Experimental and Theoretical Study between CN radical and Acetonitrile CH_3CN Relevant to Astrochemical Environments

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Outline

- Astrophysical and Astrobiological interests

- Experimental Techniques

- Results and Discussions

Astrophysical and Prebiotic interests: Nitrogen species in interstellar medium (ISM)

- Nitrogen: 5th element in interstellar medium

≈ 50 detected species($T = 7 – 20$ K ; $N = 10^4 – 10^6$ cm^{-3})

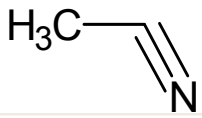
NH	CN	N_2	NH_2	HCN	HNC	N_2H^+
NH_3	HCNH+	NO	H_2CN	HCCN	C_3N	CH_2CN
CH_2NH	HC_3N	N_2O	HC_2NC	NH_2CN	C_3NH	CH_3CN
CH_3NC	HC_3NH^+	CH_2CNH	C_5N	CH_3NH_2	C_3H_7CN	HC_5N
CH_3C_3N	C_2H_5CN	CH_3CONH_2	HC_7N	CH_3C_5N	HC_9N	$HC_{11}N$
HC_2N	HC_3N	HC_4N	H_2CN	C_2H_7CN	CH_3CHNH	HCCNC
HCNO	CNCHO	NH_2CHO	CN^-	CH_3CONH_2	NH_2CH_2CN	HOCN

CN: Reactive radical, 2nd molecule detected in ISM after CH
Typical Abundance with respect to $H_2 = 5\times10^{-9}$

Detected in comets (1940), ISM(1941), Solar system (1982)

Nitrogen species: Amino acids (DNA, RNA) → Prebiotic chemistry→ Precursor

Astrophysical and Prebiotic interests: Studied reaction in this work

Acetonitrile  **+ CN → Products**

Acetonitrile:
one study at T > 300K
(Zabarnick et al. 1989)

Temperature
23 K – 354 K

Only two studies of CN with nitrogen species at low temperatures

Motivation of this work:

- *Limited **available** data*
- *Interstellar **chemistry** of these species*
- ***Prebiotic** role*
- *Effect of **temperature** on the **reactivity***

Astrophysical and Prebiotic interests: Acetonitrile CH_3CN

CH_3CN Detected in gas phase in ISM (Solomon et al. 1971)

Formation in ISM:

$$CH_3^+ + HCN \rightarrow CH_3HCN^+ + e \rightarrow CH_3CN$$ Willacy et al. 1993

$$CH_3CONH_2 + h\nu \rightarrow CH_3CN + H_2O$$ Duvernay et al. 2007

A T=20K $$CH_3CH_2NH_2 + h\nu \xrightarrow{-H_2} CH_3CH = NH + h\nu \xrightarrow{-H_2} CH_3CN$$ Danger et al. 2011

Potential precursor of amino acids (DNA, RNA)

