Gas-Phase Chemistry in the Interstellar Medium: There is Still Much to Learn

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My first contact with Xander's work was in 1994 during my postdoc at UC Berkeley

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INTERSTELLAR POLYCYCLIC AROMATIC HYDROCARBONS: THE INFRARED EMISSION BANDS, THE EXCITATION/EMISSION MECHANISM, AND THE ASTROPHYSICAL IMPLICATIONS

L. J. ALLAMANDOLA,[1] A. G. G. M. TIELENS,[1,2] AND J. R. BARKER[3]

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L. J. ALLAMANDOLA,[1] A. G. G. M. TIELENS,[1,2] AND J. R. BARKER[3]

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... not very successful, indeed

LETTERS TO NATURE

Infrared emission spectra of candidate interstellar aromatic molecules

D. J. Cook, S. Schlemmer, N. Balucani, D. R. Wagner, B. Steiner & R. J. Saykally*

Department of Chemistry, University of California, Berkeley, California 94720-1460, USA
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Bah to PAHs!

INTERSTELLAR dust is responsible, through surface reactions, for the creation of molecular hydrogen, the main component of the interstellar clouds in which new stars form. Intermediate between small, gas-phase molecules and dust are the polycyclic aromatic hydrocarbons (PAHs). Such molecules could account for 2–30% of the carbon in the Galaxy[1], and may provide nucleation sites for the formation of carbonaceous dust[2,3]. Although PAHs have been proposed[4,5] as the sources of the unidentified infrared emission

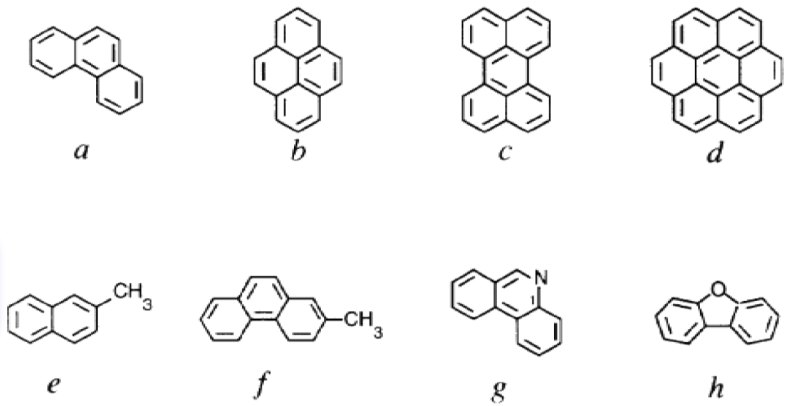


FIG. 1 Chemical structures representing the PAH molecules studied by SPIRES in this work. These include: four unsubstituted PAHs, phenanthrene (*a*, $C_{14}H_{10}$), pyrene (*b*, $C_{16}H_{10}$), perylene (*c*, $C_{20}H_{12}$) and coronene (*d*, $C_{24}H_{12}$); two methyl substituted PAHs, 2-methylnaphthalene (*e*, $C_{11}H_{10}$), and 2-methylphenanthrene (*f*, $C_{15}H_{12}$); and two hetero-substituted PAHs, phenanthridine, (*g*, $C_{13}N_9N$) and dibenzofuran (*h*, $C_{12}H_8O$). Molecules the size of coronene have recently been postulated to account for the 3.3-μm UIR band[20].

The molecular universe: an interdisciplinary programme on the physics and chemistry of molecules in space

Objective

Molecules are an important component of the universe which dominate the cooling and degree of ionization of interstellar gas clouds and, hence, regulate star and planet formation. The exploration of paths towards chemical complexity in space has direct bea ring on the origin and evolution of life. Moreover, molecular transitions provide a sensitive probe of the dynamics and the physical and chemical conditions in a wide range of objects at scales ranging from newly formed planetary systems to galactic and ex tragalactic sizes. Near-future large scale observatories by the European Space Agency and the European Southern Observatory - in partnership with American and Far-East organizations - will open up the universe to high spatial and spectral resolution studie s of molecules and, hence, the study of the key astrophysical and astrochemical processes involved in the formation and evolution of planets, stars, and galaxies. These new missions will lead to a multitude of molecular line data in a variety of astrophysi cal environments. Identification, analysis, and interpretation of this data in terms of the physical and chemical characteristics of the astronomical sources and the origin and evolution of the molecular universe will require a concerted effort by physicis ts, chemists, and astronomers in the areas of molecular spectroscopy, collisional excitation processes, chemical reactions, and astronomical modelling on species of astrophysical relevance. The results of this expert effort need to be made easly accessible to the scientific community through web-based data archives. The Research and Training Network on the Molecular Universe provides a cohesive framework for the training and development of researchers in the early stages of their career, combining European researchers in the areas of laboratory spectroscopy, laboratory astrochemistry, molecular quantum mechanical studies, astronomical modellers, and experts on data bases and web interfaces.

Project information

MOLECULAR UNIVERSE

Grant agreement ID: 512302

Start date	End date
1 October 2004	30 September 2008

Funded under:
FP6-MOBILITY

Coordinated by:
RIJKSUNIVERSITEIT GRONINGEN
Netherlands

FP6-2002-MOBILITY-1

See other projects for this call

Funding Scheme

RTN - Marie Curie actions-Research Training Networks

Coordinator

RIJKSUNIVERSITEIT GRONINGEN

Address

Broerstraat 5
Groningen

Netherlands

Website

Administrative Contact

Alexander TIELENS (Prof.)

20 nodes among which 8 research groups in physical chemistry

My task today:
to review interstellar gas-phase chemistry

an old-fashioned topic?

an ever-green topic!

Identified interstellar and circumstellar species

2 atoms

AlF AlCl C_2 CH CH^+ CN CO CO^+ CP CS CSi HCl H_2 KCl NH NO NS NaCl OH PN SO SO^+ SiN SiO SiS HF SH FeO S_2 CF^+ O_2 PO SH^+ AlO ArH^+ NO^+ TiO HCl^+ NS^+ CrO

3 atoms

C_3 C_2H C_2O C_2S CH_2 HCN HCO HCO^+ HCS^+ HOC^+ H_2O H_2S HNC HNO MgCN MgNC N_2H^+ N_2O NaCN OCS SO_2 c-SiC_2 CO_2 NH_2 H_3^+ AlNC FeCN KCN SiNC HCP CCP SiCSi CCN TiO_2 HO_2 HCS S_2H

4 atoms

c-C_3H l-C_3H C_3N C_3O C_3S C_2H_2 CH_2D^+ HCCN $HCNH^+$ HNCO HNCS $HOCO^+$ H_2CO H_2CN H_2CS H_3O^+ NH_3 SiC

5 atoms

C_5 C_4H C … H_4

H_2COH^+

6 atoms

C_5H C_5C … H_2C_3O

CH_2CNH

7 atoms

C_6H CH_2

8 atoms

CH_3C_3N $HCOOCH_3$ CH_3COOH C_7H H_2C_6 CH_2OHCHO CH_2CHCHO C_2H_6 CH_2CCHCN NH_2CH_2CN

$(NH_2)_2C$O

9 atoms

CH_3C_4H CH_3CH_2CN $(CH_3)_2O$ CH_3CH_2OH HC_7N C_8H CH_3CONH_2 C_8H^- CH_2CHCH_3 CH_3CH_2SH

CH_3NHCHO HC_7O

10 atoms

CH_3C_5N $(CH_3)_2CO$ NH_2CH_2COOH CH_3CH_2CHO CH_2OHCH_2OH CH_3OCH_2OH

≥ 11 atoms

HC_9N CH_3C_6H C_6H_6 $HC_{11}N$ $CO(CH_2OH)_2$ $HCOOC_2H_5$ CH_3COOCH_3 $CH_3CH(O)CH_2$ C_3H_7CN $C_{14}H_{10}^+$ C_{60} C_{60}^+

More than 200 molecules identified in the interstellar/circumstellar medium (only *ca*. 10-20 on ice)

➲ Occam's razor:
gas-phase reactions must be important

destruction routes are in the gas-phase

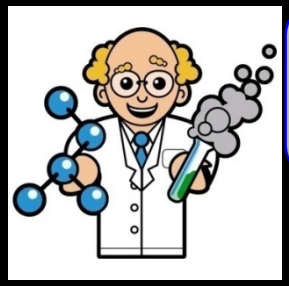
+ PAHs family

1) What is the status of our knowledge of gas-phase reactions in the interstellar medium?

2) Can we expect new significant contributions to the understanding of the chemistry of interstellar objects from gas-phase chemistry?

1) What is the status of our knowledge of gas-phase reactions in the interstellar medium?

The chemical evolution of the interstellar medium: how do we study it?



Laboratory experiments

modelling

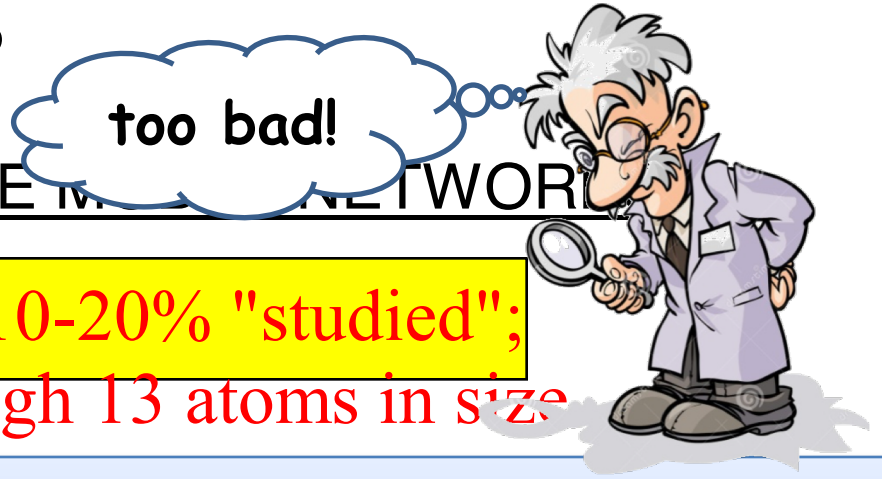
observations

Several thousands elementary reactions including:

- dissociation, excitation & ionization processes
- neutral-neutral reactions
- ion-molecule reactions
- heterogeneous processes

a large fraction of these processes still need to be characterized in lab experiments

taken from Eric Herbst 2006



GAS-PHASE M… NETWORK

4,400 reactions; 10-20% "studied";
450 species through 13 atoms in size

in 13 years this percentage has not

And those which have not been studied??
… analogy with similar reactions or chemical intuition (and some imagination)…

Successes for quiescent cores:

Those which have been studied ➲
… rarely have been studied under the appropriate conditions (low T, low P) …

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

interstellar clouds: 1) low T (as low as 10 K)
2) low number density (as low as 10^4 cm^{-3})

these are not favorable conditions for chemical transformations

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions...

interstellar clouds: 1) low T (as low as 10 K) 2) low number density (as low as 10^4 cm^{-3})

these <u>are not</u> favorable conditions for chemical transformations

these conditions <u>are an absolute nightmare for lab experiments</u>

low density ⊂ few molecular encounters, little probability for chemical reactions to take place; absence of termolecular collisions (1 every 10^9 years)

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

in addition to that, most of the 8000 elementary reactions included in the astrochemical models involve either one or two transient species that must be produced in situ in lab experiments in a controlled manner

