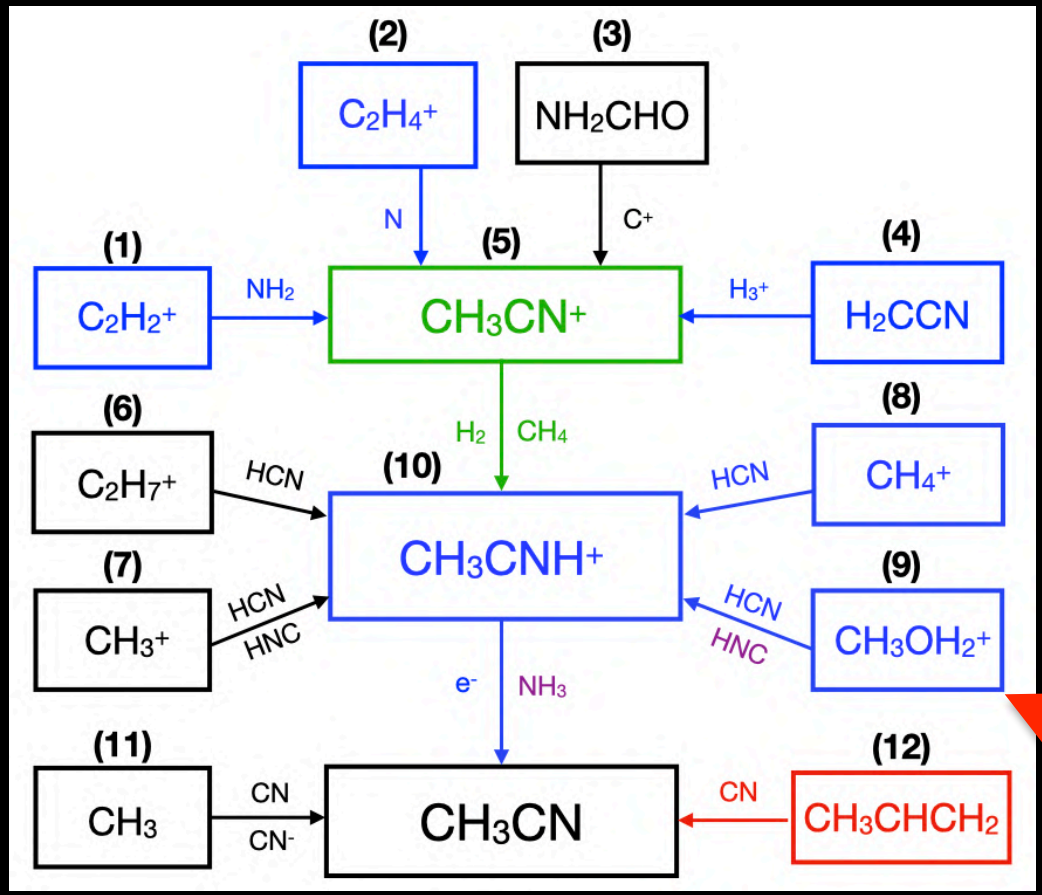


CH_3CN^+ formation

CH_3CNH^+ formation

CH_3CN formation

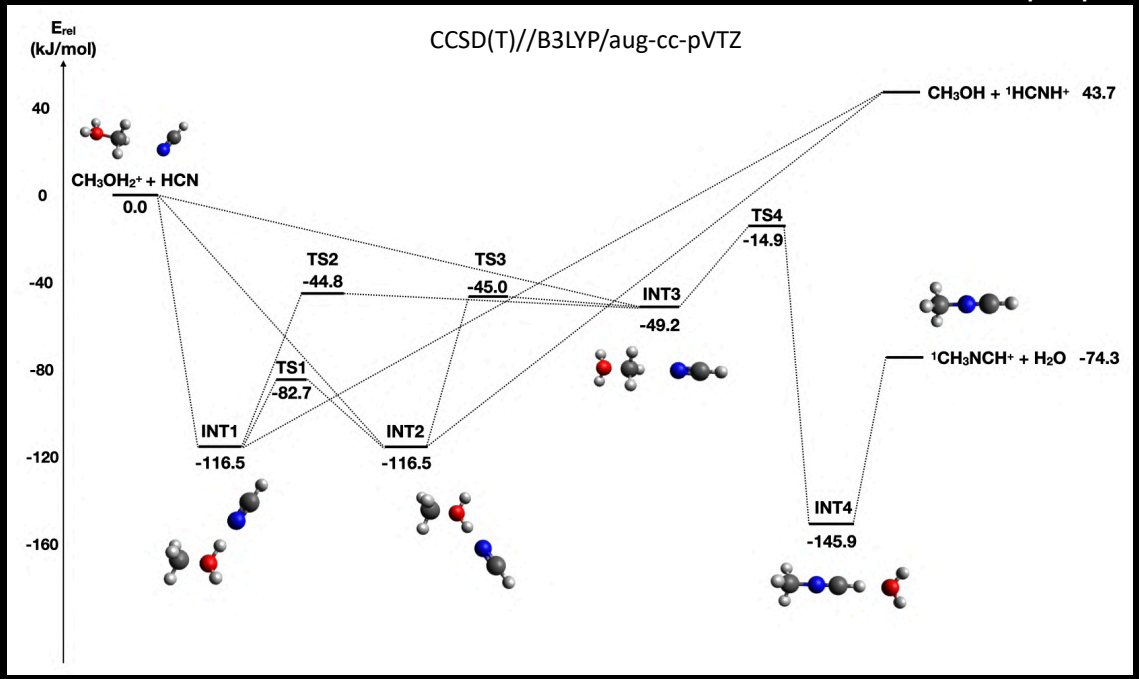
EXAMPLE OF NEW CALCULATIONS: $CH_3OH_2^+$ + HCN REACTION

Potential Energy Surface (PES)

Giani et al. in prep

Studied experimentally by Meotner and Karpas in 1986:

- Formation of C_2H_4N product which they suggest to be CH_3NCH^+, based on proton affinity considerations
- The rate constant measured at 340 K is 2.3×10^{-11} cm^3 s^{-1}



EXAMPLE OF NEW CALCULATIONS: $CH_3OH_2^+$ + HCN REACTION

PES + Capture Theory and RRKM

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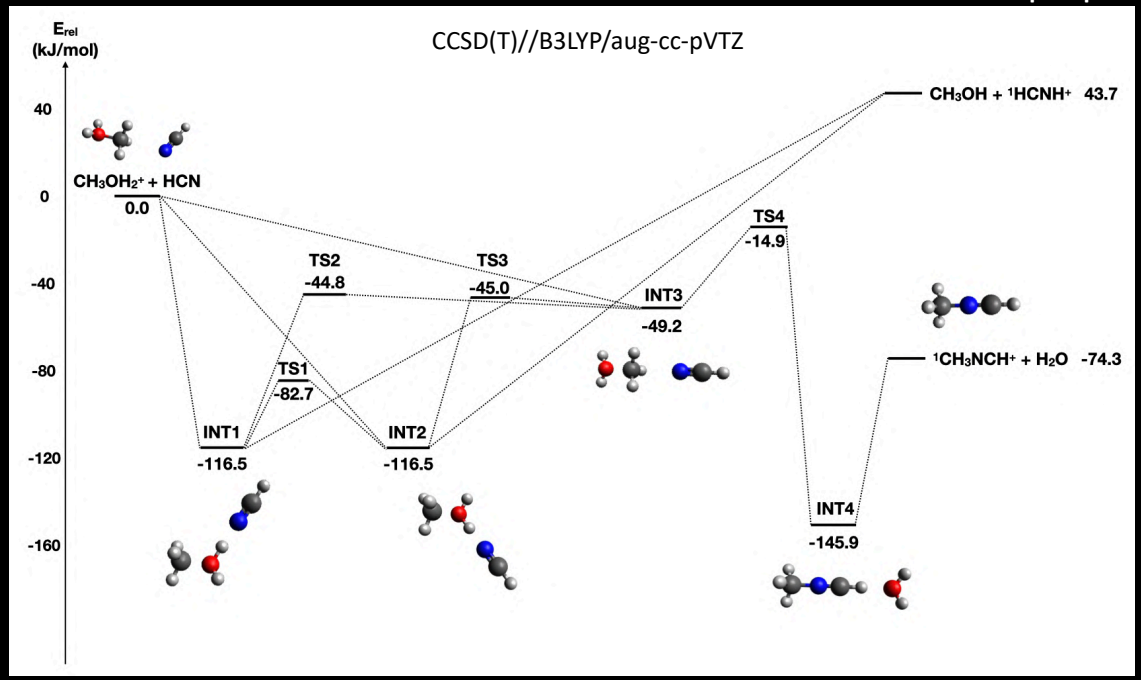
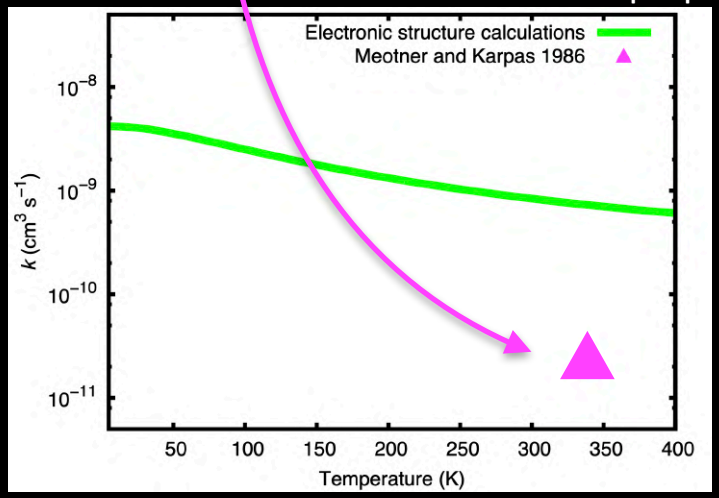