$$CH_3CN + NH_3 + h\nu \rightarrow NH_2CH_2CN + H_2$$

Danger et al. 2011
Motoki et al. 2013

↓

Amino acetonitrile

↑

$NH_2CH_2CN + 2H_2O \rightarrow$ Glycine

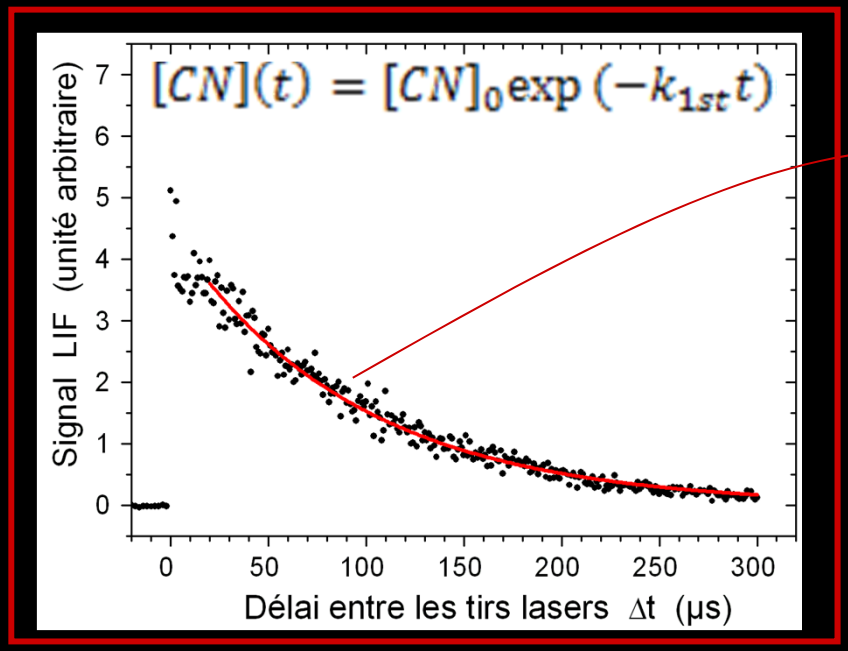
Amino acids ⇨ **Origin of life**

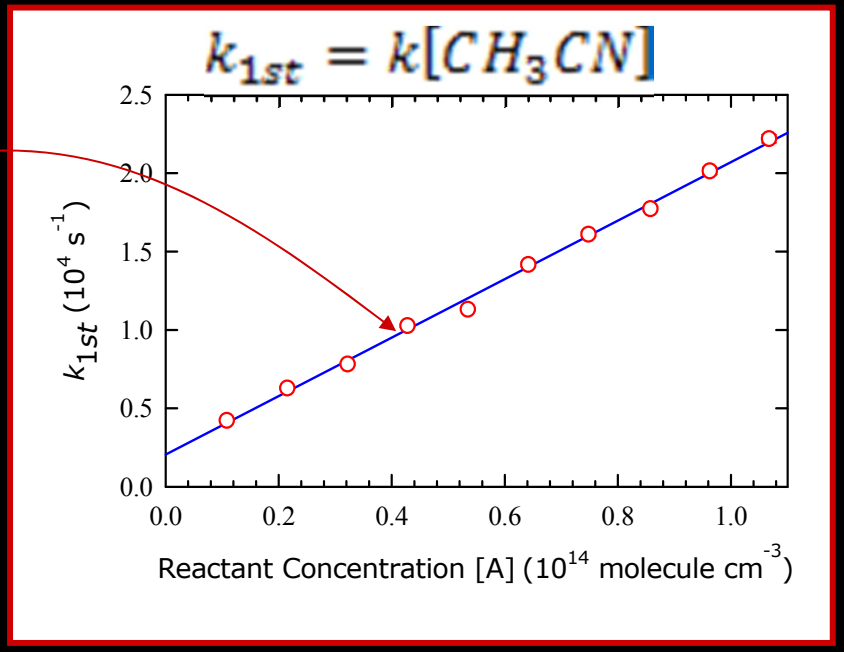
Measuring Rate constants of the studied reaction

CN + CH_3CN → Products

$$\frac{d[CN]}{dt} = -k[CH_3CN][CN]$$

$[CH_3CN]>>>[CN]$ $[CH_3CN]=cte$

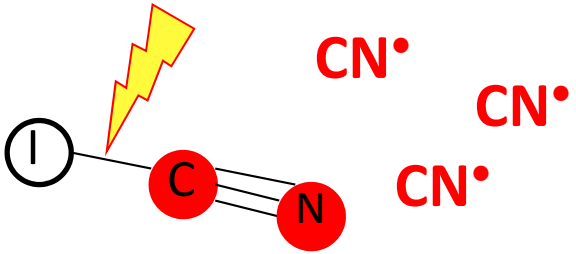




Experimental Techniques: PLP-LIF

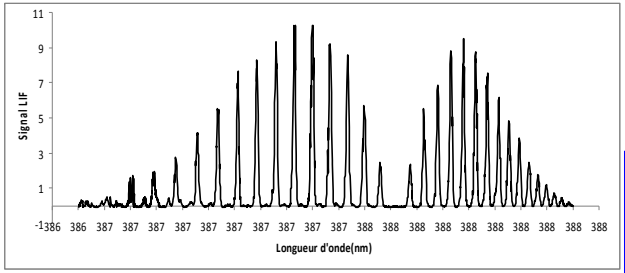
PLP (Pulsed Laser Photolysis)

Generation of CN ($X^2\Sigma^+$) at 266 nm from ICN

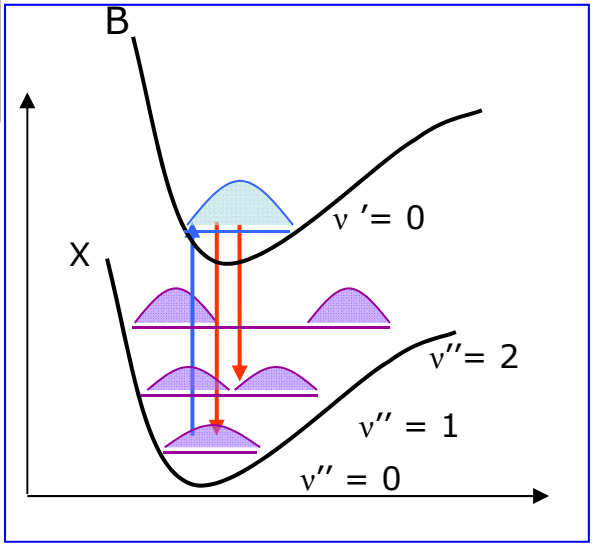


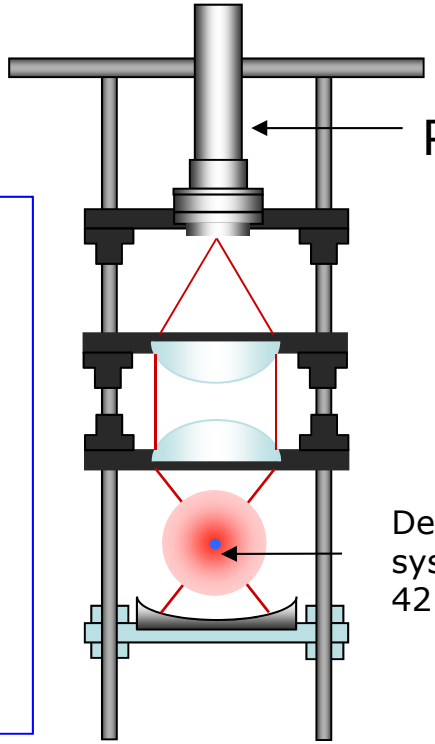
LIF (Laser Induced Fluorescence)

Dye laser (Exalite in dioxane) pumped by a YAG laser at 355 nm– Excitation of CN around 387 nm and fluorescence detection at 421.6 nm