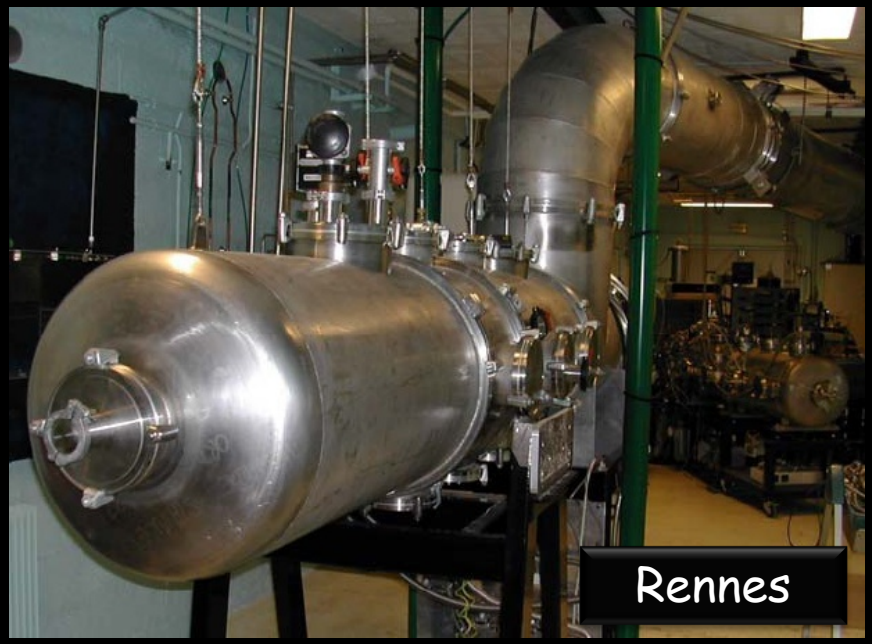
e.g. $O + C_3O \rightarrow C_2O + CO$

$C_2H^+ + HCO \rightarrow CO + C_2H_2^+$

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

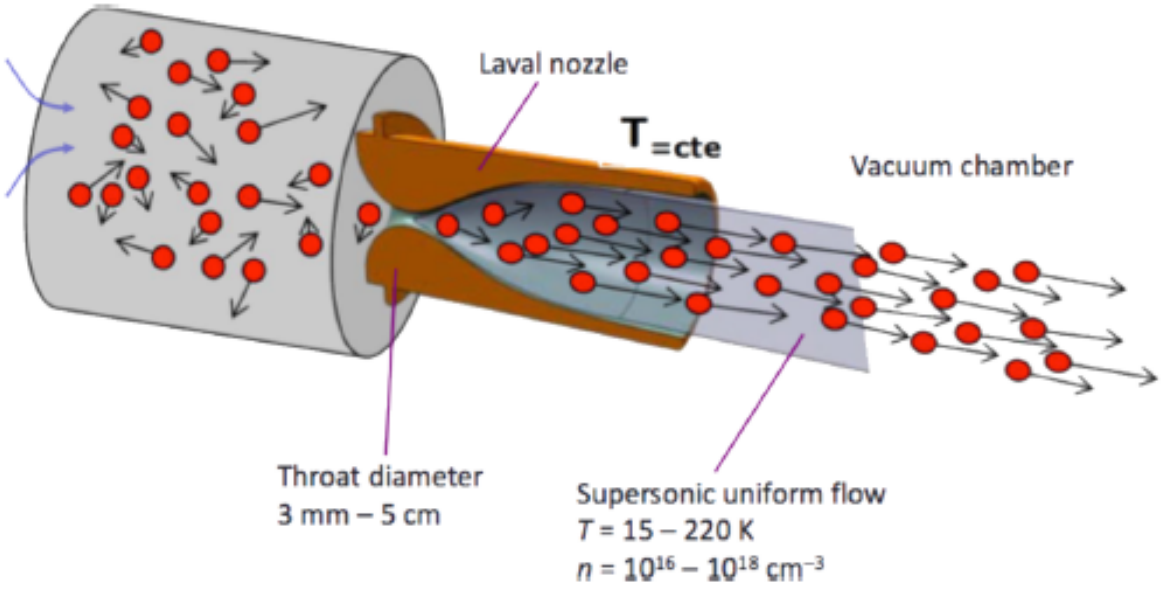
we have three pillars

❶ CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique



credit: S. Le Picard

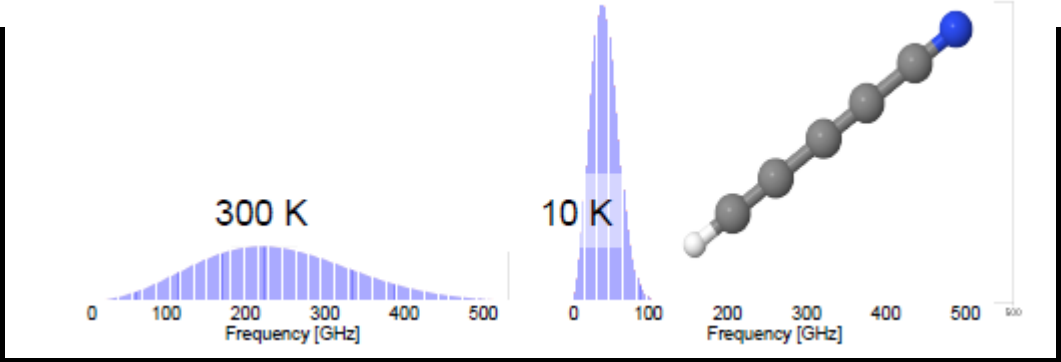
low T, as low as those of interest in the ISM



Laval nozzle controls expansion of carrier gas: avoids problems of other cooling methods:

- expansion/cooling is rapid – condensation avoided
- expansion controlled – collisions maintain thermal equilibrium
- essentially a rapid temperature jump

credit: Ian Sims



Fantastic experimental technique that has twice revolutionised our common sense in astrochemistry: at the beginning of the 90's by proving that neutral-neutral reactions can be very fast at the low T of cold interstellar objects and now (see later)

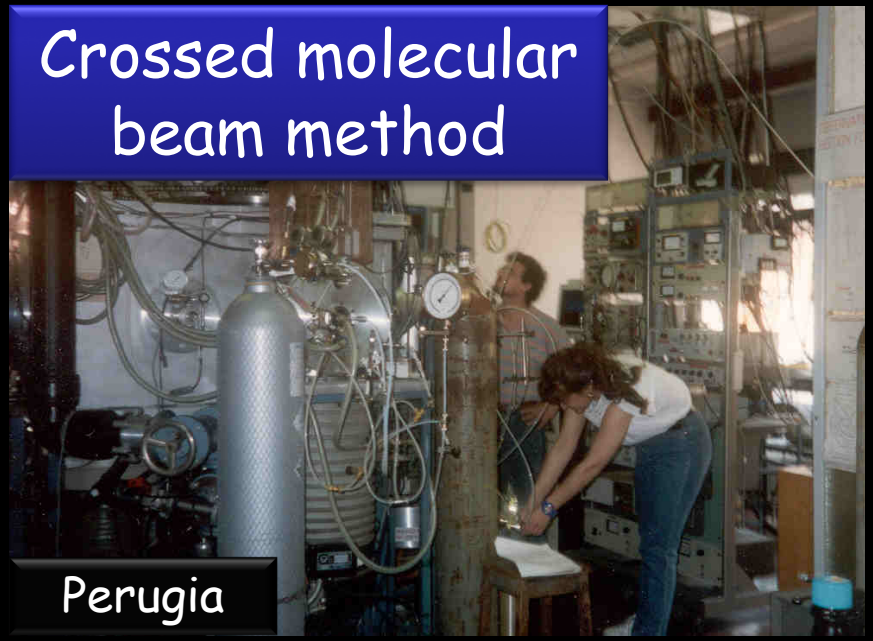
BUT it does not provide a single-collision environment

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

we have three pillars

❷ collision free experiments (molecular beam experiments)

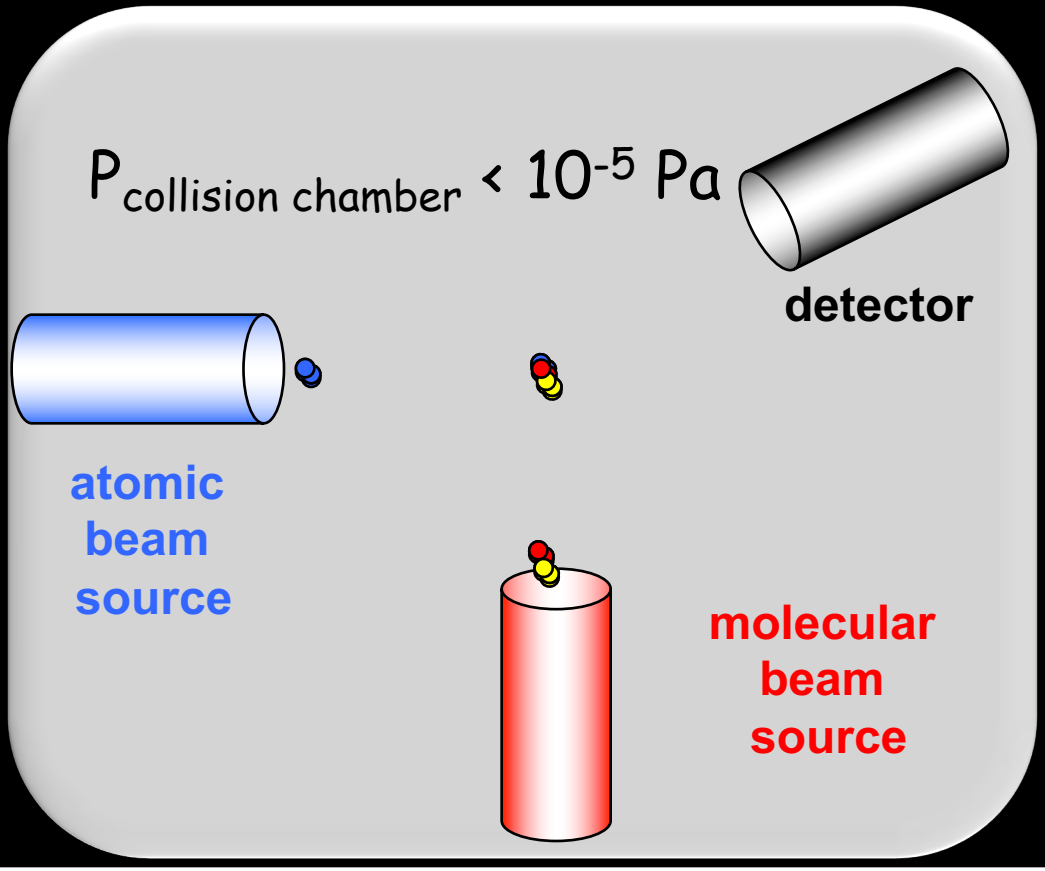
Crossed molecular beam method



Perugia

very low pressure (reactions under single collision conditions)

The crossed molecular beam method: an experimental technique to study bimolecular reactions under single collision conditions



the colliding species are prepared by expanding the gases into two distinct molecular beams which cross each other at a specific angle and collision energy

➲ **the species of each beam are made to collide only with the molecules of the other beam at the collision center**; the formed **products fly undisturbed towards the detector**

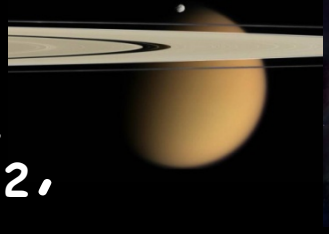
▶ because of the large mean free path, **the products do not undergo secondary or wall collisions** before arriving at the detector chamber

▶ this allows us to observe the consequences of (many) identical well-defined single molecular collisions ➲ **PRIMARY PRODUCTS**

Neutral-neutral reactions of astrophysical relevance investigated in Perugia:

- $O + C_2H_2$, C_2H_4, CH_2CCH_2, CH_3CCH, CH_3CHCH_2, H_2S C_6H_6, $C_6H_5CH_3$
- $OH + H_2$, CO
- $O + CH_3$, C_3H_5

- $CN + C_2H_2$, CH_3CCH, C_2H_4
- $N(^2D) + H_2$, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6, $C_6H_5CH_3$