Giani et al. in prep



Computed rate constant more than one order of magnitude higher than the experimental value

Entrance potential not accurate? → **Semi-empirical model**

EXAMPLE OF NEW CALCULATIONS: $CH_3OH_2^+$ + HCN REACTION

PES + Capture Theory and RRKM + semi-empirical model

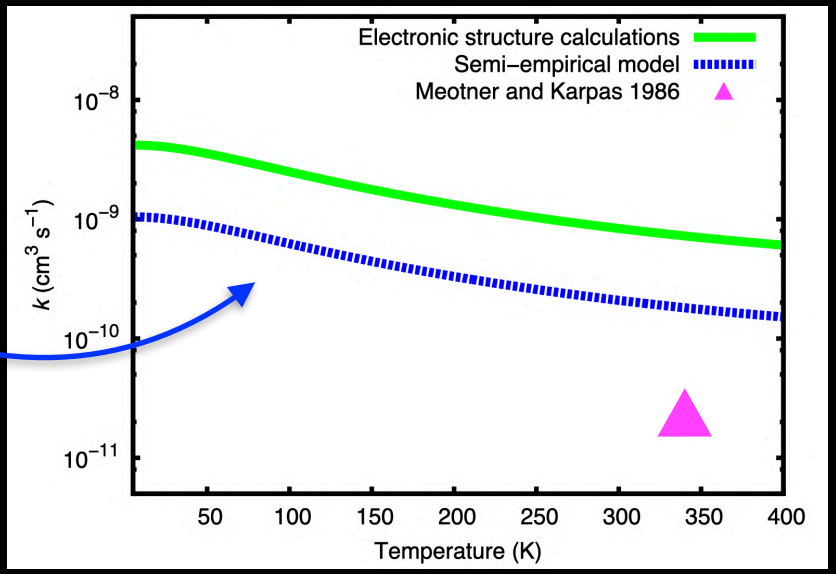
Pirani et al. 2008

$$V_{TOT} = V_{elec} + V_{non-elec}$$

$$V_{\mathrm{ILJ}} = \varepsilon \left[\frac{4}{n(R)-4} \left(\frac{R_m}{R} \right)^{n(R)} - \frac{n(R)}{n(R)-4} \left(\frac{R_m}{R} \right)^{4} \right] \longrightarrow V_{rep} + V_{ind} + V_{disp}$$

$$V_{elec} = \frac{1}{4\pi\varepsilon_0} \sum_i \sum_j \frac{q_i q_j}{r_{ij}} \longrightarrow \text{Averaged all over the relative configurations}$$

Still one order of magnitude higher



EXAMPLE OF NEW CALCULATIONS: $CH_3OH_2^+$ + HCN REACTION

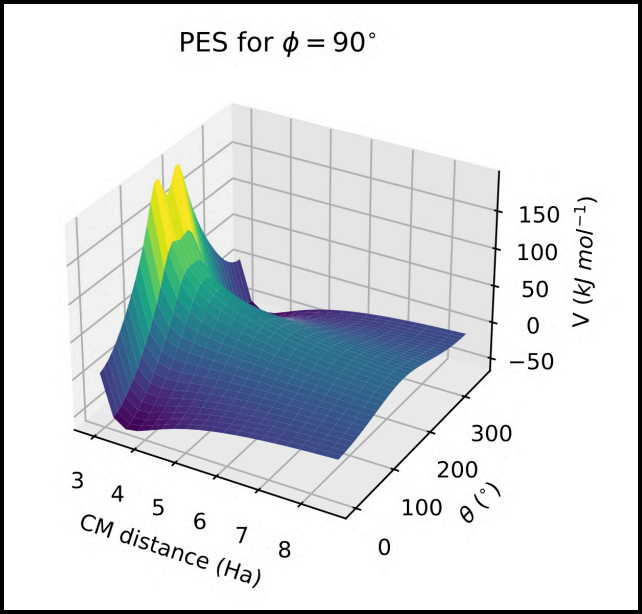
PES + Capture Theory and RRKM + semi-empirical model + steric effect

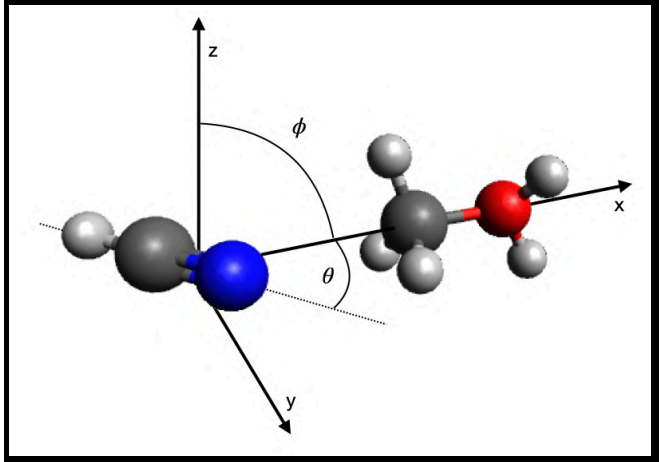
Pirani et al. 2008

$$V_{TOT} = V_{elec} + V_{non-elec}$$

$$V_{ILJ} = \varepsilon \left[\frac{4}{n(R)-4} \left(\frac{R_m}{R} \right)^{n(R)} - \frac{n(R)}{n(R)-4} \left(\frac{R_m}{R} \right)^{4} \right] \longrightarrow V_{rep} + V_{ind} + V_{disp}$$

$$V_{elec} = \frac{1}{4\pi\varepsilon_0} \sum_i \sum_j \frac{q_i q_j}{r_{ij}} \longrightarrow \text{Evaluated at each specific configuration of the reactants}$$