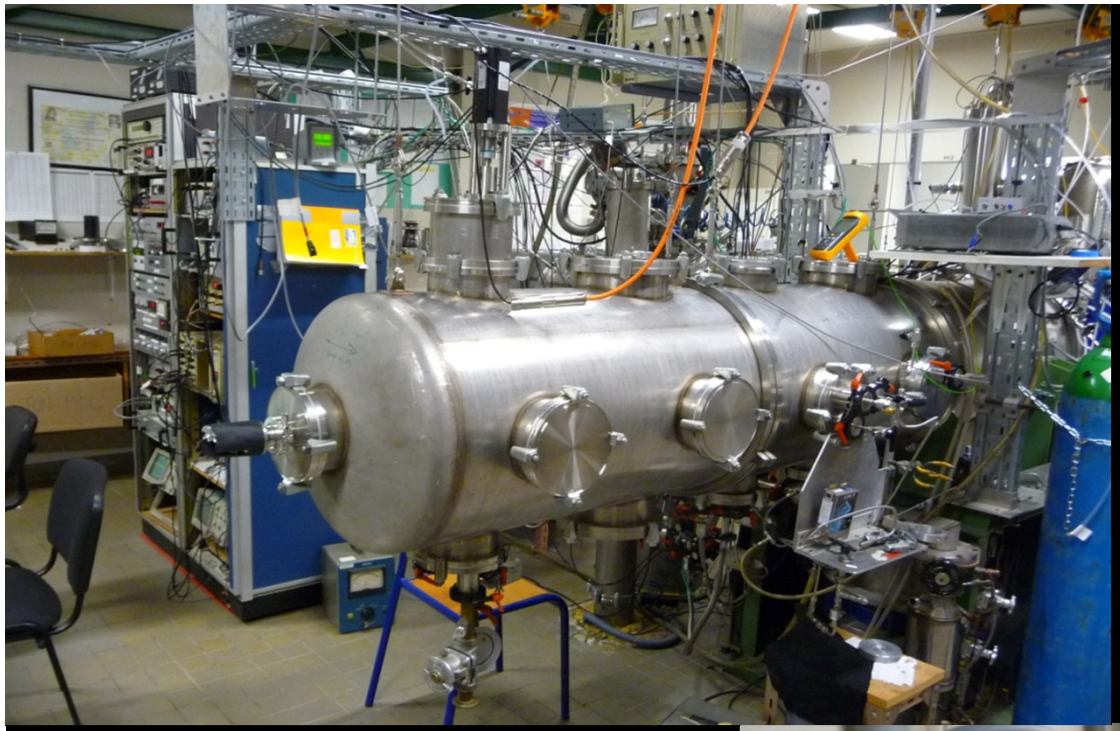


Spectre de CN à 123 K





Detection system at 421.6 nm



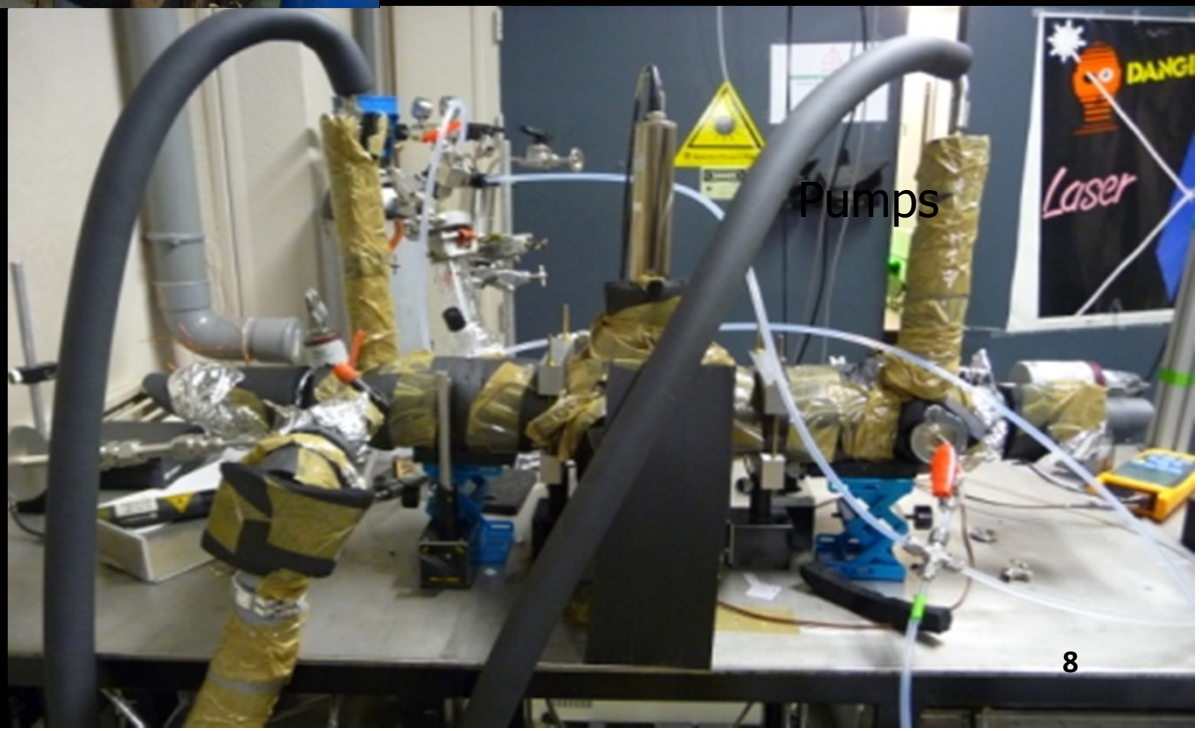
CRESU

T= 23 K – 168 K

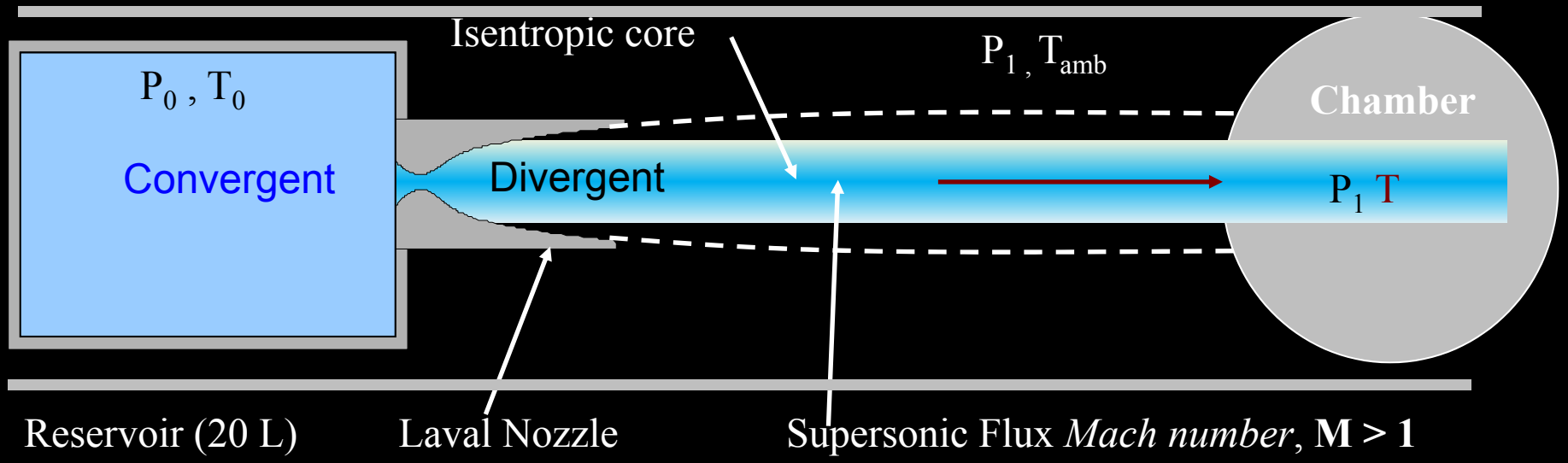
and 297 K subsonic configuration

Cryogenic cell

T= 258 K – 354 K