- $C + C_2H_2$, C_2H_4, CH_3CCH
- $C_2(X^1\Sigma_g^+, a^3\Pi_u) + C_2H_2$

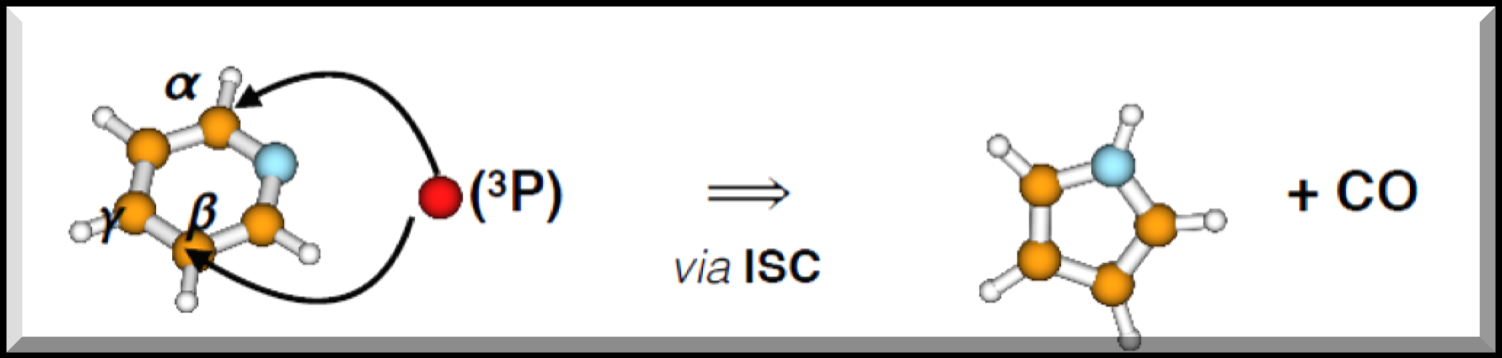
- $C(^1D) + CH_4$

- $S(^1D) + C_2H_2, C_2H_4, CH_4$

An experimental study of the pyridine (C_5H_5N) + O atom reaction: gas-phase destruction routes of a long searched molecule in extra-terrestrial environments

Demian Marchione[1]*, Pedro Recio-Ibañez[1], Adriana Caracciolo[1], Piergiorgio Casavecchia[1], Nadia Balucani[1]

[1] Department of Chemistry, Biology and Biotechnologies, University of Perugia – Perugia, Italy



$O(^3P) + C_5H_5N$		$O(^3P) + C_6H_6$	
Preliminary branching ratios		**Branching ratios**	
$C_5H_4NO + H$ (1)	1 %	$C_6H_5O + H$	69 %
$C_5H_4NO + H$ (2)	1 %	C_6H_5OH	4 %
Ring degrad.	98 %	Ring degrad.	27 %

Neutral-neutral reactions of astrophysical relevance investigated in Perugia:

- O + C_2H_2, C_2H_4, CH_2CCH_2, CH_3CCH, CH_3CHCH_2, H_2S C_6H_6, $C_6H_5CH_3$
- OH + H_2, CO
- O + CH_3, C_3H_5

- CN + C_2H_2, CH_3CCH, C_2H_4
- $N(^2D)$ + H_2, H_2O, CH_4, C_2H C_2H_4, C_2H_6, C_6H_6, $C_6H_5CH_3$

+ the huge amount of work by Ralf Kaiser (Univ Hawaii)

e.g. C, Si, B, CN, CH, C_2, C_3, C_2H, SiH, etc

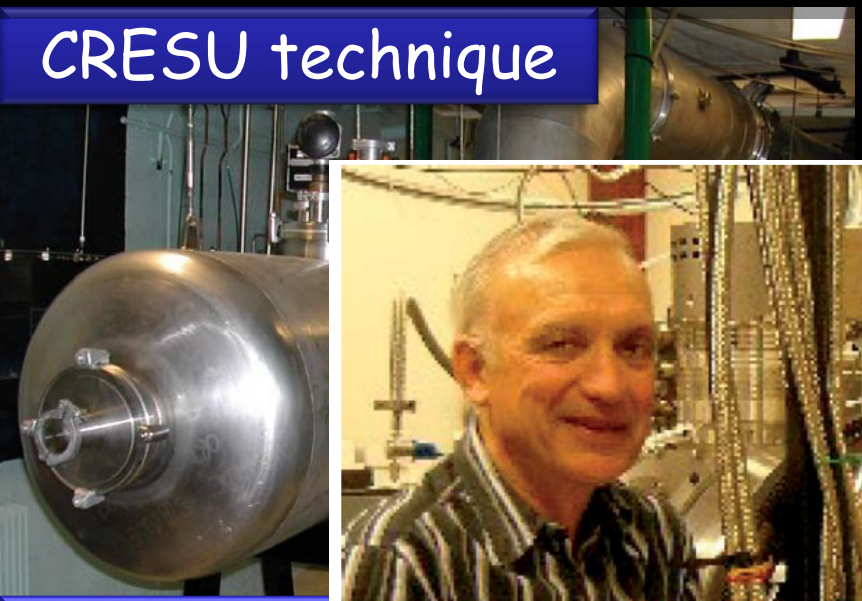
Fantastic experimental technique that has revealed the reaction product branching ratios by reproducing the single collision conditions of interstellar objects (challenging experiments)

BUT

it does not reproduce the low T (collision energy) conditions of interstellar objects

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

CRESU technique



low T, as low as those
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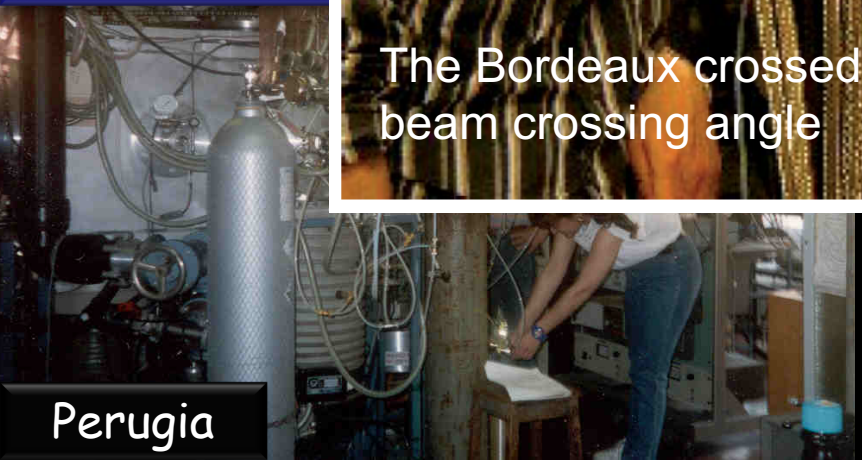

Perugia

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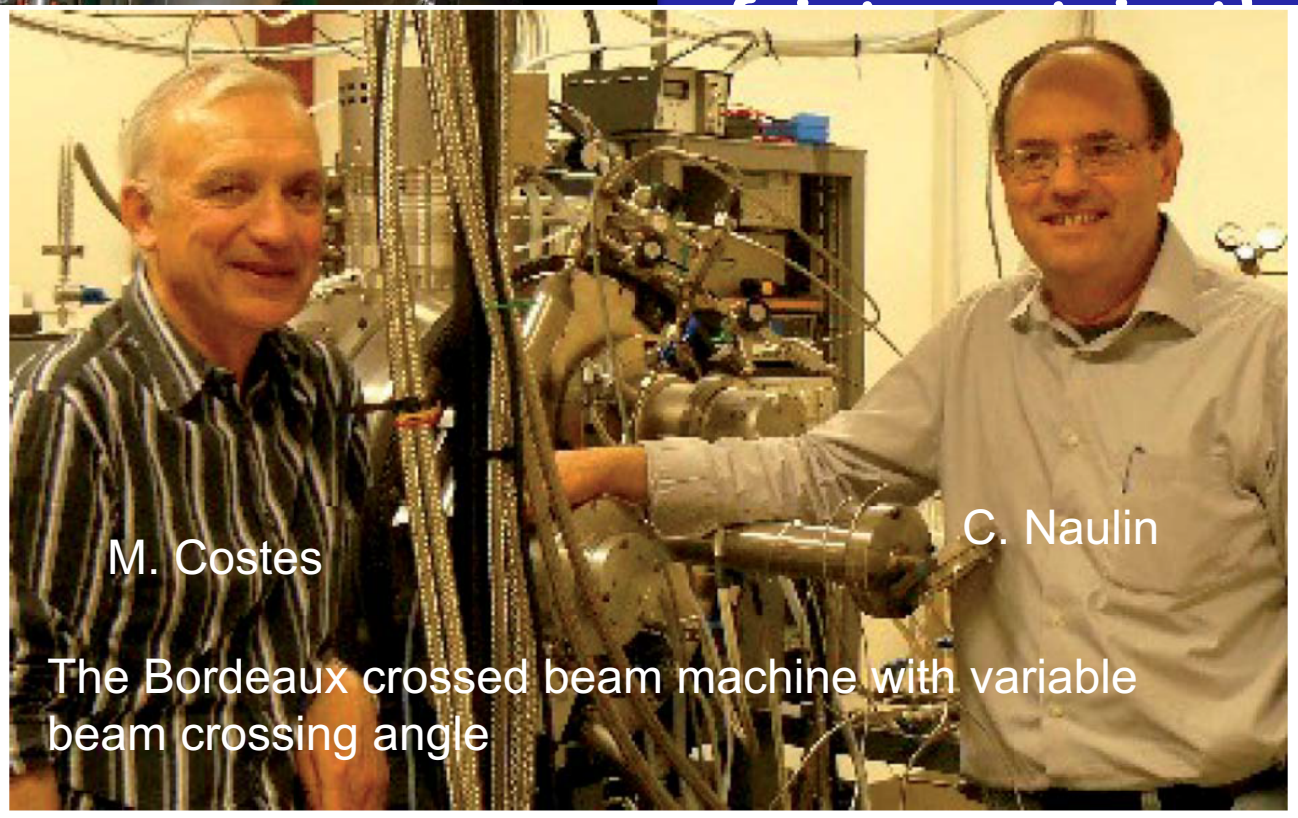
the ISM (collision free experiments)



M. Costes

C. Naulin

The Bordeaux crossed beam machine with variable beam crossing angle

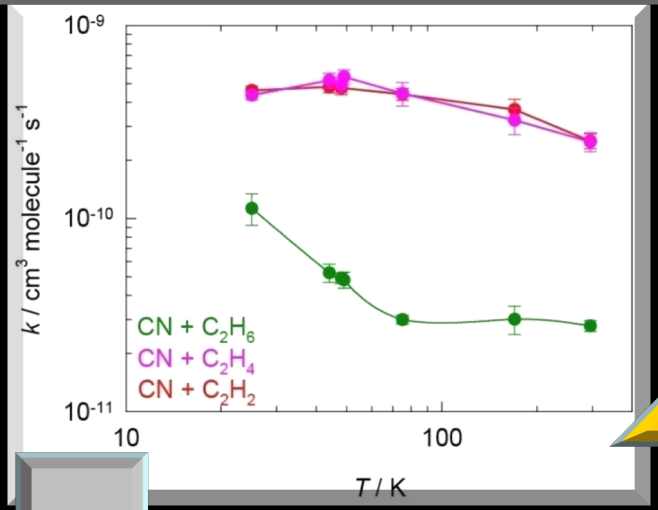
What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

we have three pillars

❸ quantum chemistry calculations

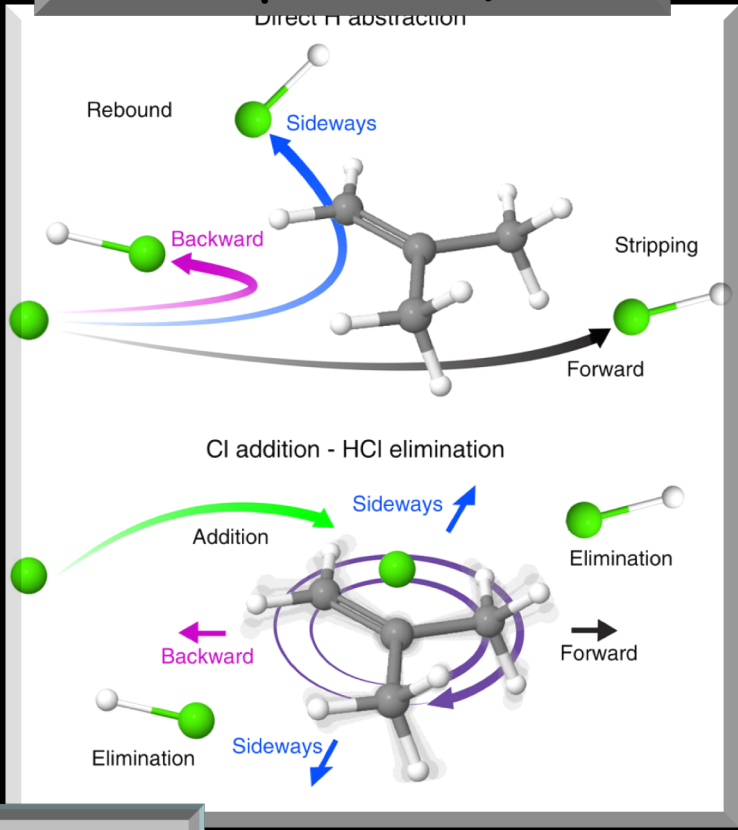
a) There are no versatile experimental techniques achieving both low T and P