N atom pointing the carbon

↓

Attractive

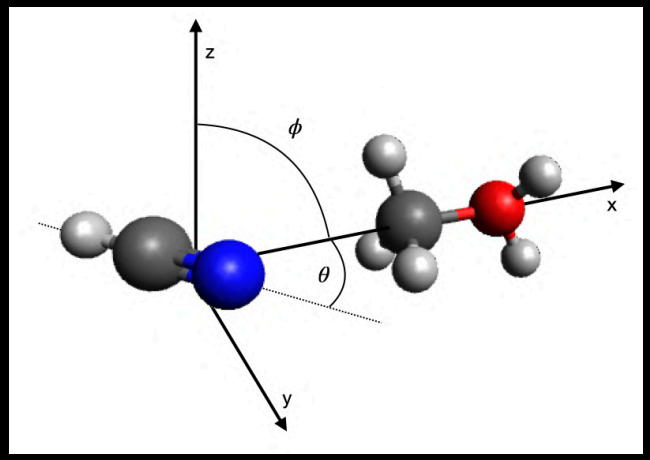
H atom pointing the carbon

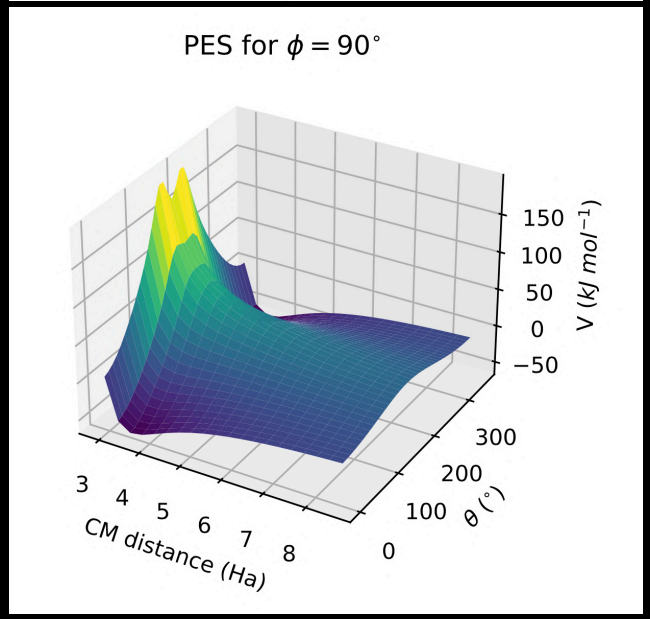
↓

Repulsive

EXAMPLE OF NEW CALCULATIONS: $CH_3OH_2^+$ + HCN REACTION

PES + Capture Theory and RRKM + semi-empirical model + steric effect



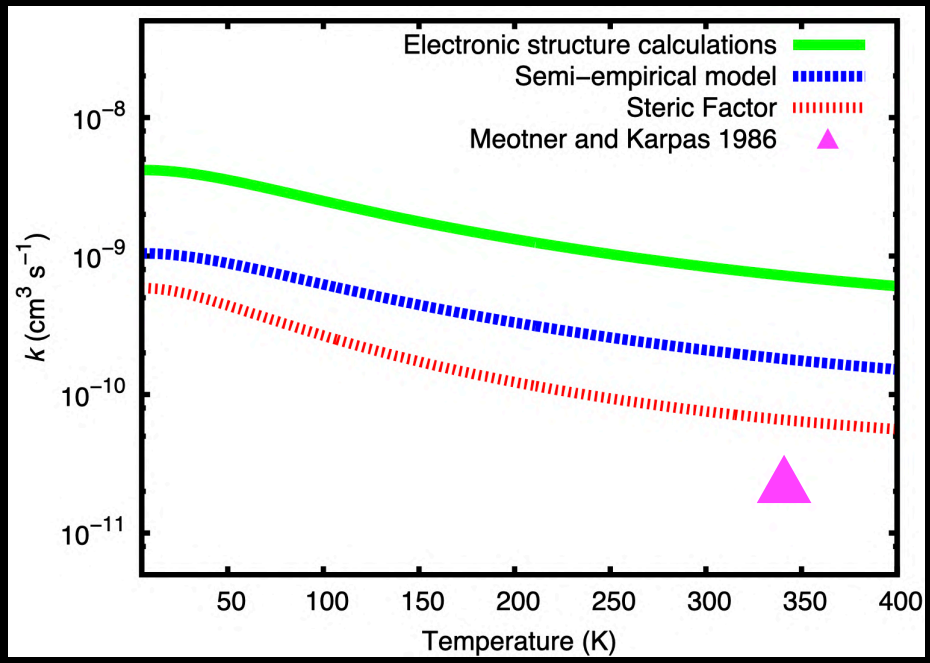


Only half (58%) of the collisions are reactive, which results in a steric factor of 0.58

Final result (red curve):

$K_{calculated}$ (340 K) = 6.5×10^{-11}

$K_{measured}$ (340 K) = 2.3×10^{-11}



CH_3CN GAS-PHASE NETWORK: CRITICAL REVIEW OF THE LITERATURE

- The **red** reaction is removed
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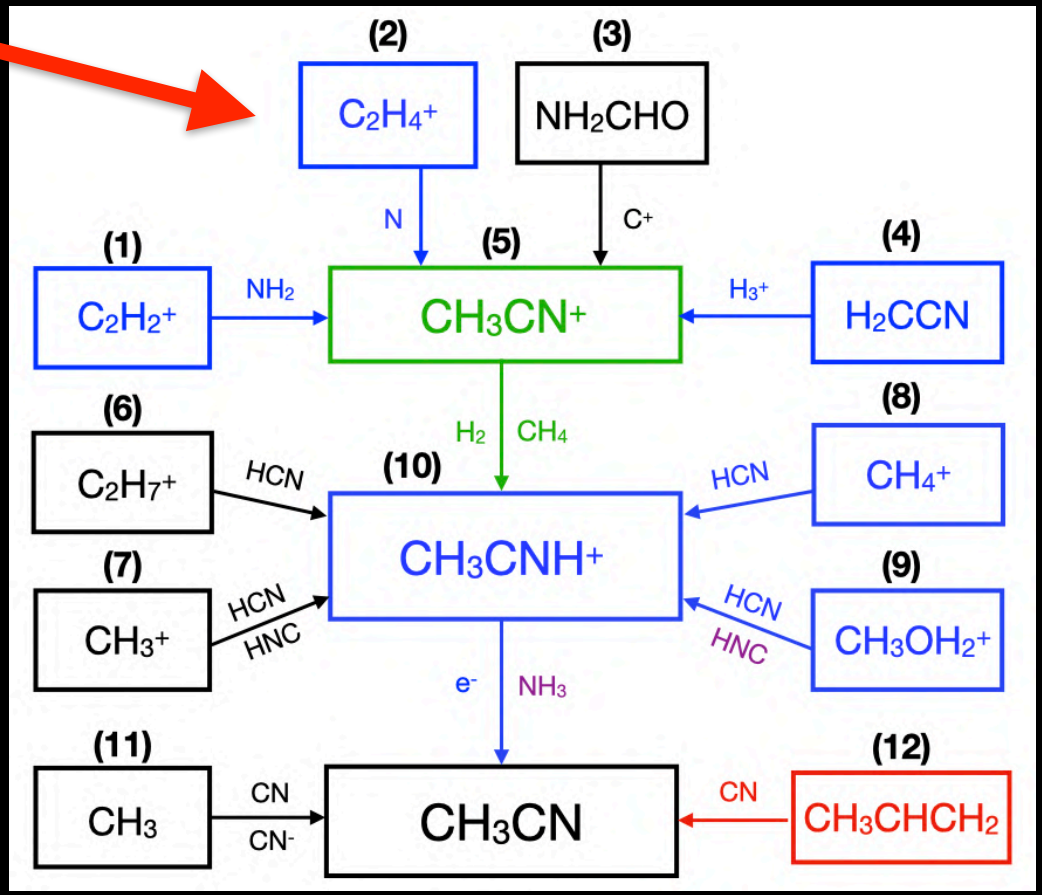
- The **green** reactions are verified



CH_3CN^+ formation

↓

CH_3CNH^+ formation

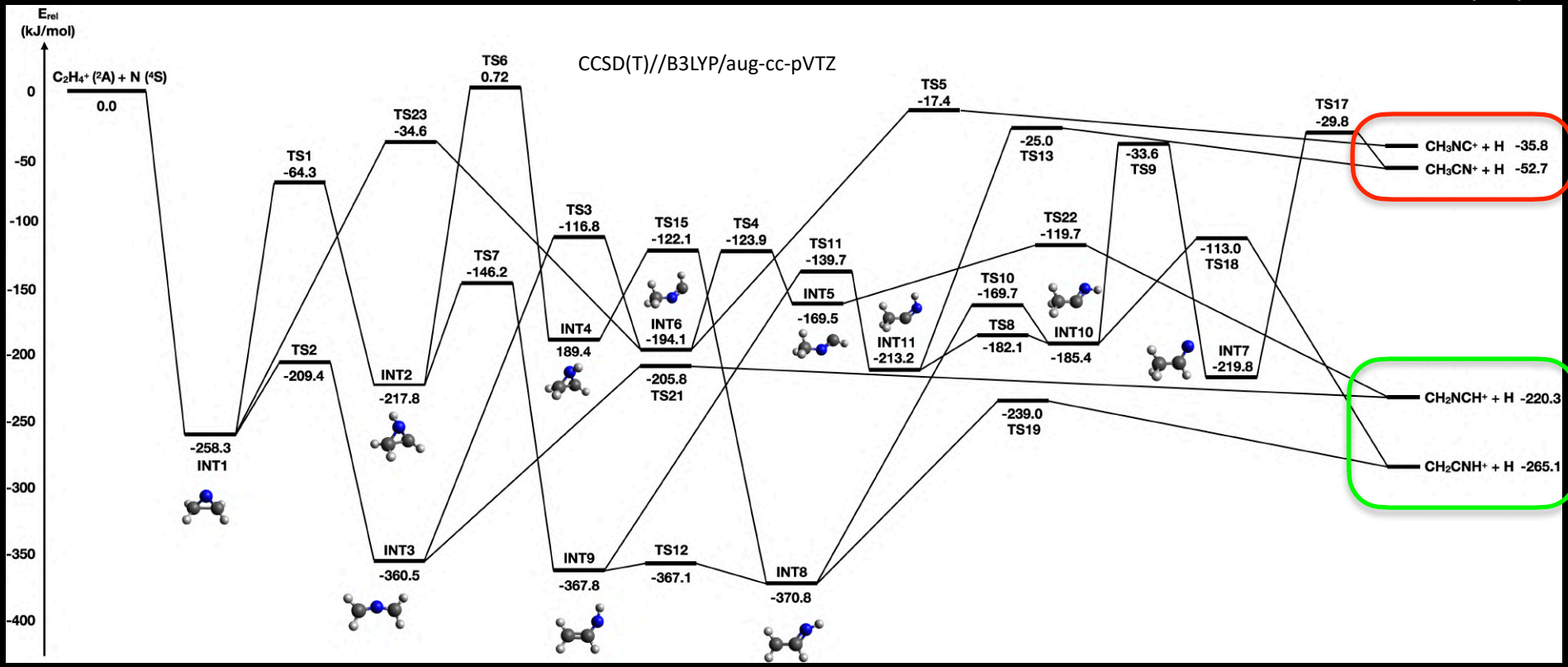
↓

CH_3CN formation

EXAMPLE OF NEW CALCULATIONS: $C_2H_4^+$ + N REACTION

PES

Giani et al. in prep



Experiment by Scott et al. (1999):