CRESU: Cinétique de Réaction en Ecoulement Supersonique Uniforme



P_0, pressure inside reservoir
T_0, temperature inside reservoir

P_1, pressure inside flow, (i.e. inside chamber)
T_1, temperature inside flow

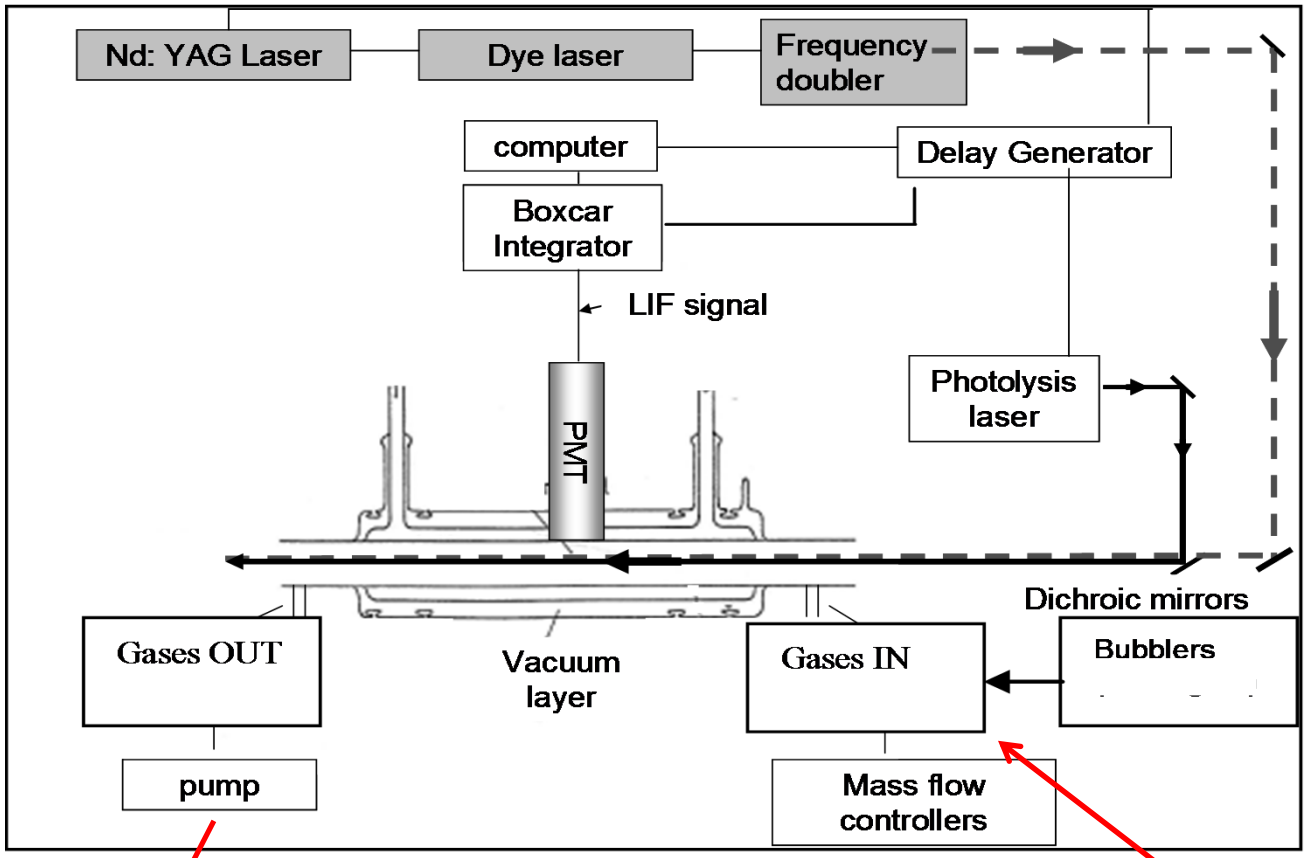
$$\frac{T}{T_0} = 1 + \frac{\gamma + 1}{2} M^2$$