Rate coefficients at low T (CRESU)

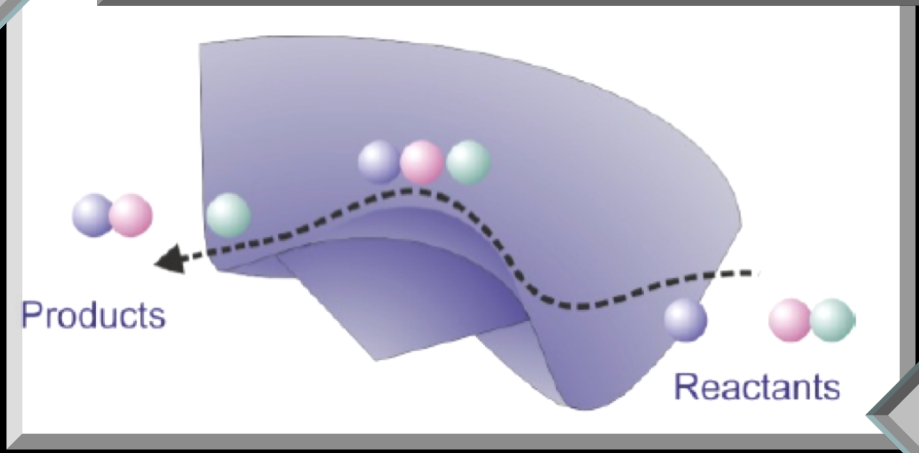


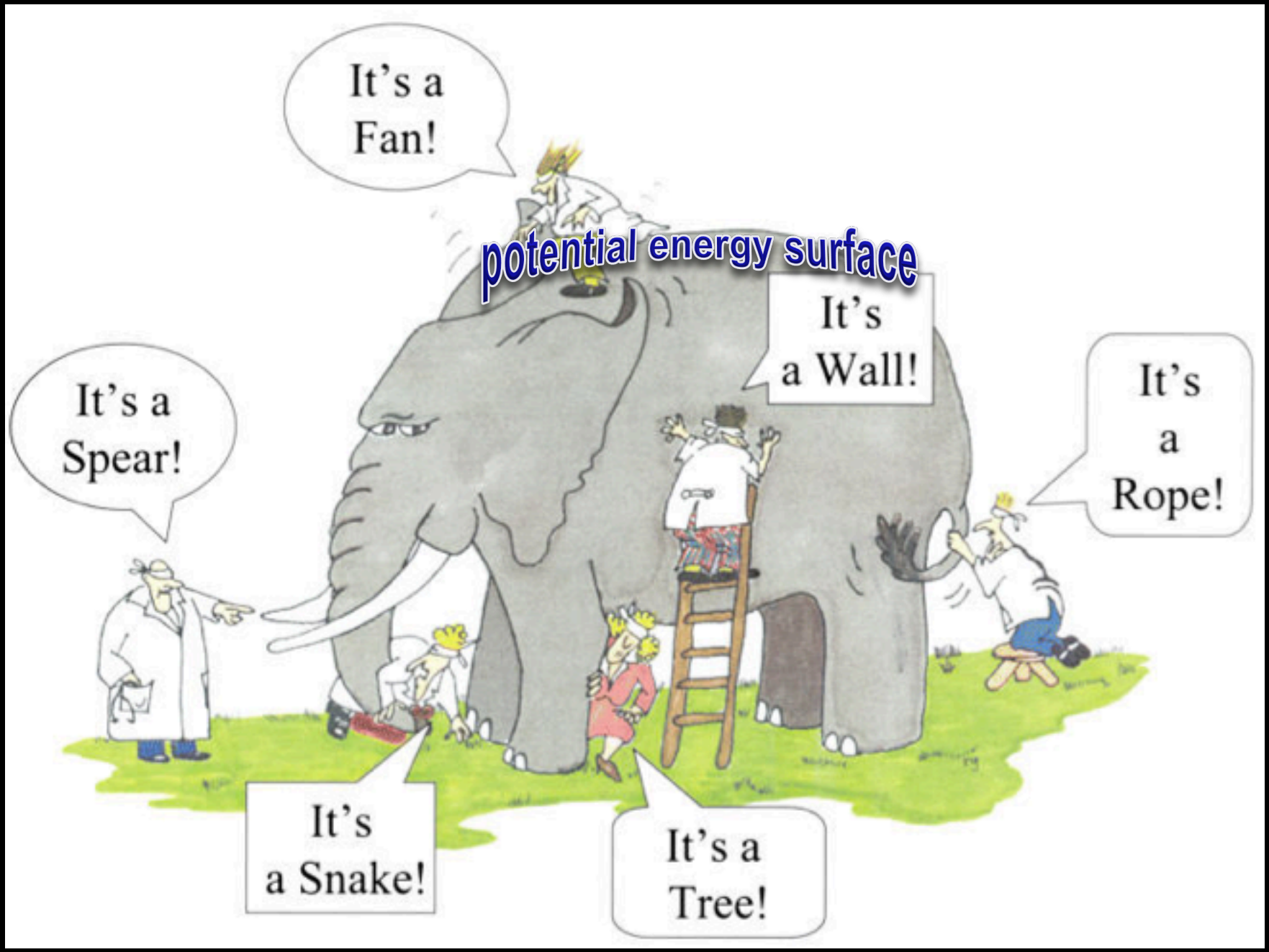
Calculate anything you need

Reaction mechanism + product branching ratios (crossed molecular beam experiments)



Accurate potential energy surface




It's a Fan!
potential energy surface
It's a Wall!
It's a Spear!
It's a Rope!
It's a Snake!
It's a Tree!

In a few cases we have finally assembled the elephant…

nature chemistry

ARTICLES

PUBLISHED ONLINE: 12 JANUARY 2014 | DOI: 10.1038/NCHEM.1835

The rate of the $F + H_2$ reaction at very low temperatures

Meryem Tizniti[1], Sébastien D. Le Picard[1], François Lique[2], Coralie Berteloite[1], André Canosa[1], Millard H. Alexander[3]* and Ian R. Sims[1]*

The prototypical $F + H_2 \rightarrow HF + H$ reaction possesses a substantial energetic barrier (~800 K) and might therefore be expected to slow to a negligible rate at low temperatures. It is, however, the only source of interstellar HF, which has been detected in a wide range of cold (10–100 K) environments. In fact, the reaction does take place efficiently at low temperatures due to quantum-mechanical tunnelling. Rate constant measurements at such temperatures have essentially been limited to fast barrierless reactions, such as those between two radicals. Using uniform supersonic hydrogen flows we can now report direct experimental measurements of the rate of this reaction down to a temperature of 11 K, in remarkable agreement with state-of-the-art quantum reactive scattering calculations. The results will allow a stronger link to be made between observations of interstellar HF and the abundance of the most common interstellar molecule, H_2, and hence a more accurate estimation of the total mass of astronomical objects.

The potential energy surface and the non-BO method employed by M. Alexander had already been tested against crossed molecular beam experiments (for decades!!)

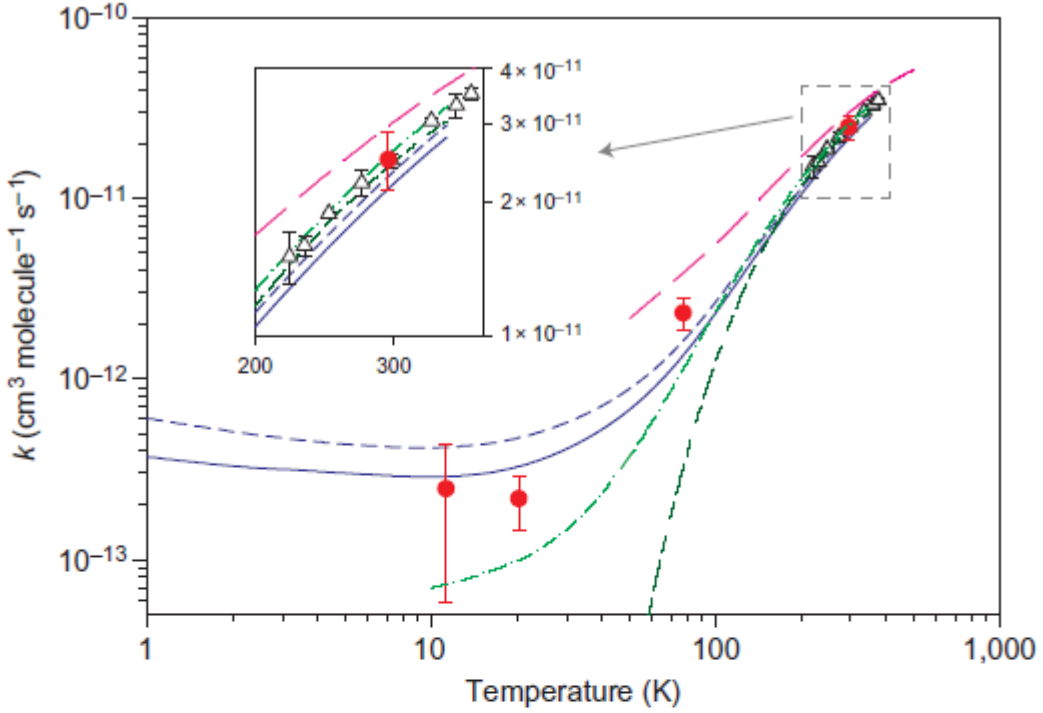


Figure 3 | Comparison of rate coefficients k for the $F(^2P_J) + n\text{-}H_2 \rightarrow HF + H$ reaction as a function of temperature. Symbols present experimental results: from this work (filled red circles, with error bars corresponding to 95% confidence limits) and from Stevens and colleagues[25] (open triangles, with their quoted uncertainties). The solid and dashed blue lines represent the predictions of our scattering calculations with, respectively, inclusion and exclusion of non-BO coupling. In these calculations we assume a ratio of *ortho* ($j = 1$) to *para* ($j = 0$) H_2 of 3:1. Also shown is the Arrhenius temperature dependence proposed by Persky and Kornweitz[28] (alternating short-long dashed dark green line), the predictions of the single-PES quantum scattering calculations of Zhu and colleagues[22] (long-dashed magenta line) and the quantum reactive scattering calculations of Aquilanti and colleagues[10,29] (light green dashed-dotted line) performed on their PES III, which is a modification of the original Stark-Werner PES.

You can trust it 100%

NATURE CHEMISTRY | VOL 6 | FEBRUARY 2014 |

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

we have three pillars

❸ quantum chemistry calculations

a) There are no versatile experimental techniques achieving both low T and P: a theoretical description of the reactive process via electronic structure calculations of the relevant potential energy surface + kinetics calculations can provide the rate coefficients under the conditions of interest; the comparison with available experimental data tests the accuracy of the calculations

b) There are no experimental data at all: a theoretical description of the reactive process via electronic structure calculations of the relevant potential energy surface + kinetics calculations can provide an educated guess of the reaction rate coefficients

2) Can we expect new significant contributions to the understanding of the chemistry of interstellar objects from gas-phase chemistry?