➡ In the paper the product is CH_2CNH^+, but

In KIDA and UMIST the reported product is

CH_3CN^+

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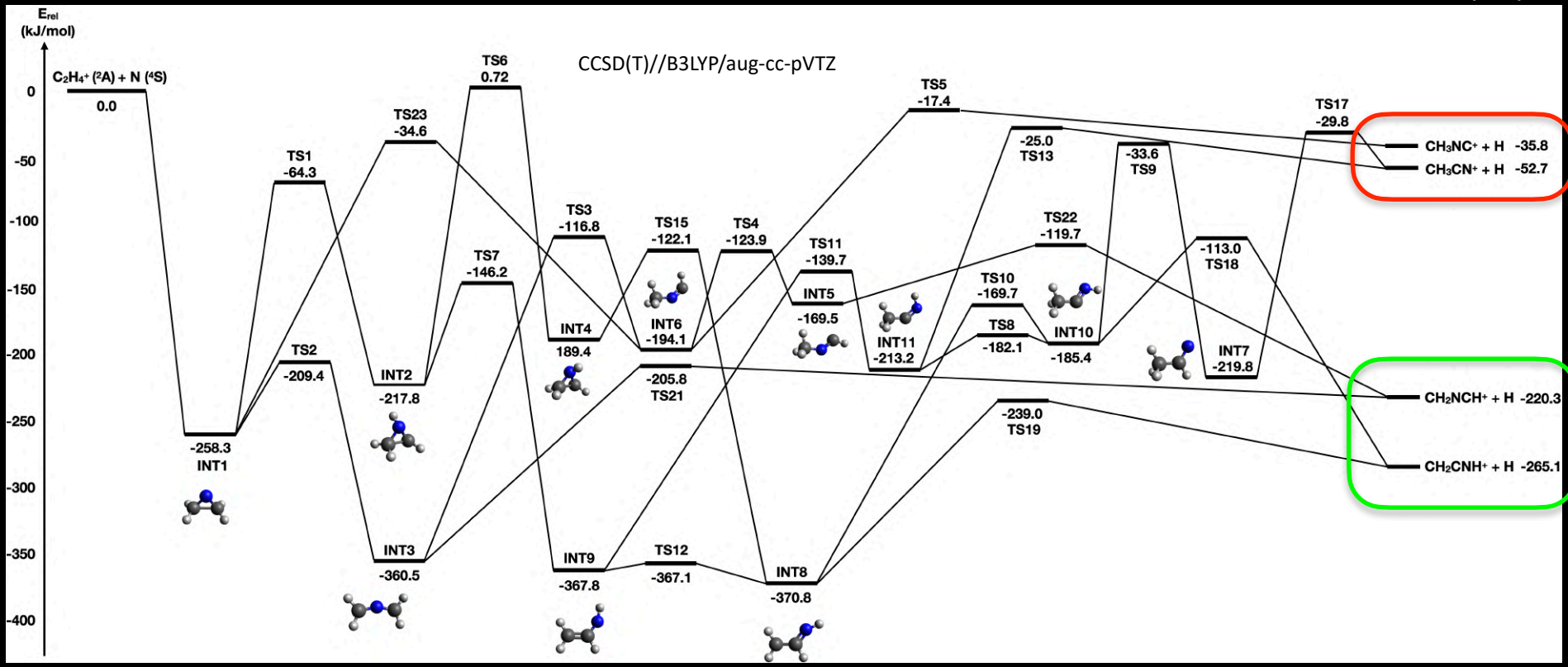


Experiment by Scott et al. (1999):

➡ In the paper the product is CH_2CNH^+, but In KIDA and UMIST the reported product is CH_3CN^+

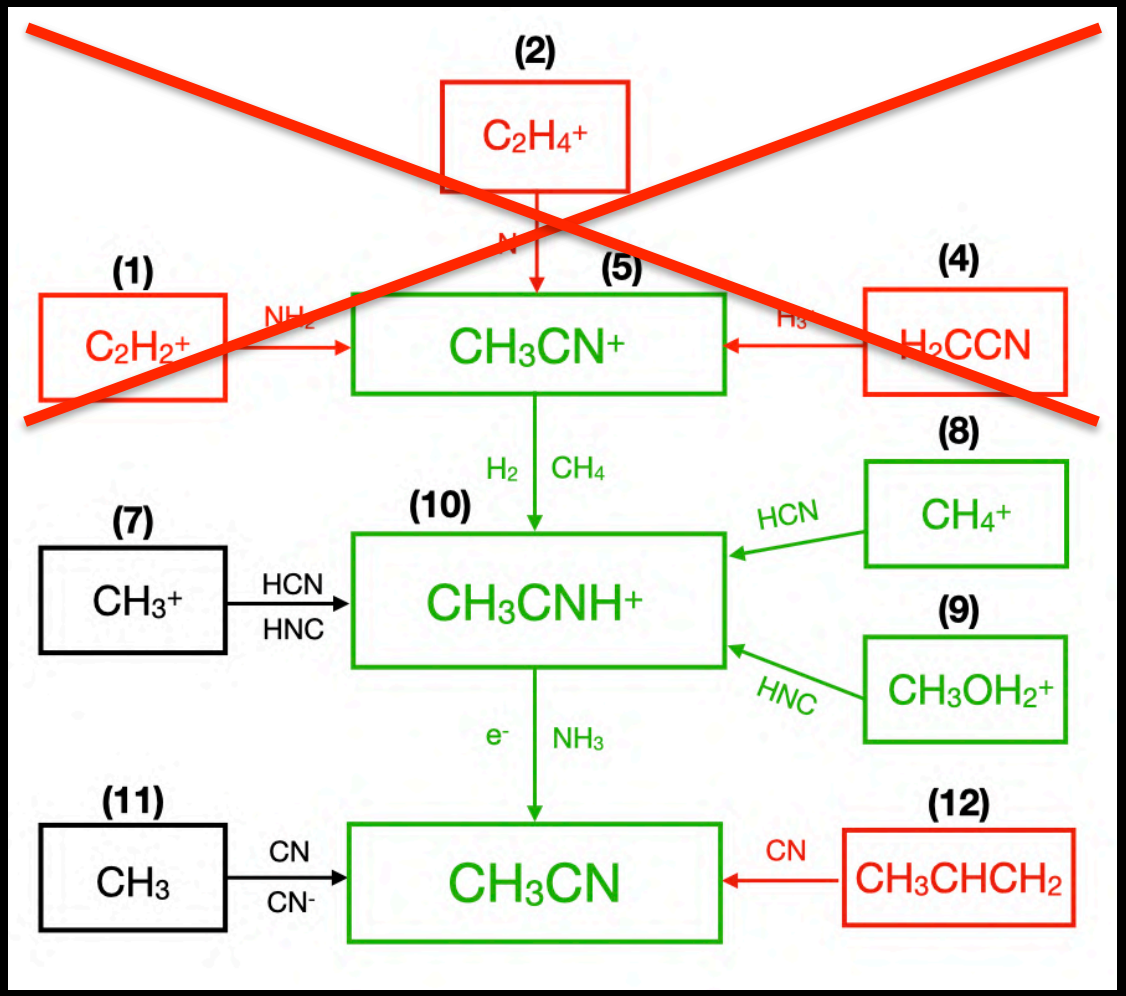
Results:

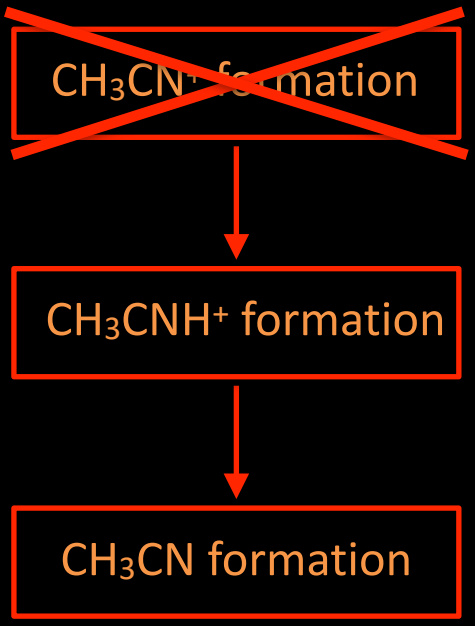
➡ In the databases the reaction product is not correct

➡ The main product is CH_2NCH^+ and not CH_3CN^+

CH_3CN GAS-PHASE NETWORK: CRITICAL REVIEW OF THE LITERATURE

RESULTS

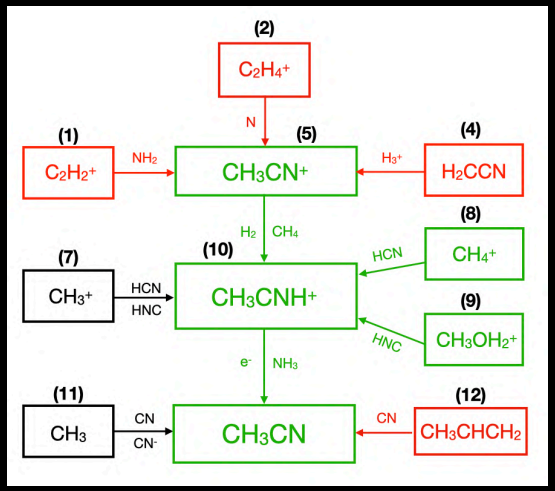


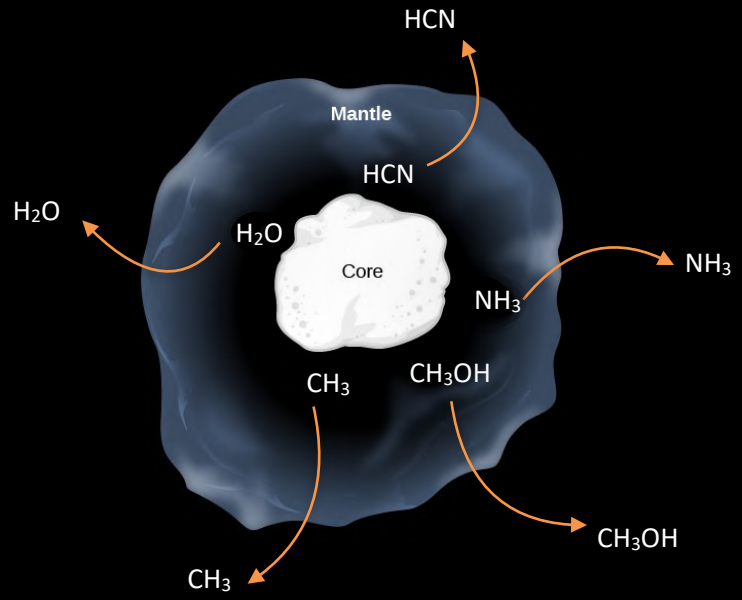


HOW IS CH_3CN FORMED IN COLD MOLECULAR CLOUDS?