- Due to the supersonic speed, the flow is decoupled from the walls of the chamber. Diffusion is completely negligible $\Rightarrow$ *No Condensation*

Ideal Chemical Reactor for Low Temperature Studies

Limitations:
$K > 2\times10^{-13}$ $cm^3 molécule^{-1}$ s^{-1}

Experimental Techniques: Cryogenic Cell



Room Temperature or ≠ T

Using a cryogenic liquid

258 K <T< 354 K regulated by using a Cryostat

Gas exit

↓

Vacuum

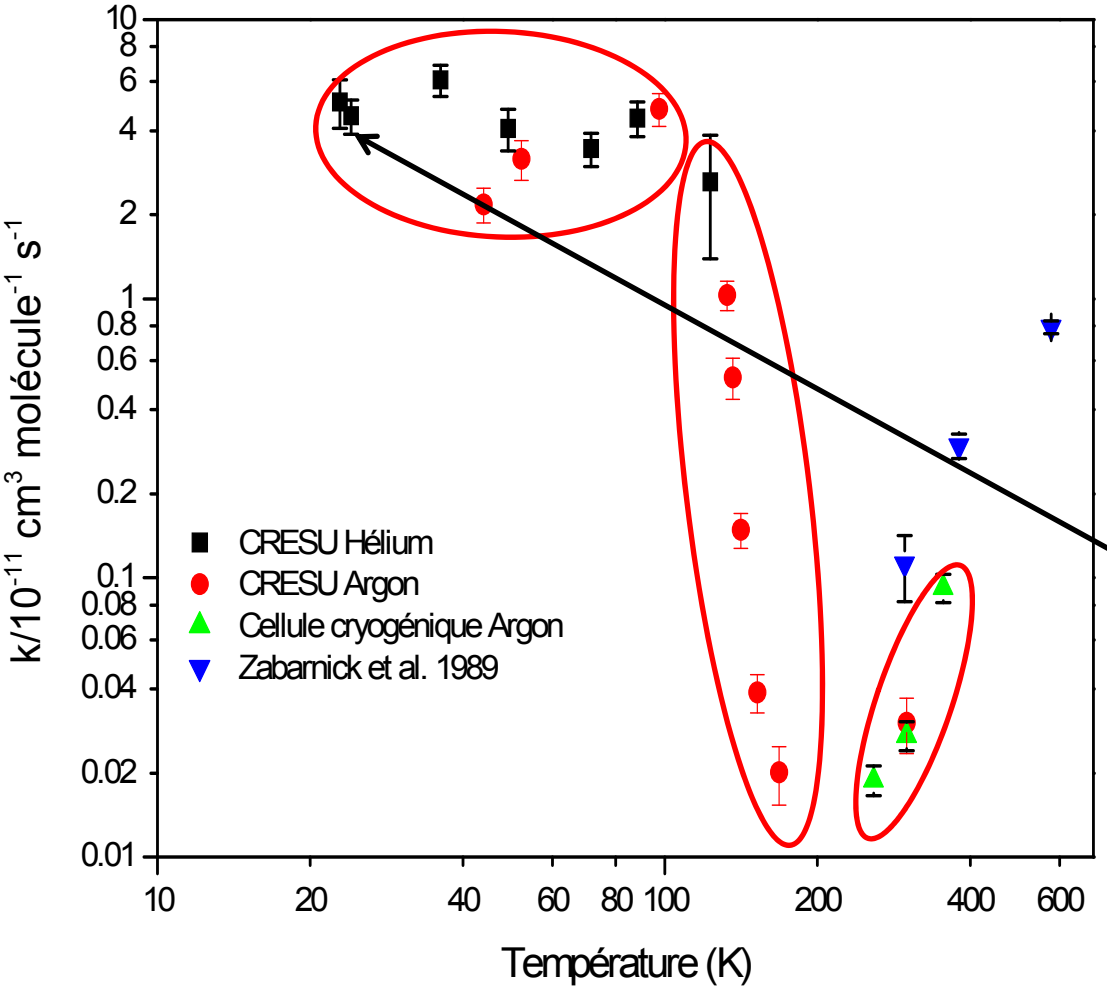
Slow Flow

Pressure: 10 – 760 Torr

Gas Entrance:
buffer gas(He, Ar), reactant and ICN

Results: CN+ Acetonitrile

Sleiman C., El Dib G., Gonzalez Rubio S. & Canosa A. (2014, in prep)



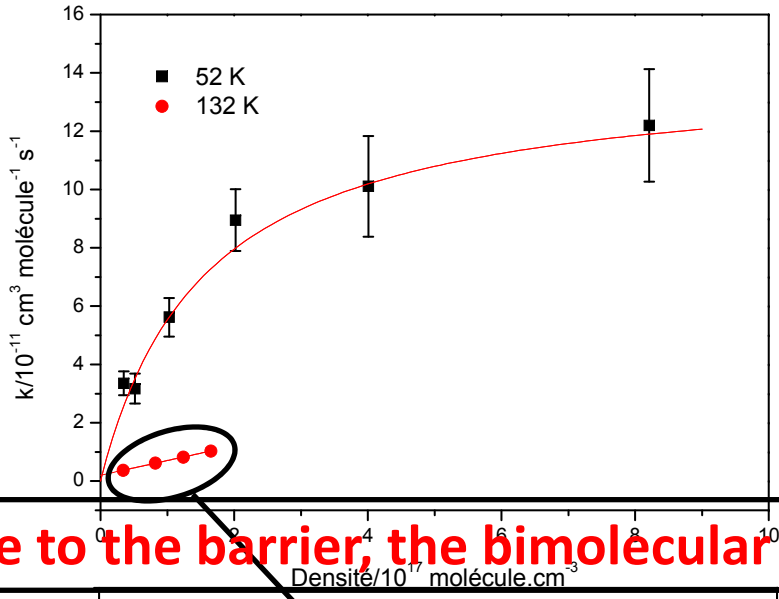
- T> 200 K, usual Arrhenius behavior
- Presence of an activation barrier