1) recent CRESU results

the effects of pre-reactive complexes and tunnelling on rate coefficients

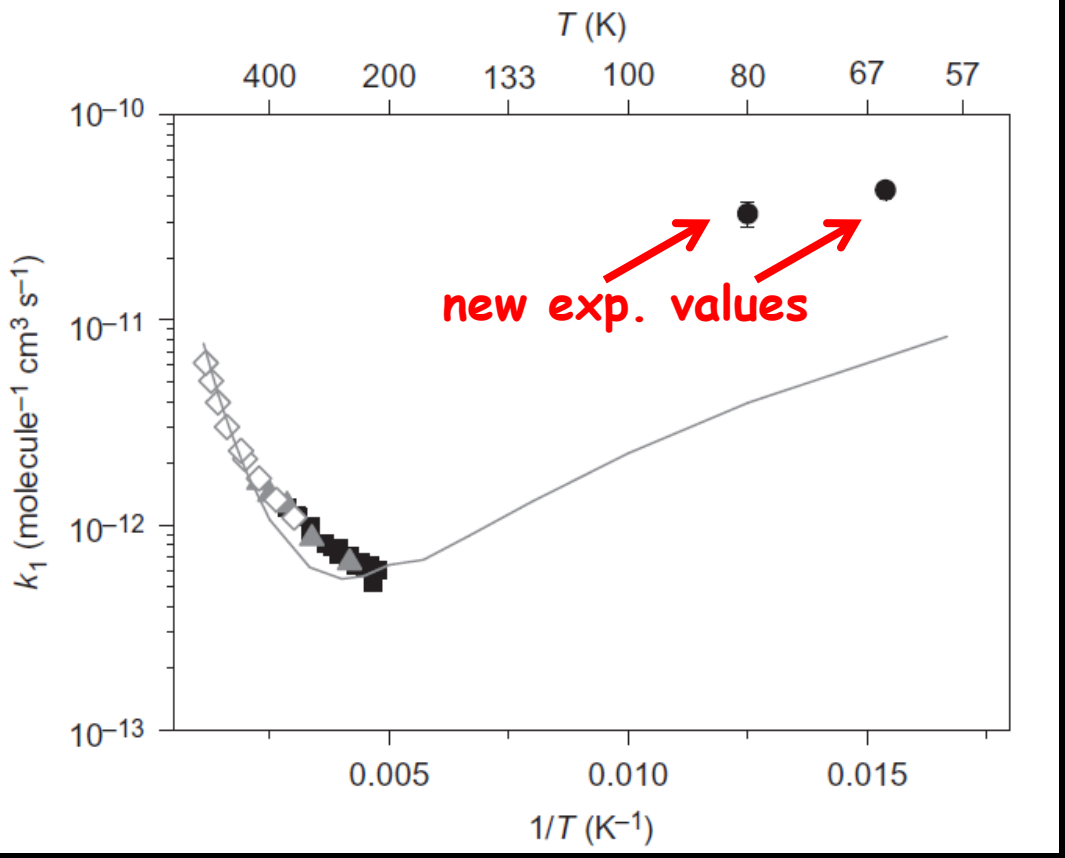
nature chemistry

ARTICLES

PUBLISHED ONLINE: 30 JUNE 2013 | DOI: 10.1038/NCHEM.1692

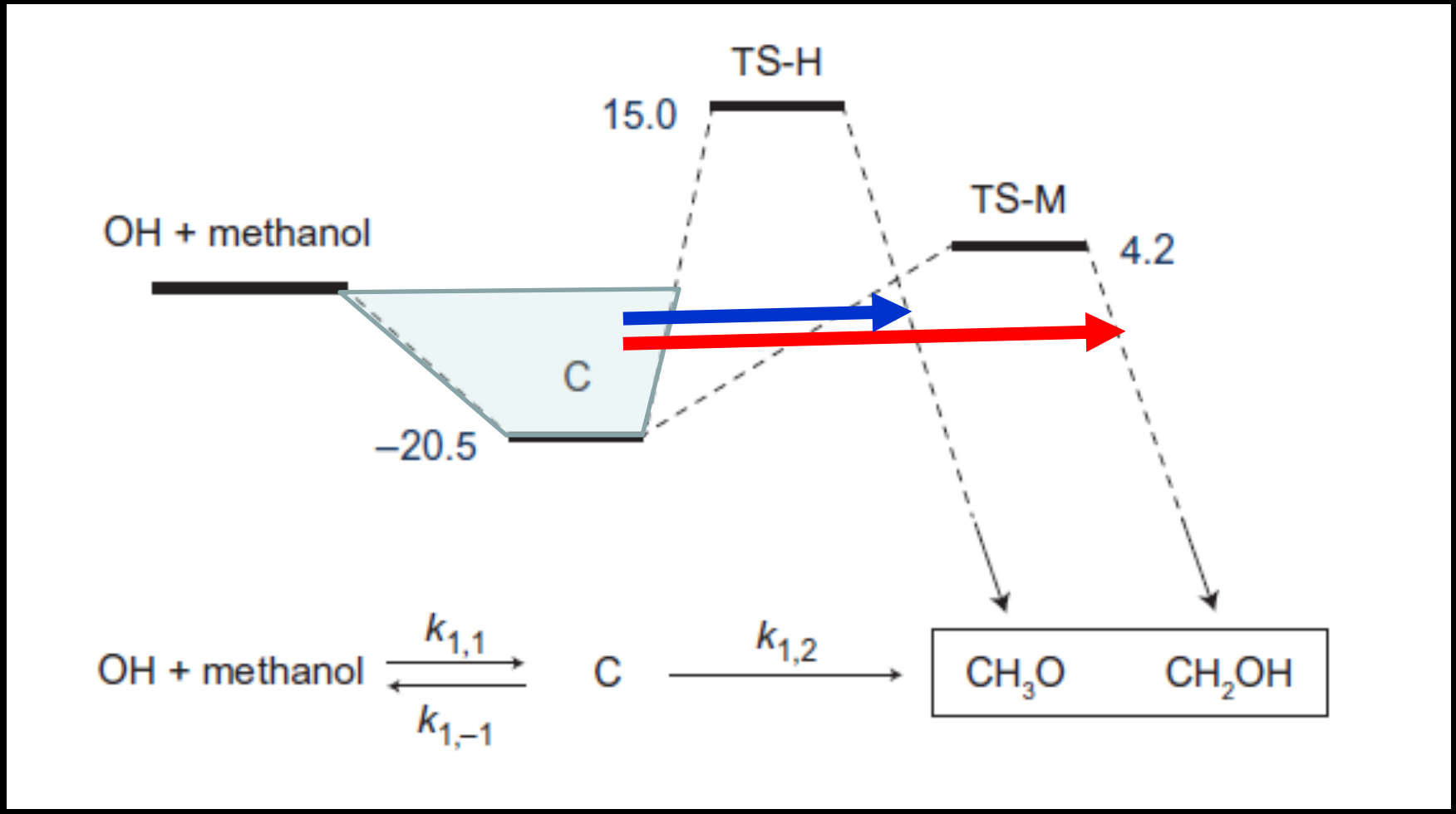
Accelerated chemistry in the reaction between the hydroxyl radical and methanol at interstellar temperatures facilitated by tunnelling

Robin J. Shannon[1], Mark A. Blitz[1,2], Andrew Goddard[1] and Dwayne E. Heard[1,2]*



Despite the presence of an entrance barrier, the rate coefficient at 63 K was found to be larger than the one at 200 K.

Deviations from Arrhenius behavior are quite common. In some cases they are associated to the tunnelling effect…



According to master equation calculations explicitly considering tunnelling effects, at temperatures lower than 200 K the lifetime of the van der Waals complex is very long and tunnelling towards CH_3O+H becomes the dominant channel (99%)

The Astrophysical Journal, 823:25 (8pp), 2016 May 20 doi:10.3847/0004-637X/823/1/25
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REACTIVITY OF OH AND CH_3OH BETWEEN 22 AND 64 K: MODELING THE GAS PHASE PRODUCTION OF CH_3O IN BARNARD 1b

M. Antiñolo[1,2], M. Agúndez[3], E. Jiménez[1,2], B. Ballesteros[1,2], A. Canosa[4], G. El Dib[4], J. Albaladejo[1,2], and J. Cernicharo[3]

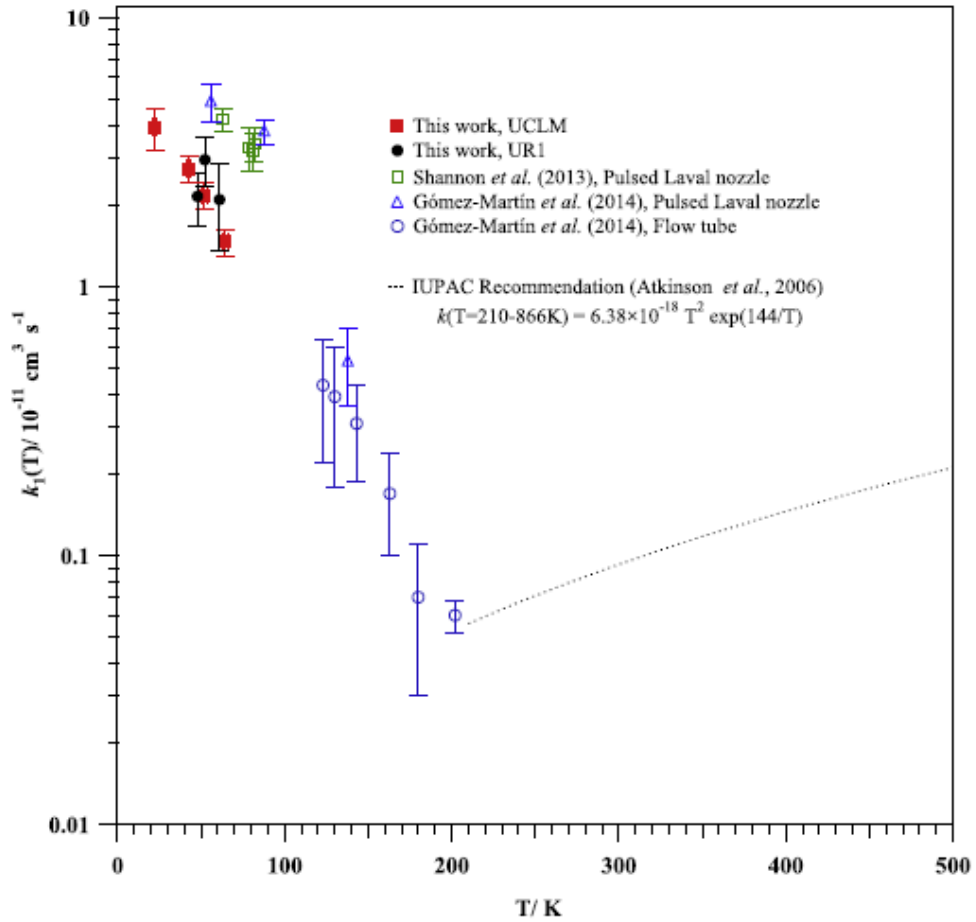


Figure 3. Rate coefficients for the reaction of OH with CH_3OH as a function of temperature. Filled symbols are kinetic data presented in this work and empty symbols are values reported in the literature.

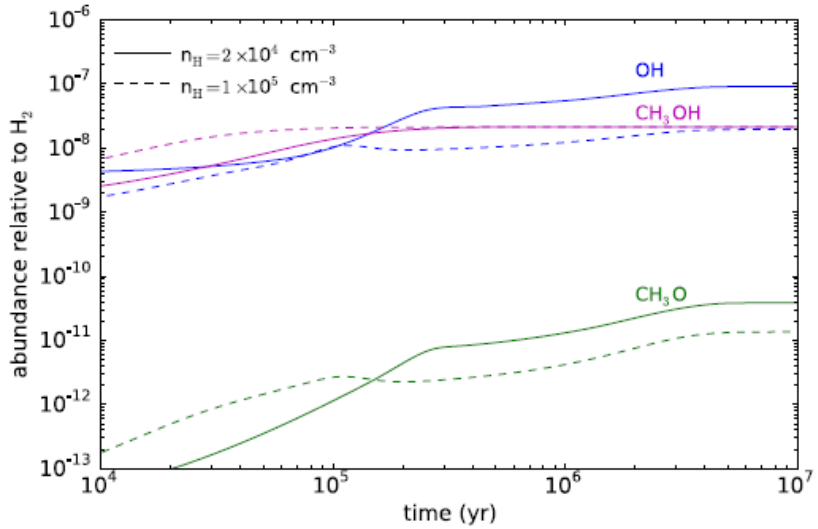


Figure 4. Calculated abundances of OH, methanol, and CH_3O relative to H_2 are shown as a function of time. Solid and dashed lines correspond to densities of H nuclei of 2×10^4 cm^{-3} and 1×10^5 cm^{-3}, respectively.