Two paradigms:

1. **Gas-phase**:

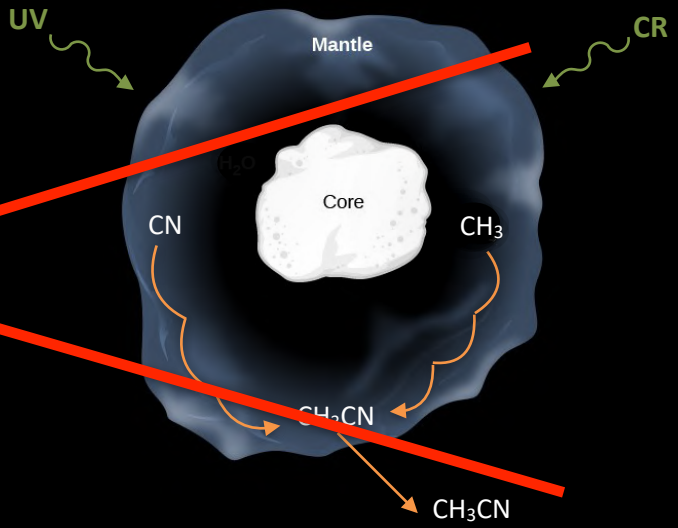




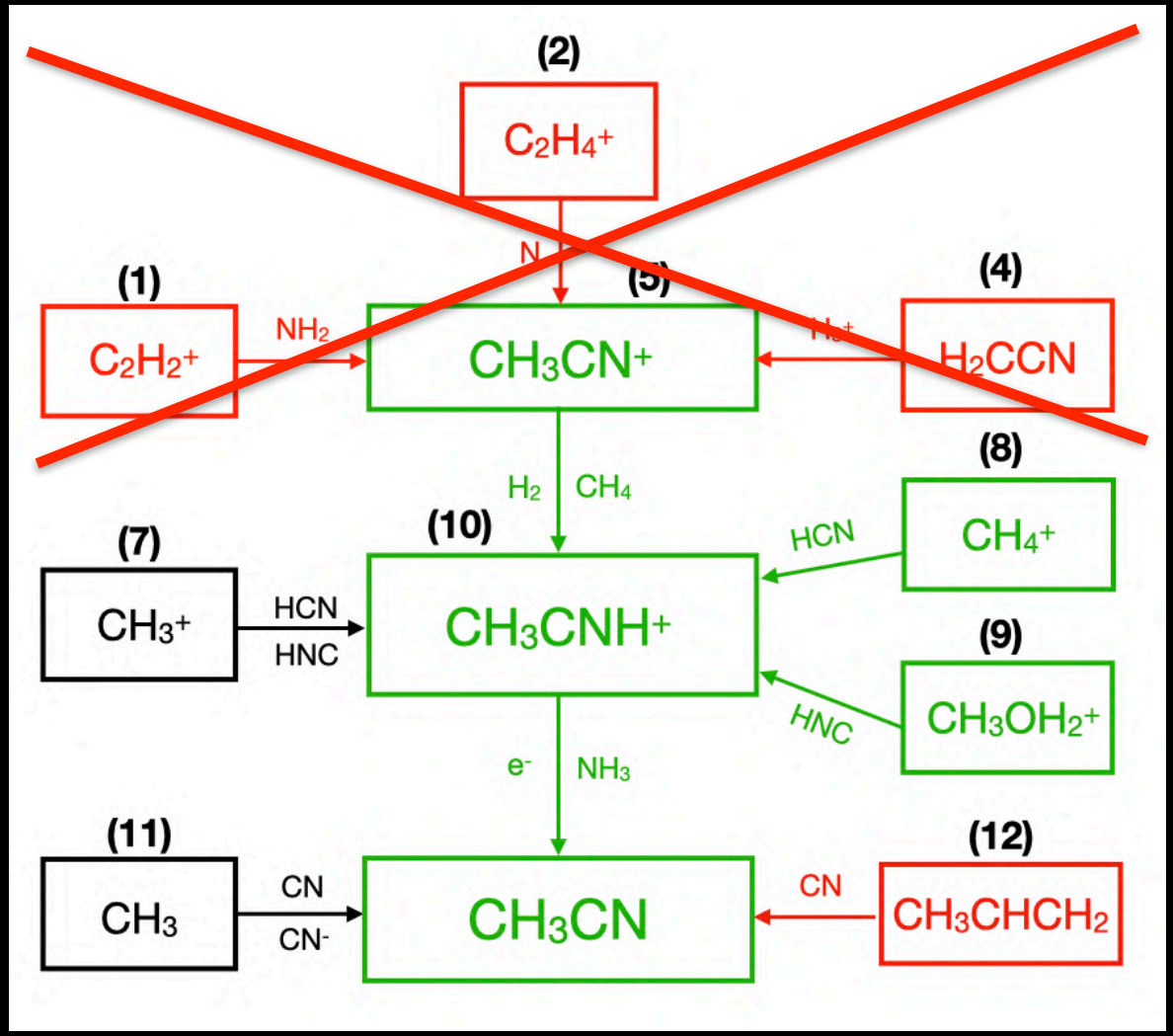
2. **Grain surface (diffusive or non diffusive)**:

radical formation on mantles, diffusion (at least 20-30 K) and surface reactions.

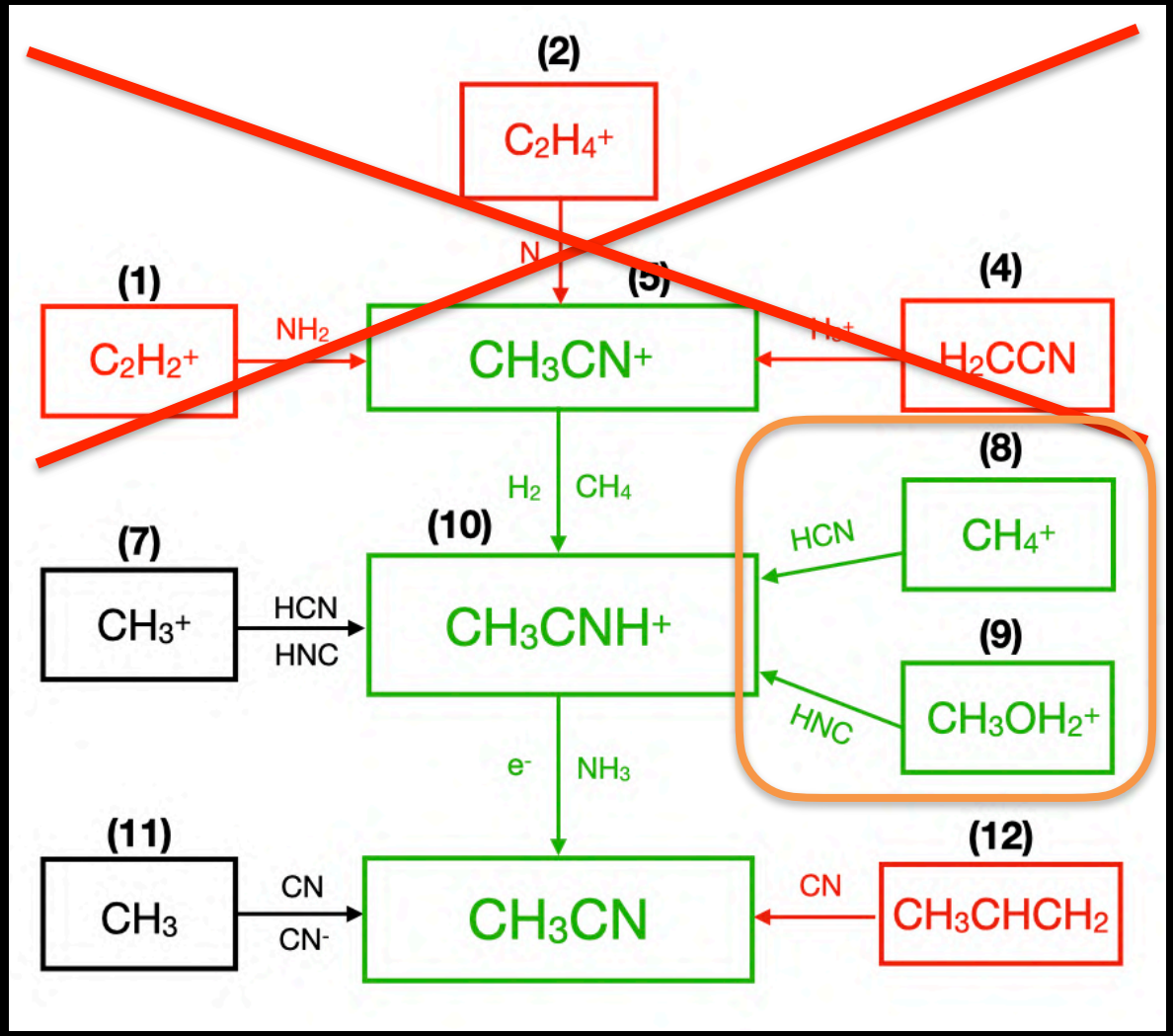
NO DIFFUSION



HOW IS CH_3CN FORMED IN COLD MOLECULAR CLOUDS?