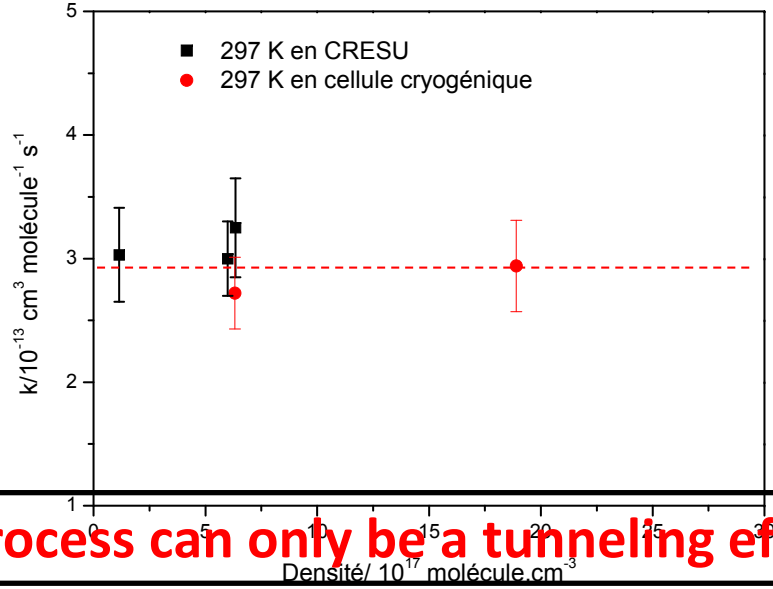
- 123 <T< 170 K, Dramatic increase by *two orders of magnitude*

- T < 123 K, rate coefficient still increases but at a lower level, reaching a value of $(5.08\pm0.86)\times10^{-11}$ cm^{3}molec.$^{-1}$s^{-1} at 23 K

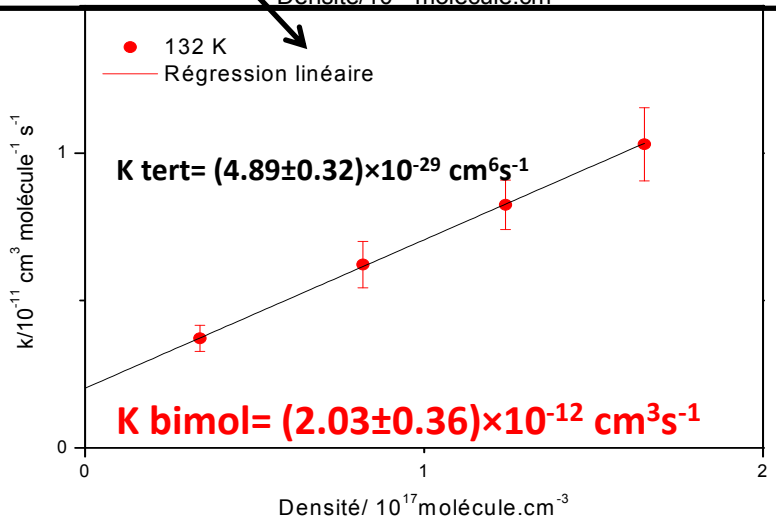
- Change in the mechanism at low temperature

Results: CN + Acetonitrile, Pressure dependence





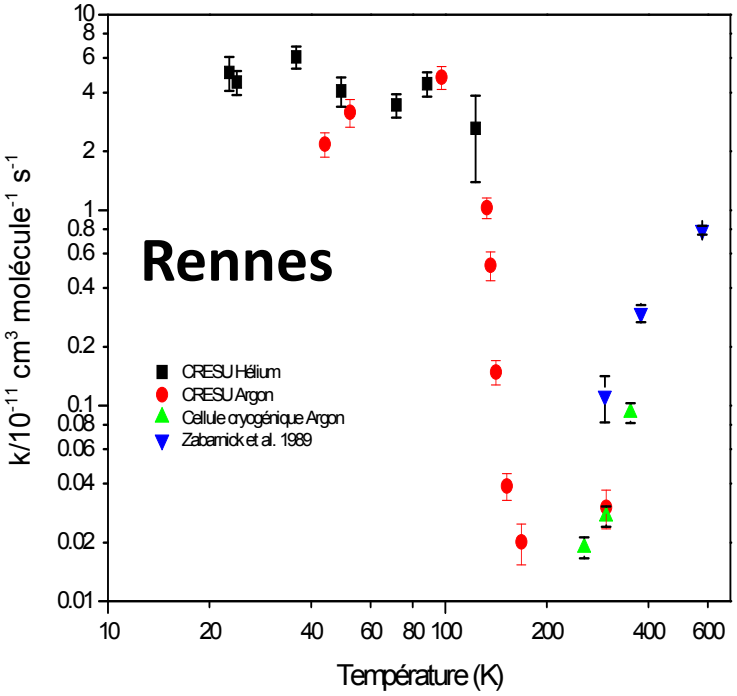
Due to the barrier, the bimolecular process can only be a tunneling effect