ACCOUNTS of chemical research

Article

Cite This: *Acc. Chem. Res.* XXXX, XXX, XXX−XXX

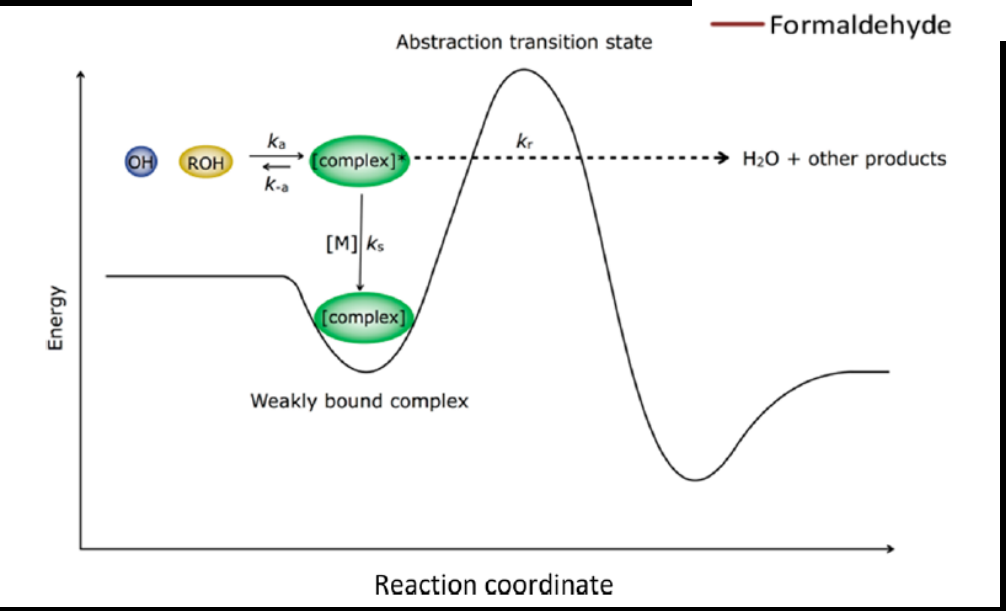
pubs.acs.org/accounts

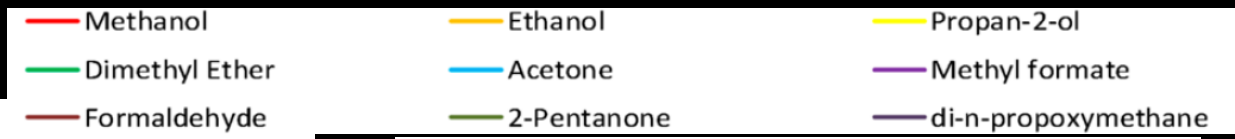
Rapid Acceleration of Hydrogen Atom Abstraction Reactions of OH at Very Low Temperatures through Weakly Bound Complexes and Tunneling

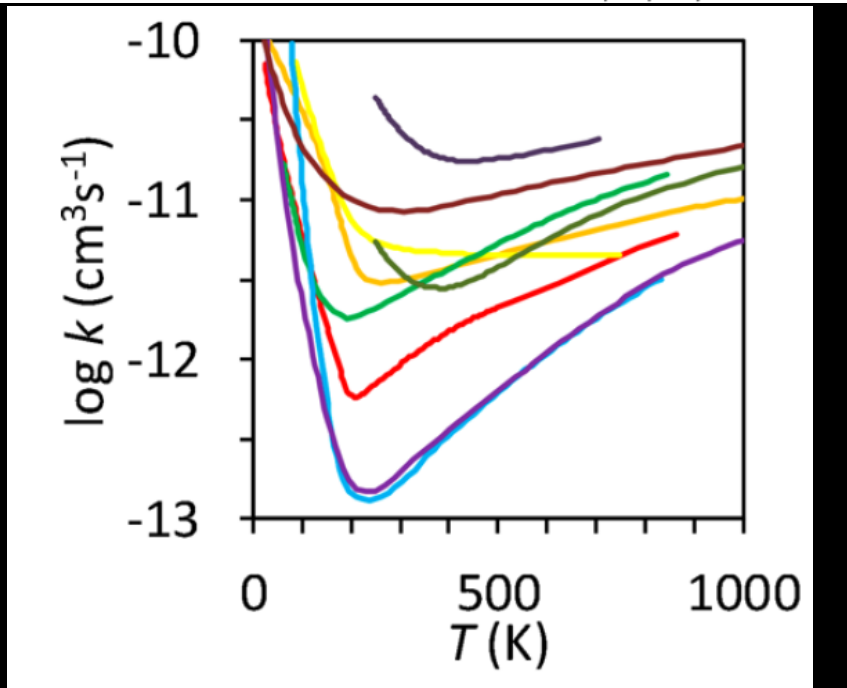
Published as part of the Accounts of Chemical Research special issue "Hydrogen Atom Transfer".

Dwayne E. Heard*

School of Chemistry and National Centre for Atmospheric Science, University of Leeds, Leeds LS2 9JT, United Kingdom







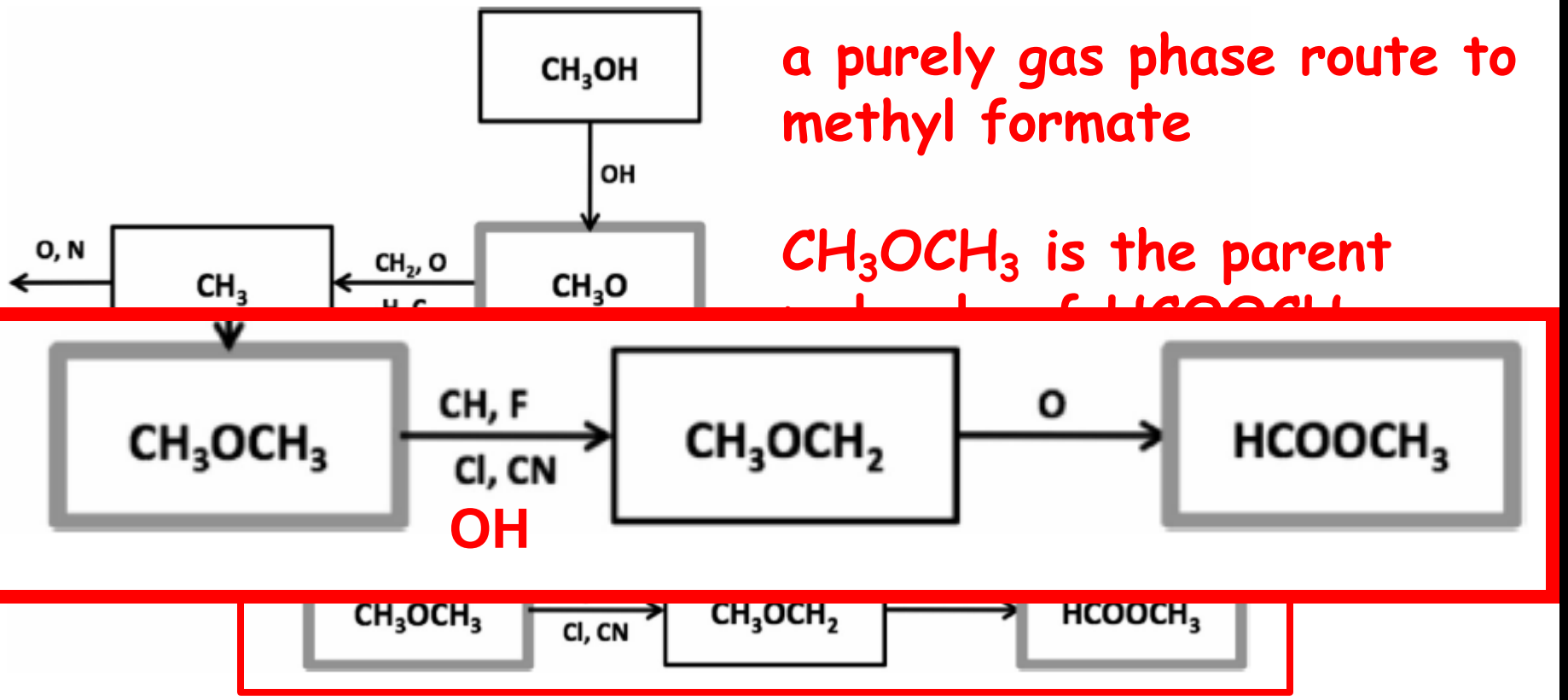
Given the abundance of OH, we now have new formation routes (in 2 steps)

Monthly Notices
of the
ROYAL ASTRONOMICAL SOCIETY

MNRAS **449,** L16–L20 (2015) doi:10.1093/mnrasl/slv009

Formation of complex organic molecules in cold objects: the role of gas-phase reactions

Nadia Balucani,[1,2,3] Cecilia Ceccarelli[2,3★] and Vianney Taquet[4]

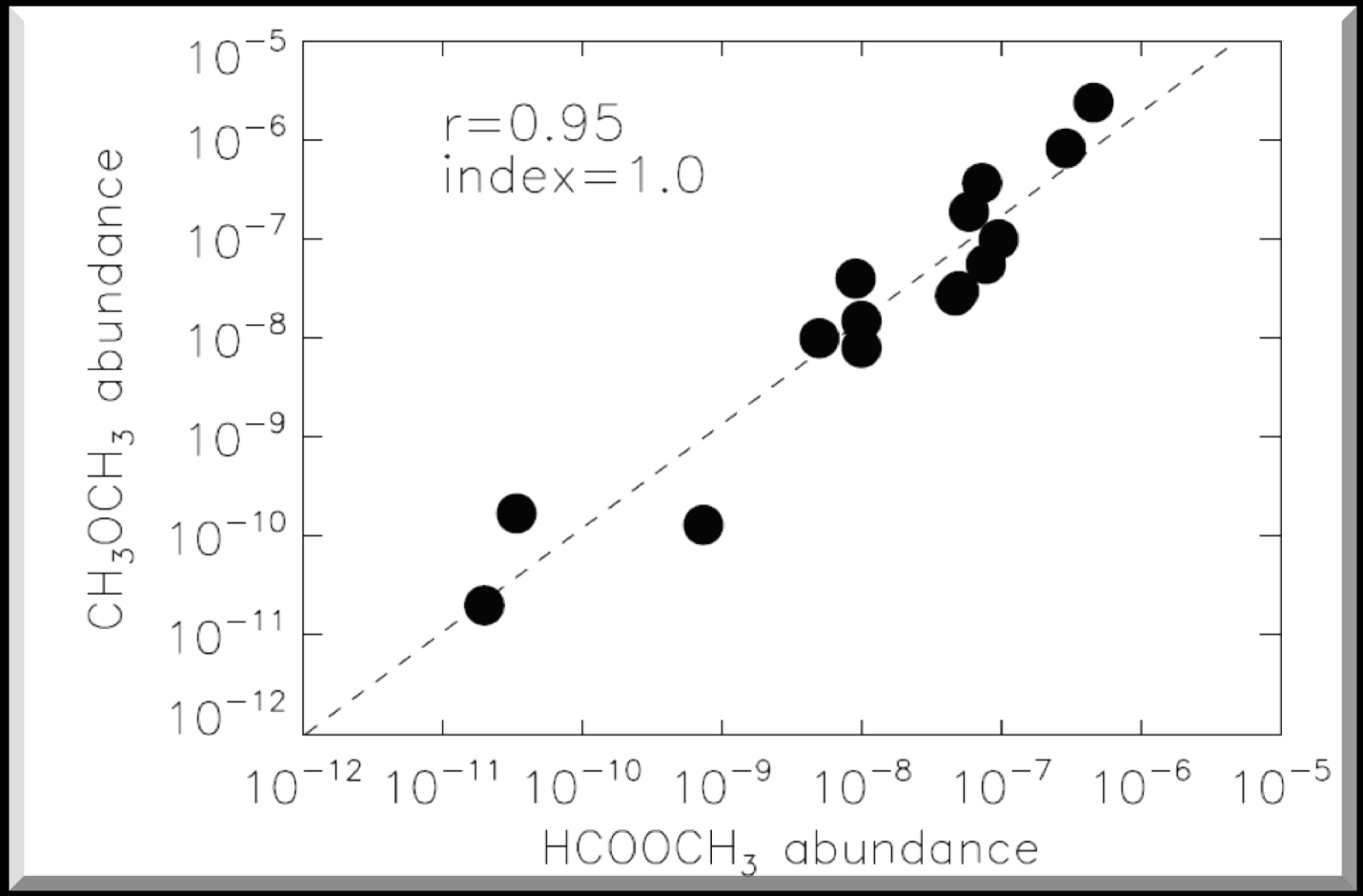


a purely gas phase route to methyl formate

CH_3OCH_3 is the parent

Abundance of dimethyl ether as a function of the abundance of methyl formate in different ISM sources