HOW IS CH_3CN FORMED IN COLD MOLECULAR CLOUDS?



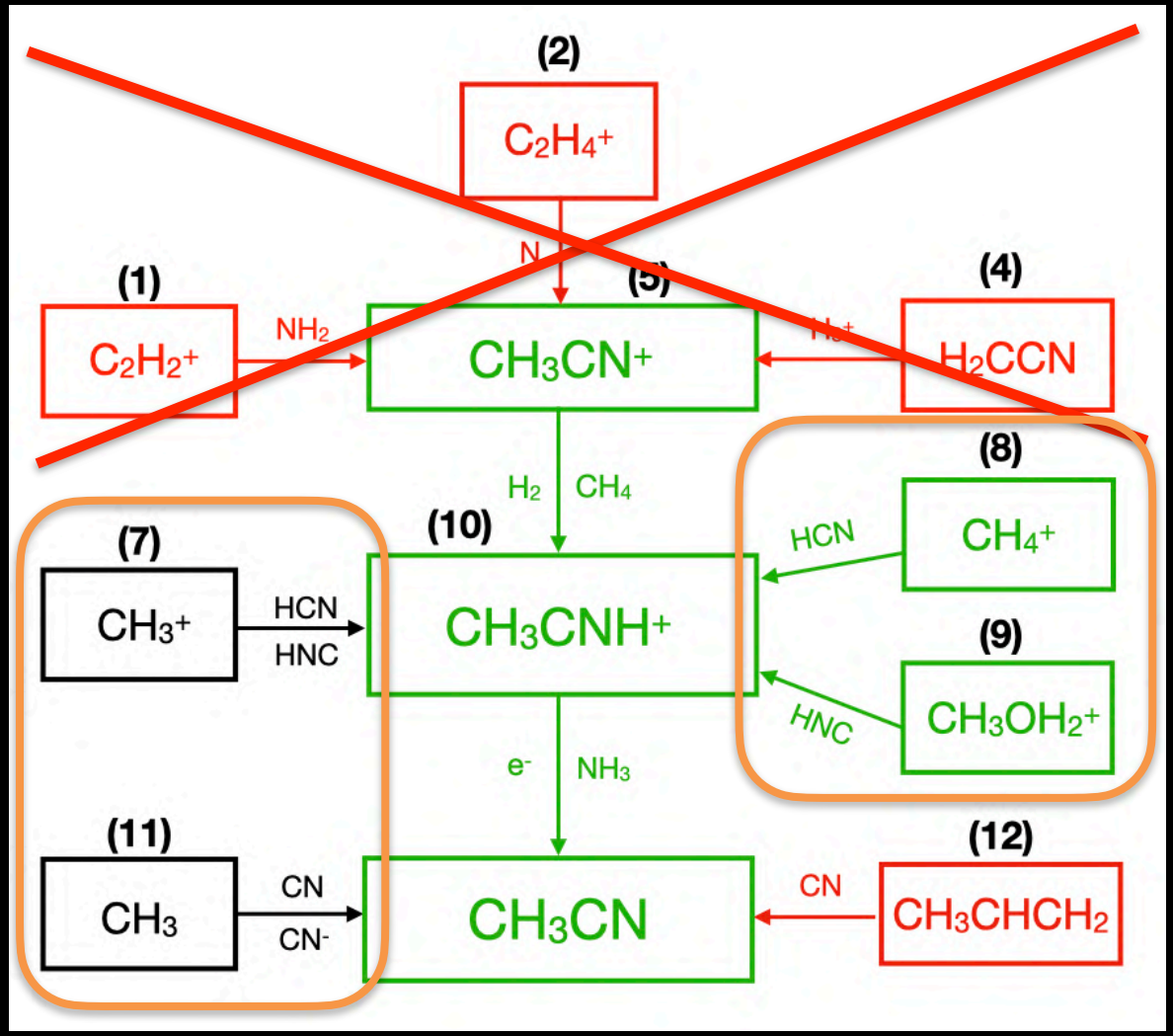
Low abundance of CH_4 and CH_3OH

HOW IS CH_3CN FORMED IN COLD MOLECULAR CLOUDS?

Radiative Association Reactions

↓

Different method to be studied



Low abundance of CH_4 and CH_3OH

MODELING OF THE MOLECULAR CLOUD

Importance of the radiative association reaction rates

The most important are:

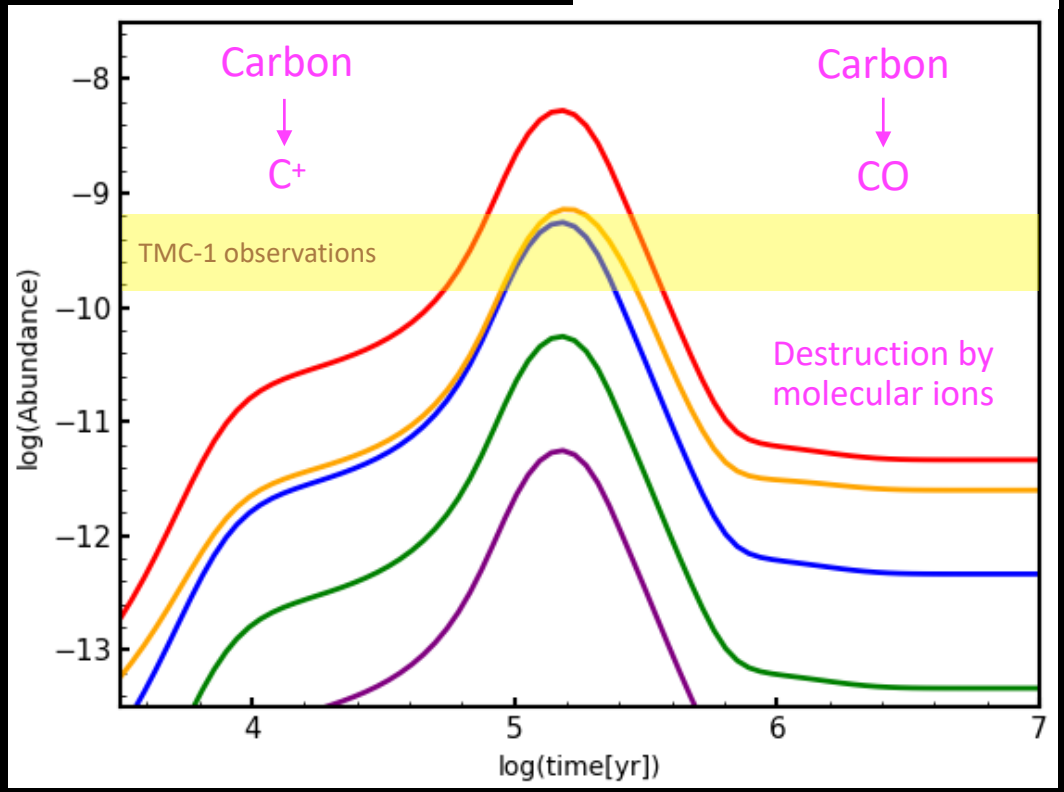
1) $CH_3^+ + HCN \rightarrow CH_3CNH^+ + h\nu$

2) $CH_3^+ + HNC \rightarrow CH_3CNH^+ + h\nu$

	Rate Reaction 1	Rate Reaction 2
■	10^{-9}	10^{-9}
■	10^{-10}	10^{-9}
■	10^{-10}	10^{-10}
■	10^{-11}	10^{-11}
■	10^{-12}	10^{-12}

KIDA values

CH_3CN abundance wrt H



If their rate constants are lowered by a factor 100 no CH_3CN formed in the gas phase

→ **The importance of computing correct radiative association rate constants**

CONCLUSIONS AND PERSPECTIVES

- Of 14 reactions in the KIDA/UMIST database only 6 are correct, of which two newly proposed.
- Theoretical calculations are essential to provide reliable reaction products and rate constants.
- Radiative association reactions are crucial. A different treatment is necessary to derive reliable values.
- *Giani et al. in prep: stay tuned!*

Thanks for your attention!