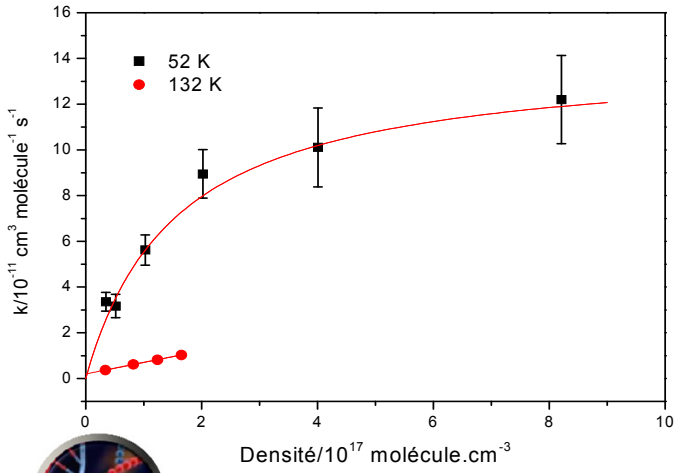


- **T= 297 K, no pressure dependence**
- **At 52 K and 132 K: pressure dependence**
- **Pressure dependence →Termolecular process**

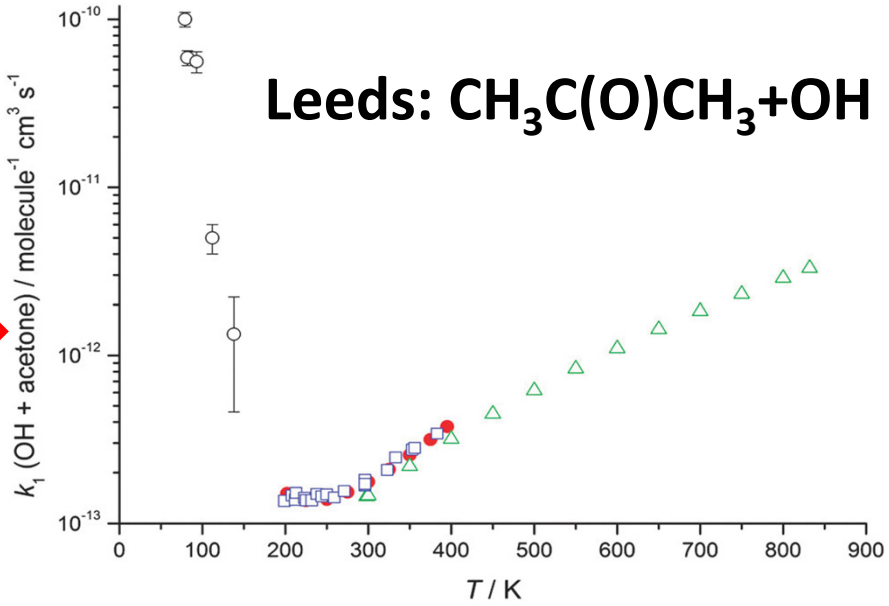
- **Extrapolating at P=0, shows competition between a bimolecular and a termolecular process**