r = correlation coefficient + *power-law index*



Jaber, Ceccarelli, Kahane, Caux
ApJ 2014, 791:29

The genealogical tree of ethanol

an astrochemical connection among interstellar CH_3CH_2OH and $HCOOH$, CH_3COOH, CH_2OHCHO

see the poster by Fanny Vazart

The Astrophysical Journal, 854:135 (10pp), 2018 February 20 https://doi.org/10.3847/1538-4357/aaa41e
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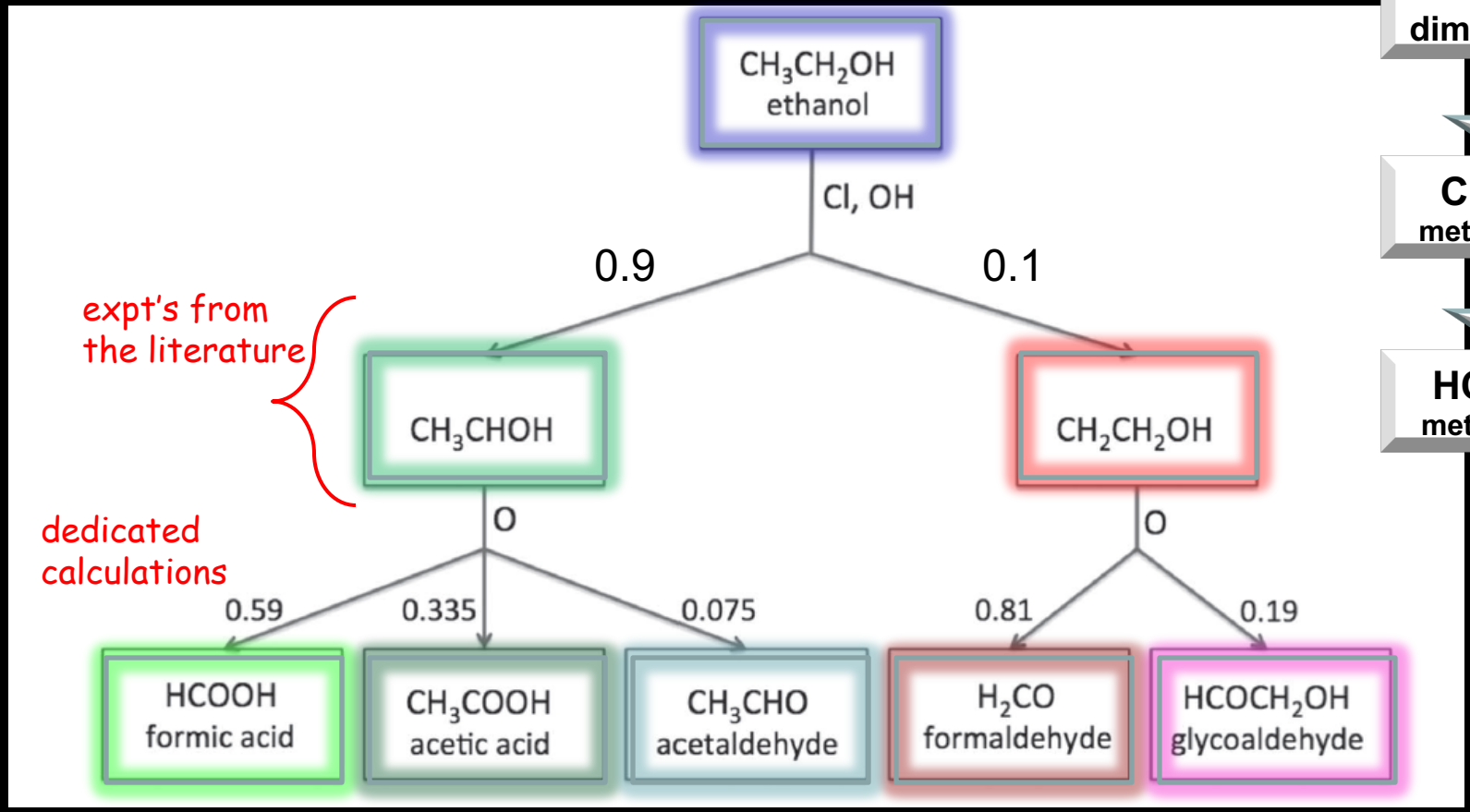
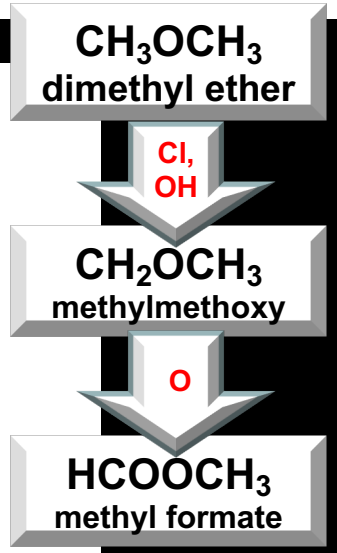
OPEN ACCESS

The Genealogical Tree of Ethanol: Gas-phase Formation of Glycolaldehyde, Acetic Acid, and Formic Acid

Dimitrios Skouteris[1], Nadia Balucani[2,3,4], Cecilia Ceccarelli[3], Fanny Vazart[1], Cristina Puzzarini[4,5], Vincenzo Barone[1], Claudio Codella[4], and Bertrand Lefloch[3]





The reaction Cl + CH_3CH_2OH

J. Phys. Chem. A **1999**, *103*, 9805−9814

Absolute and Site-Specific Abstraction Rate Coefficients for Reactions of Cl with CH_3CH_2OH, CH_3CD_2OH, and CD_3CH_2OH between 295 and 600 K

Craig A. Taatjes*

Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, California 94551-0969

Lene K. Christensen, Michael D. Hurley, and Timothy J. Wallington*

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Received: July 20, 1999; In Final Form: October 5, 1999

TABLE 2: Measured HCl Yields, ϕ_{HCl}, for Cl Reactions with Selectively Deuterated Ethanols[a]

temp (K)	CD_3CH_2OH	CH_3CD_2OH	CD_3CD_2OH
295	0.95 ± 0.1	0.16 ± 0.04	<0.05
400	1.03 ± 0.1	0.18 ± 0.05	<0.05
450	0.92 ± 0.1	0.20 ± 0.05	
500	0.99 ± 0.1	0.26 ± 0.08	
550	0.95 ± 0.1		
600		0.22 ± 0.05	

[a] Error bars are $\pm 2\sigma$ and include estimates of systematic error.

The reaction OH + CH_3CH_2OH

THE JOURNAL OF PHYSICAL CHEMISTRY A

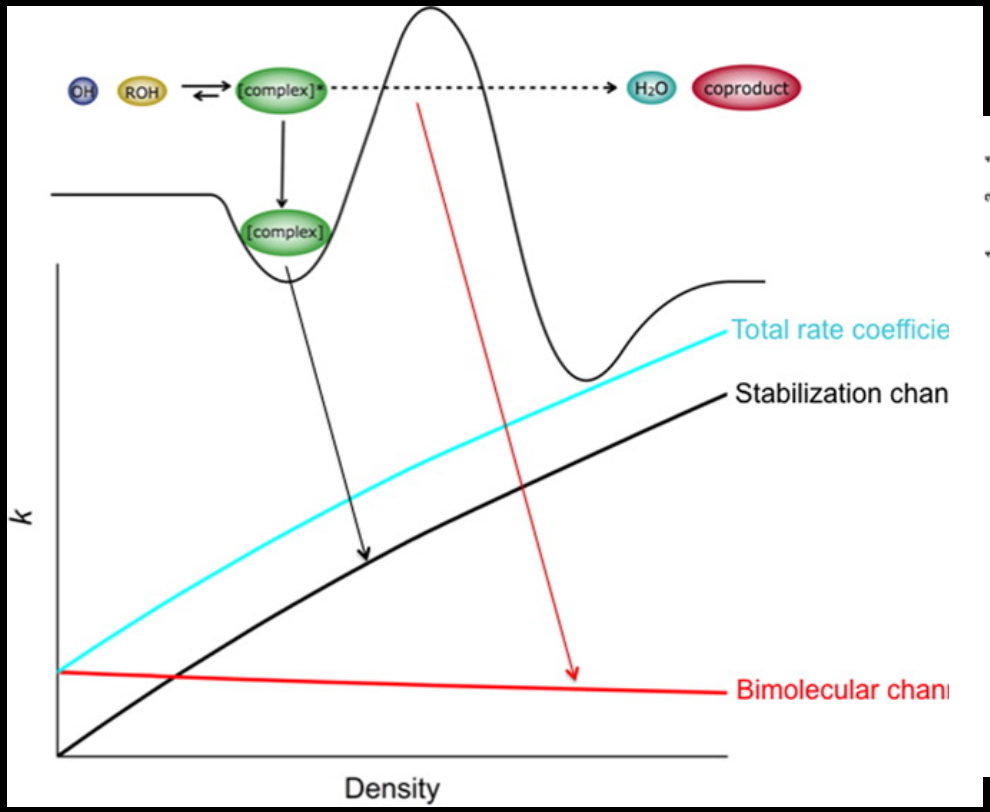
Article

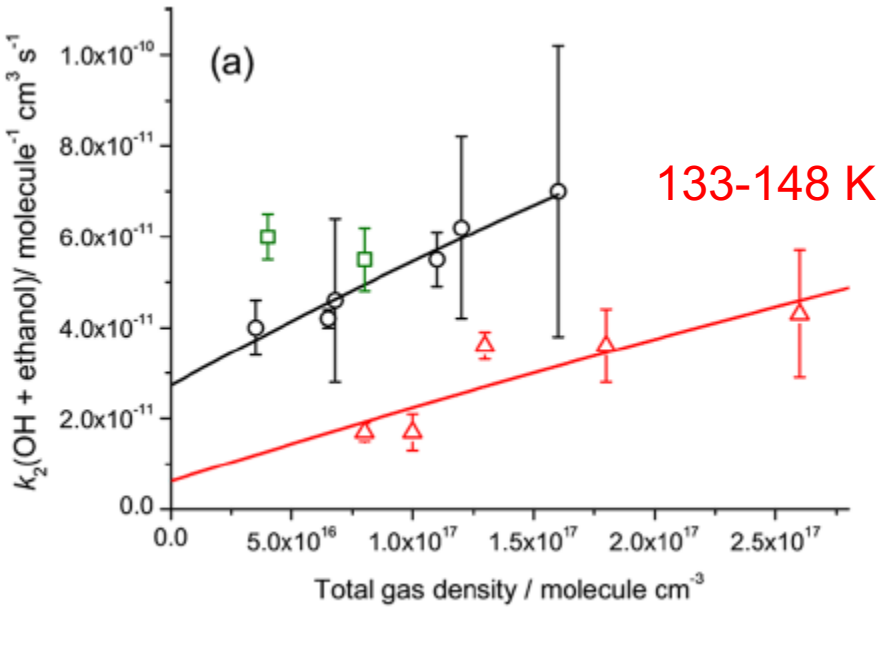
pubs.acs.org/JPCA

Measurements of Rate Coefficients for Reactions of OH with Ethanol and Propan-2-ol at Very Low Temperatures