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CH_3CN: revised gas-phase network

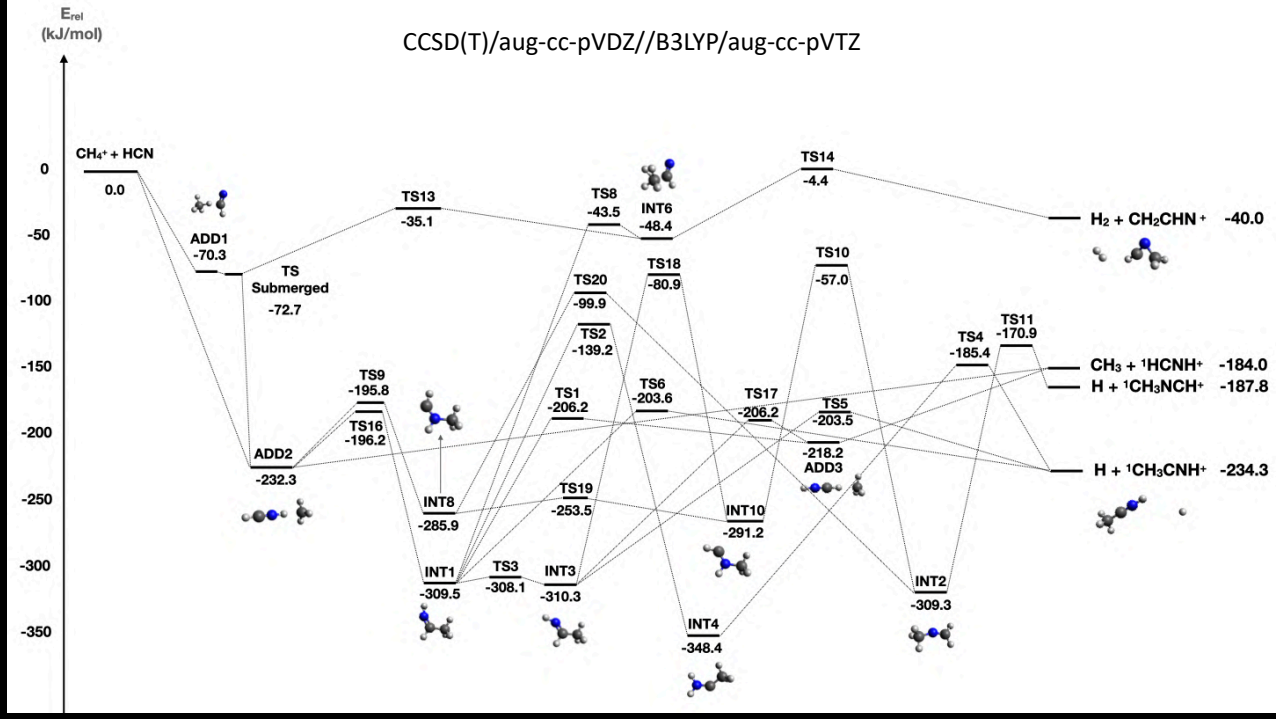
		Revised network						KIDA			UDfA		
		Reaction			α	β	γ	T [K]	α	β	γ	α	β	γ
(i) Routes to CH_3CN^+														
1	+	$C_2H_2^+ + NH_2$	→	$CH_3CN^+ + H$	0.5	9.9×10^{-10}	4.6	10-300	0.5	9.9×10^{-10}	4.6	-	-	-
	+			$CCH + NH_3^+$	0.5	9.9×10^{-10}	4.6	10-300	0.5	9.9×10^{-10}	4.6	-	-	-
2	*	$C_2H_4^+ + N$	→	$CH_3CN^+ + H$	-	-	-	-	3.0×10^{-10}	0.0	0.0	-	-	-
4	+	$H_2CCN + H_3^+$	→	$CH_3CN^+ + H_2$	1.0	2.9×10^{-9}	5.8	10-300	1.0	2.9×10^{-9}	5.8	-	-	-
(ii) Routes to CH_3CNH^+														
5a		$CH_3CN^+ + H_2$	→	$CH_3CNH^+ + H$	5.7×10^{-10}	0.0	0.0	10-300	-	-	-	5.7×10^{-10}	0.0	0.0
5b		$CH_3CN^+ + CH_4$	→	$CH_3CNH^+ + CH_3$	1.7×10^{-9}	0.0	0.0	10-300	-	-	-	1.7×10^{-9}	0.0	0.0
6		$C_2H_7^+ + HCN$	→	$CH_3CNH^+ + CH_4$	2.2×10^{-10}	-0.5	0.0	10-300	-	-	-	2.2×10^{-10}	-0.5	0.0
				$HCNH^+ + CH_3CH_3$	2.0×10^{-9}	-0.5	0.0	10-300	-	-	-	2.0×10^{-9}	-0.5	0.0
7a	+	$CH_3^+ + HCN$	→	$CH_3CNH^+ + h\nu$	9.0×10^{-9}	-0.5	0.0	10-300	9.0×10^{-9}	-0.5	0.0	9.0×10^{-9}	-0.5	0.0
7b	+	$CH_3^+ + HNC$	→	$CH_3CNH^+ + h\nu$	9.0×10^{-9}	-0.5	0.0	10-300	9.0×10^{-9}	-0.5	0.0	-	-	-
8	*	$CH_4^+ + HCN$	→	$CH_3 + HCNH^+$	3.9×10^{-9}	0.0	0.0	10-300	-	-	-	-	-	-
	*			$CH_3CNH^+ + H$	3.2×10^{-11}	0.0	0.0	10-300	3.3×10^{-9}	0.0	0.0	-	-	-
9b	*	$CH_3OH_2^+ + HNC$	→	$CH_3CNH^+ + H_2O$	3.0×10^{-11}	0.0	0.0	10-300	-	-	-	-	-	-
	*		→	$CH_3OH + HCNH^+$	1.0×10^{-9}	0.0	0.0	10-300	-	-	-	-	-	-
(iii) Routes to CH_3CN														
10a	*	$CH_3CNH^+ + NH_3$	→	$CH_3CN + NH_4^+$	8.7×10^{-10}	0.0	0.0	10-300	-	-	-	-	-	-
10b	*	$CH_3CNH^+ + e^-$	→	$CH_3CN + H$	-	-	-	-	1.3×10^{-7}	-0.5	0.0	5.3×10^{-7}	-0.7	0.0
	*		→	$H_2CCN + H + H$	-	-	-	-	8.8×10^{-8}	-0.5	0.0	-	-	-
	*		→	$CH_3 + HCN$	-	-	-	-	6.0×10^{-8}	-0.5	0.0	2.8×10^{-7}	-0.7	0.0
	*		→	$CH_3 + HNC$	-	-	-	-	6.0×10^{-8}	-0.5	0.0	-	-	-
11a	+	$CH_3 + CN$	→	$CH_3CN + h\nu$	-	-	-	-	1.0×10^{-16}	0.0	0.0	1×10^{-16}	0.0	0.0
11b	+	$CH_3 + CN^-$	→	$CH_3CN + e^-$	1.0×10^{-9}	0.0	0.0	10-300	1.0×10^{-9}	0.0	0.0	1×10^{-9}	0.0	0.0

CH_4^+ + HCN reaction

Three exothermic channels:

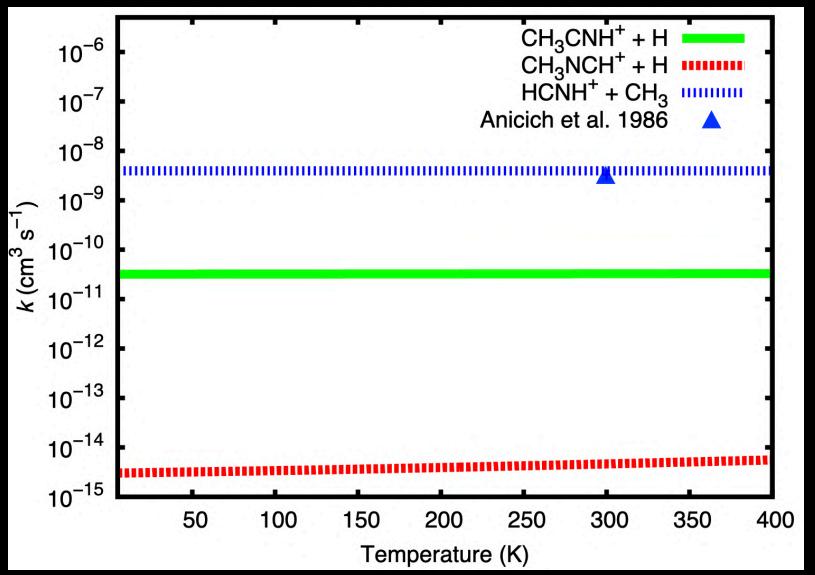
- Proton transfer to form CH_3 + $HCNH^+$
- Reaction to form CH_3CNH^+
- Reaction to form CH_3NCH^+

Products	Rate constant ($cm^3\ s^{-1}$)
$HCNH + CH_3$	3.9×10^{-9}
$CH_3CNH^+ + H$	3.2×10^{-11}
$CH_3NCH^+ + H$	3.0×10^{-15}