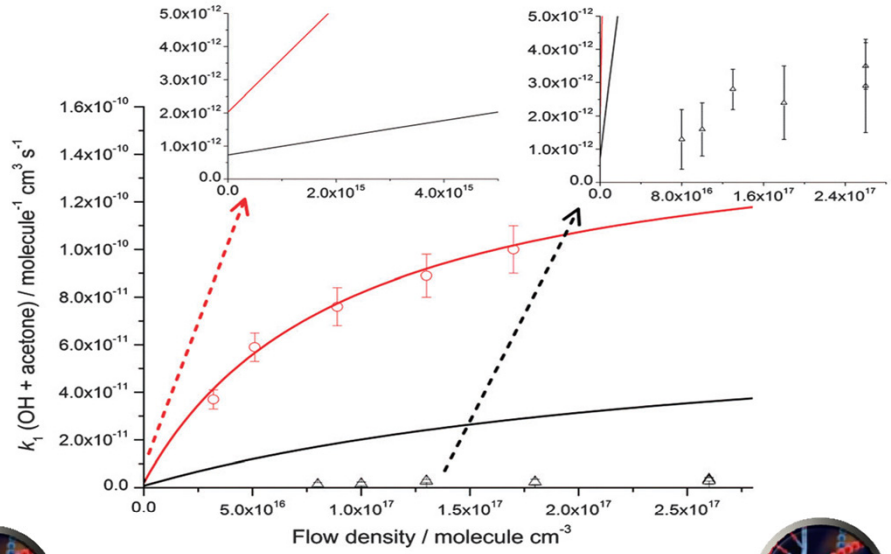
Results: Similar behavior

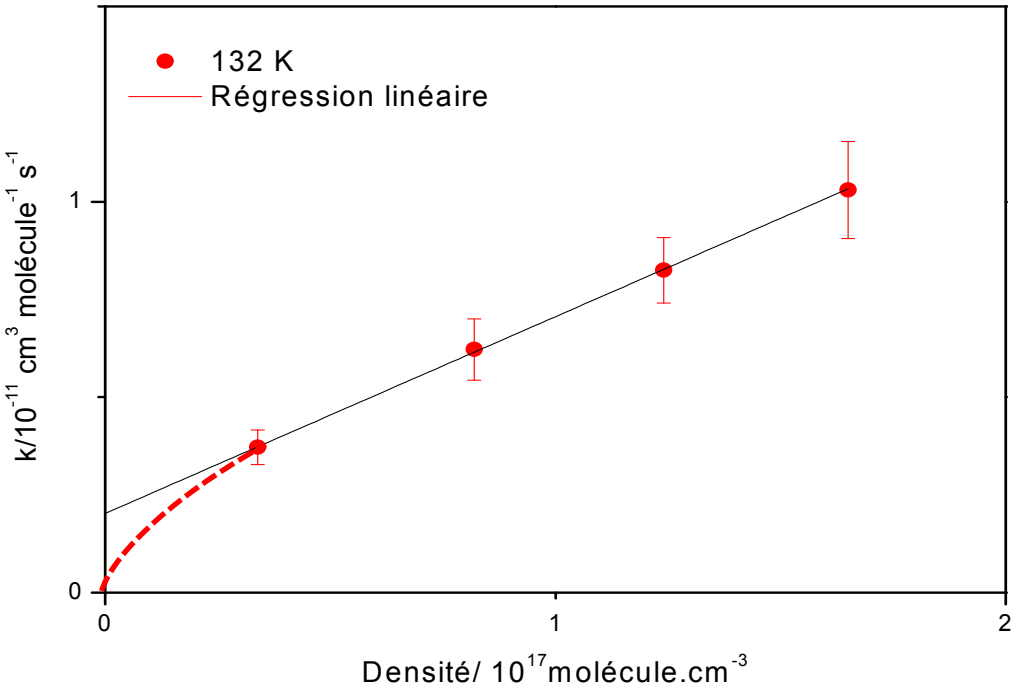




Leeds: $CH_3C(O)CH_3$+OH





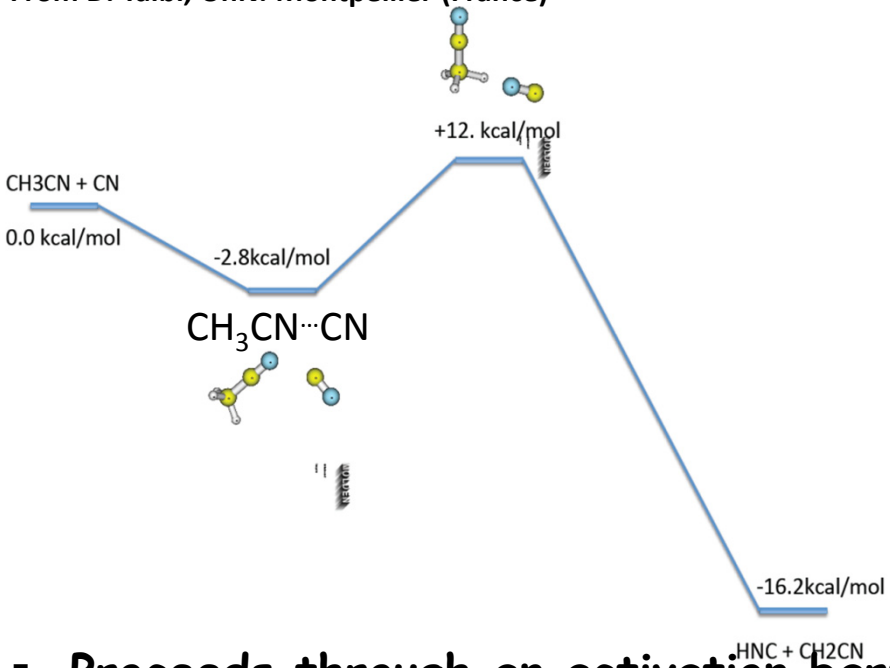


However, fall-off curves may become very broad in the low limit pressure (J. Troe and G. Ushakov)!!!

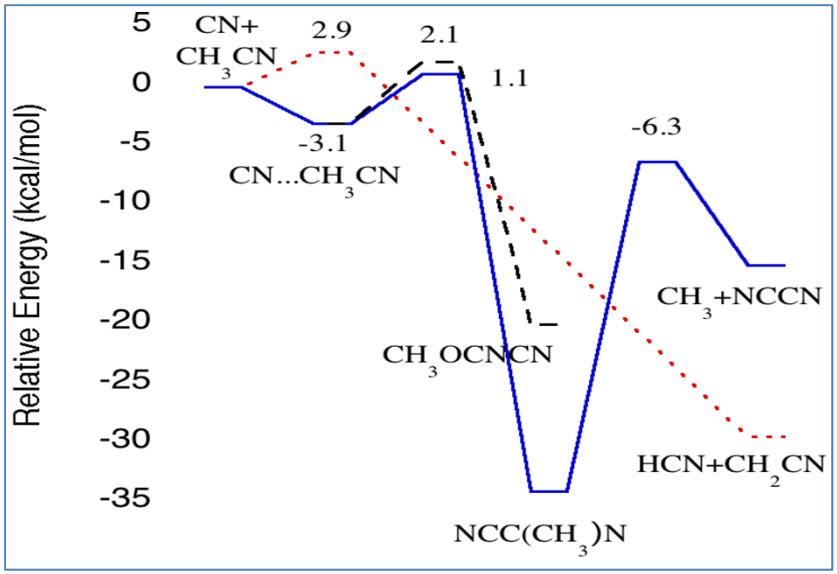
Need to perform more experiments at very low pressures

Results: CN + Acetonitrile, Possible mechanism

From D. Talbi, Univ. Montpellier (France)



From S. Klippenstein, Argonne University (USA)



- Proceeds through an activation barrier via weekly bonded complex ($CH_3CN\cdots CN$ or $CN\cdots CH_3CN$)

- At T > 200 K, the complex is short-lived. Dissociation to the reactants
- A large energy barrier is observed and is compatible with the Arrhenius behaviour for 250 < T < 350 K

- At T < 200 K, complex stabilized by the buffer gas : $k_{diss} << k_{formation}$

- Competition between a bimolecular and a termolecular process.

Conclusions and Perspectives

- At T>200 K, Arrhenius behavior
- At T< 200 K, dramatic increase of rate constants → Change of the reaction mechanism

- Termolecular process competing with bimolecular process by tunn

- N
con

This study show that reactions which are slow at room temperature can occur a change in their mechanism and can present some interstellar implications!!!!!!

- Interesting to perform more experiments as a function of pressure at different temperatures in order to determine the contribution of tunneling effect as a function of temperature

Thank you
for your
Attention !!!