Experimentally studied by Anicich et al. (1986) at 298 K :

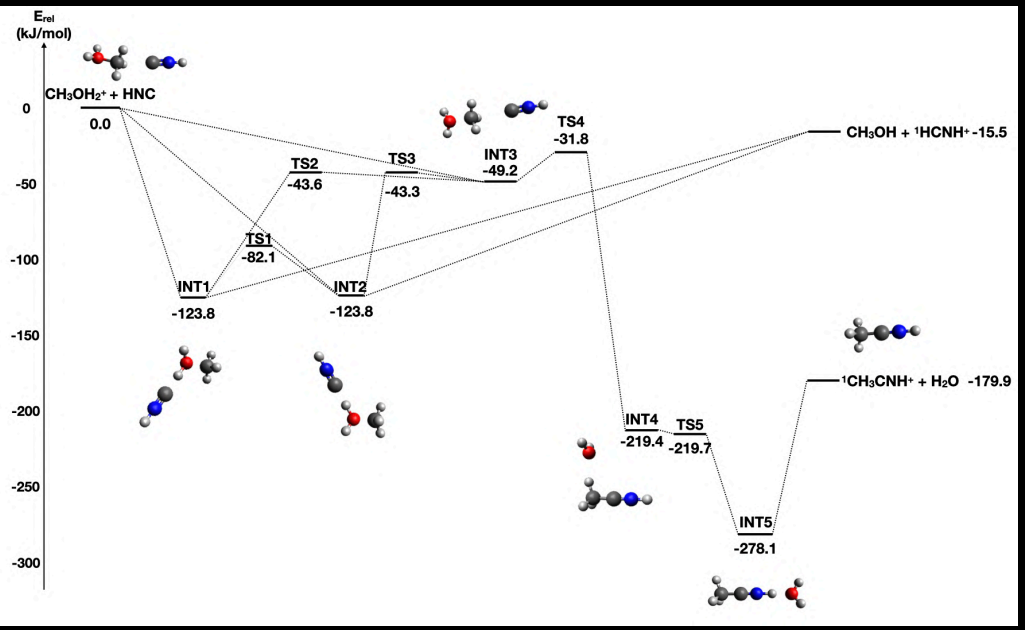
- Rate constant for the proton transfer of 3.3×10^{-9} $cm^3\ s^{-1}$, and a BR of 98%.
- KIDA reports the same rate constant for the formation of CH_3CNH^+, even if it represents the 2% of the products

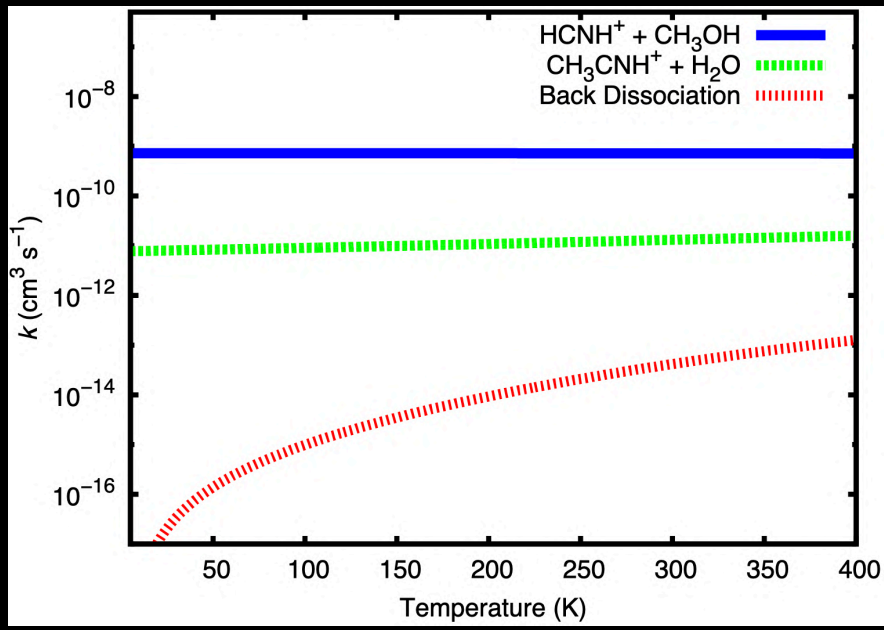


$CH_3OH_2^+$ + HNC reaction

We replied the procedure for this system:

- The proton transfer channel is exothermic by 15 kJ mol^{-1}, therefore methanol is the major product (k ~ 10^{-9} cm^3 s^{-1})
- CH_3CNH^+ is a secondary product (k ~ 10^{-11} cm^3 s^{-1})
- Back dissociation is negligible



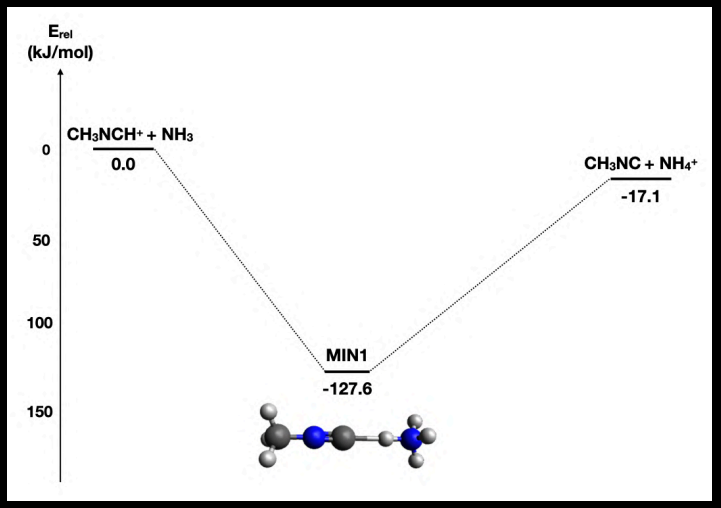


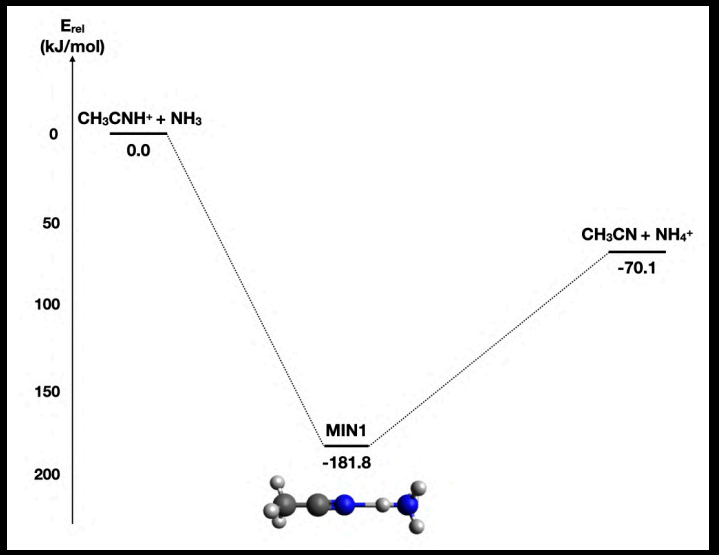
CH_3CNH^+ and CH_3NCH^+ + NH_3 reactions

The CH_3CNH^+ and CH_3NCH^+ ions have to be converted into the neutral counterparts:

- Electron recombination: Geppert et al. 2007 showed that only a fraction in the DR of CH_3CNH^+ preserves the carbon chain, but probably the product is not CH_3CN.

- Proton transfer (PT) to ammonia: usually the value of 2×10^{-9} is assumed for all the PT reactions, based on the work of Hemsworth et al 1974.





We calculated the PES and the capture rate constants:

$$K\ (CH_3CNH^+ + NH_3) = 8.7 \times 10^{-10}\ \ cm^3\ s^{-1}$$

$$K\ (CH_3NCH^+ + NH_3) = 9.9 \times 10^{-10}\ \ cm^3\ s^{-1}$$

CH_3CN: CHEMISTRY

GAS-PHASE synthesis

Two step process: radiative association of CH_3^+ and HCN, and dissociative recombination of protonated acetonitrile CH_3CNH^+ with an electron

1) $CH_3^+ + HCN \rightarrow CH_3CNH^+/CH_3NCH^+ + photon$ **Radiative association (RA)**

- Rate constant parameters α=9 × 10^9 and β=-0.5 derived using a statistical method (Herbst 1985)
- CH_3NCH^+ / CH_3CNH^+ ratio between 0.1 and 0.4 (DeFrees et al. 1985)

2) $CH_3CNH^+/CH_3NCH^+ + e^- \rightarrow CH_3CN/CH_3NC + H$ **Electron recombination (ER)**

- 65% of retention of carbon chain and 35% of fissure of one C-C or C-N bond (Geppert et al. 2007)

Products	BR
$H + H + H_2CCN$	24 %
$CH_3CN + H$	39 %
$HCN + CH_3$	18 %
$HNC + CH_3$	18 %

Loison et al. 2014

GRAIN SURFACE synthesis

CH_3CN might be directly produced within the ice mantles by the reaction of CH_3 with CN or the stepwise hydrogenation of C_2N