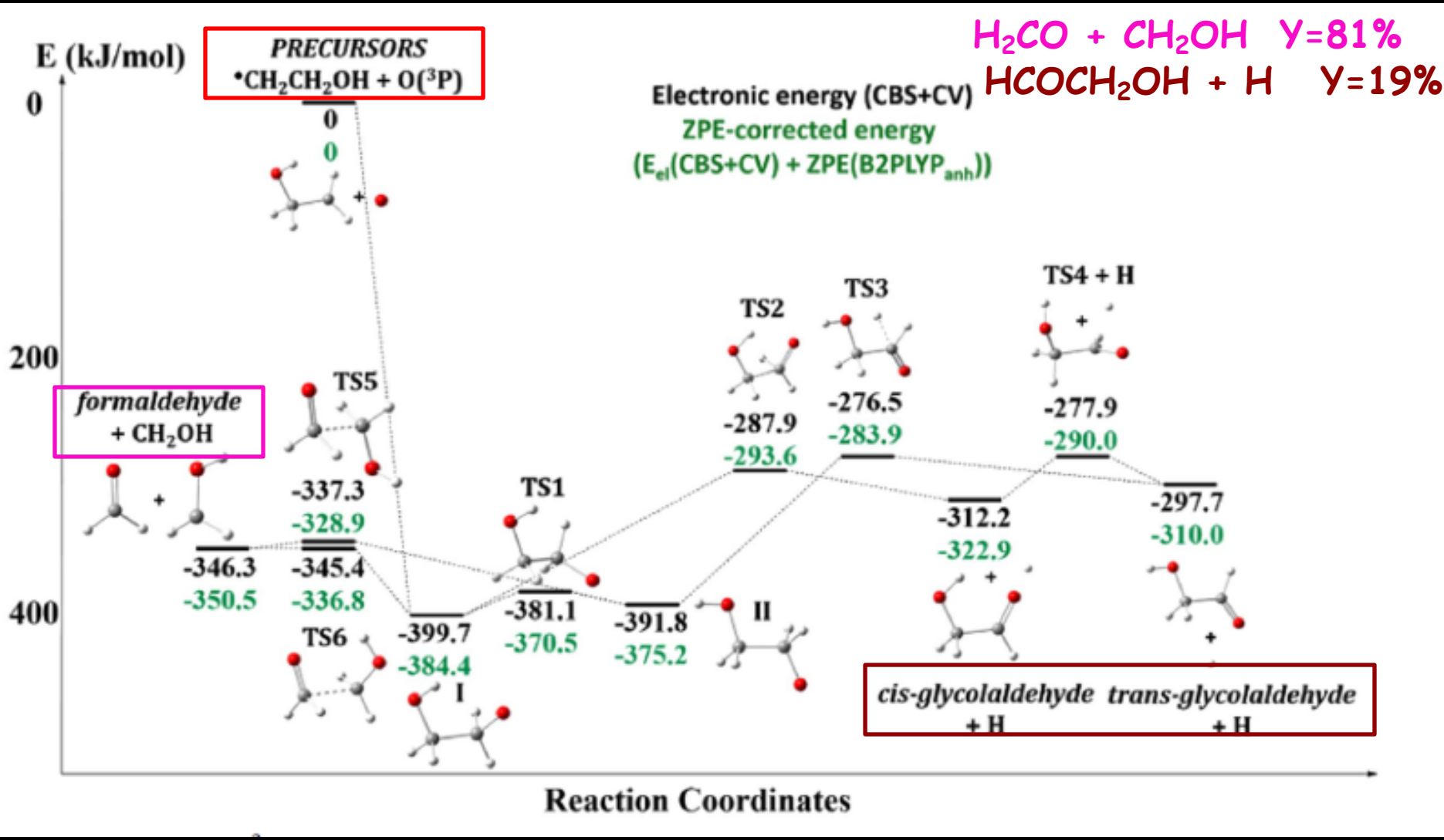
Rebecca L. Caravan, Robin J. Shannon, Thomas Lewis, Mark A. Blitz, and Dwayne E. Heard*

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.



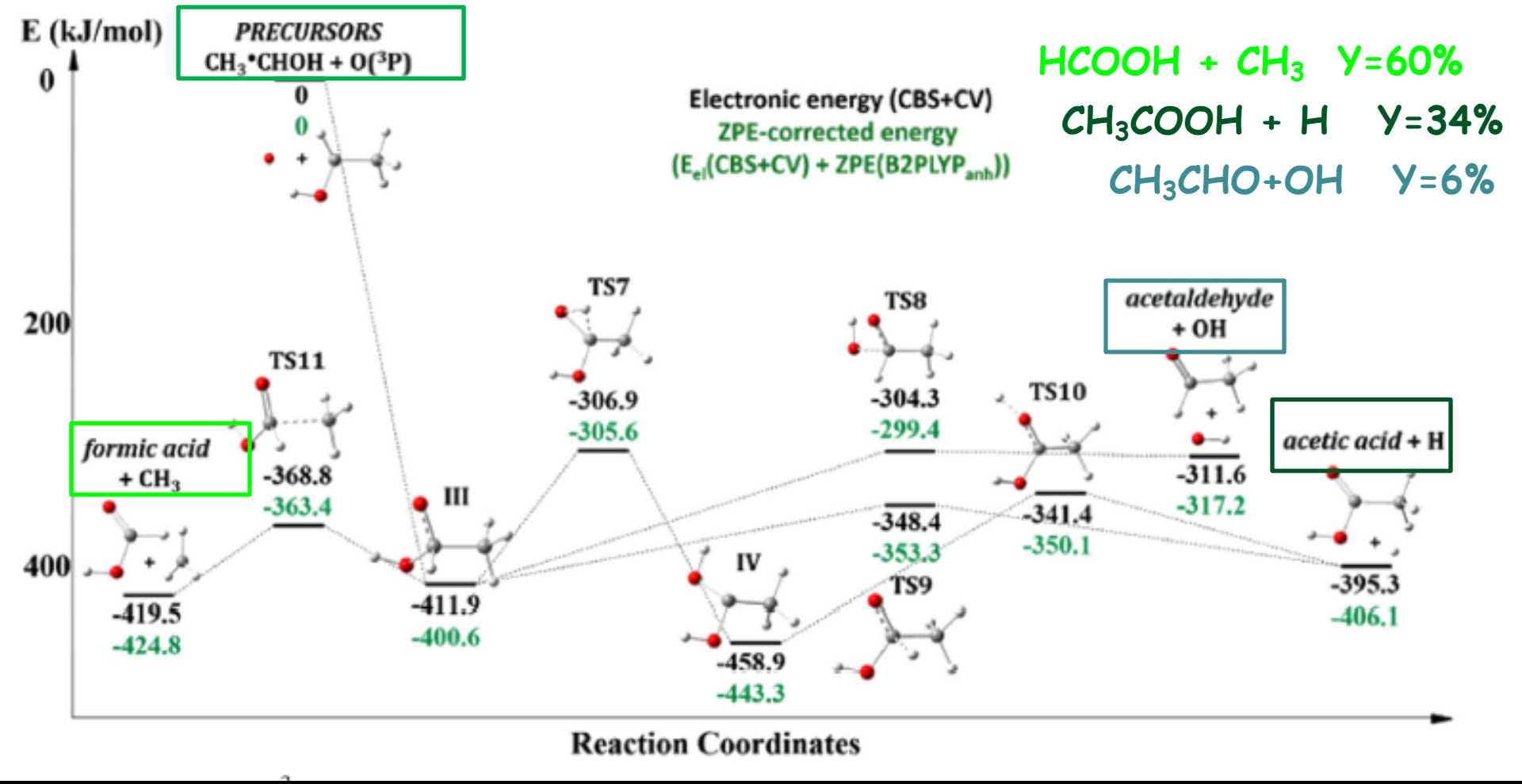


The potential energy surface for the reaction $O+CH_2CH_2OH$



Skouteris et al. ApJ 2018, 854, 135

The potential energy surface for the reaction $O+CH_3CHOH$



Skouteris et al. ApJ 2018, 854, 135

Kinetics calculations (Capture Theory + RRKM)

Reaction	α	β	γ
$CH_3CHOH + O \rightarrow HCOOH + CH_3$	3.9(−10)	0.18	0.49
$CH_3CHOH + O \rightarrow CH_3CHO + OH$	4.8(−11)	0.19	0.39
$CH_3CHOH + O \rightarrow CH_3COOH + H$	2.2(−10)	0.16	0.59
$CH_2CH_2OH + O \rightarrow HCOCH_2OH + H$	1.1(−10)	0.16	0.55
$CH_2CH_2OH + O \rightarrow H_2CO + CH_2OH$	4.6(−10)	0.17	0.51

Kinetics calculations (Capture Theory + RRKM)

Reaction	α	β	γ
$CH_3CHOH + O \rightarrow HCOOH + CH_3$	3.9(−10)	0.18	0.49
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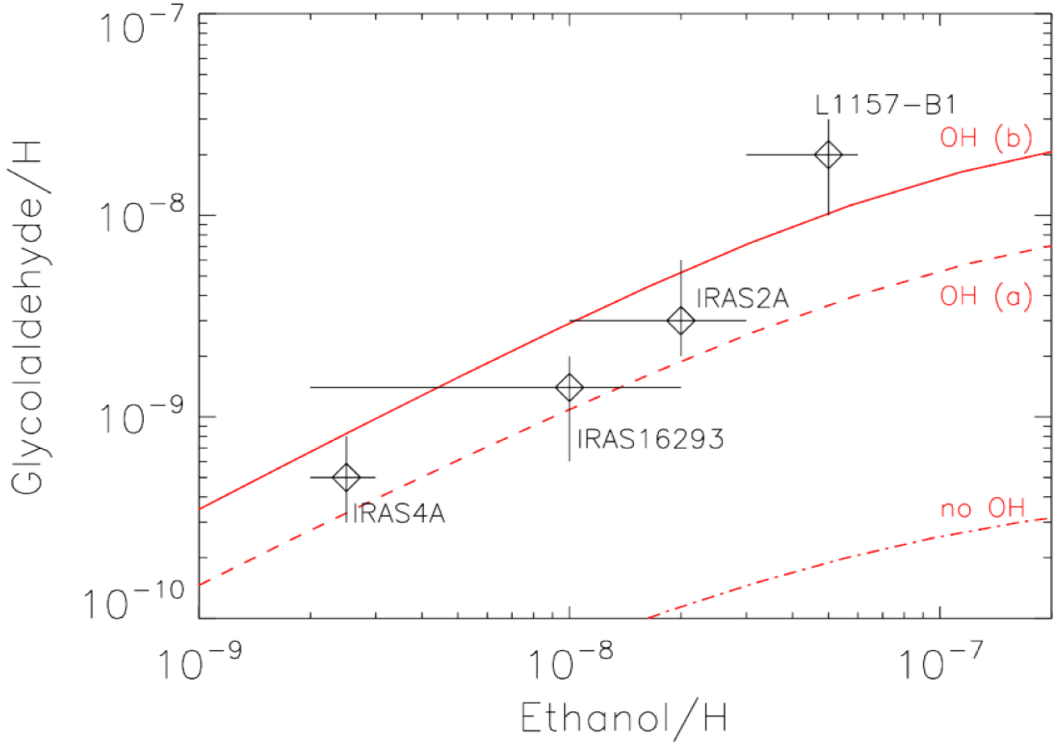
$CH_2CH_2OH + O \rightarrow H_2CO + CH_2OH$	4.6(−10)	0.17	0.51

The astrochemical model (Nahoon + revised KIDA database)



The abundance of glycolaldehyde plotted against the abundance of ethanol for four different astrochemical objects follows closely the theoretical predictions based on our model (the three red curves correspond to different branching ratios of the ethanol radicals on hydrogen abstraction by the OH radical).

2) Deuteration of interstellar complex organic molecules: a benchmark for gas-phase vs ice chemistry in star-forming regions?

Astronomy & Astrophysics manuscript no. ms
August 28, 2018
©ESO 2018

The ALMA-PILS survey: Isotopic composition of oxygen-containing complex organic molecules toward IRAS 16293–2422B

J. K. Jørgensen[1], H. S. P. Müller[2], H. Calcutt[1], A. Coutens[3], M. N. Drozdovskaya[4], K. I. Öberg[5] M. V. Persson[6], V. Taquet[7], E. F. van Dishoeck[8, 9], and S. F. Wampfler[4]

gas-phase reactions are believed to be irrelevant in influencing the degree of deuteration of interstellar complex organic molecules

THE ASTROPHYSICAL JOURNAL, 340:906–920, 1989 May 15
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DEUTERIUM FRACTIONATION IN DENSE INTERSTELLAR CLOUDS

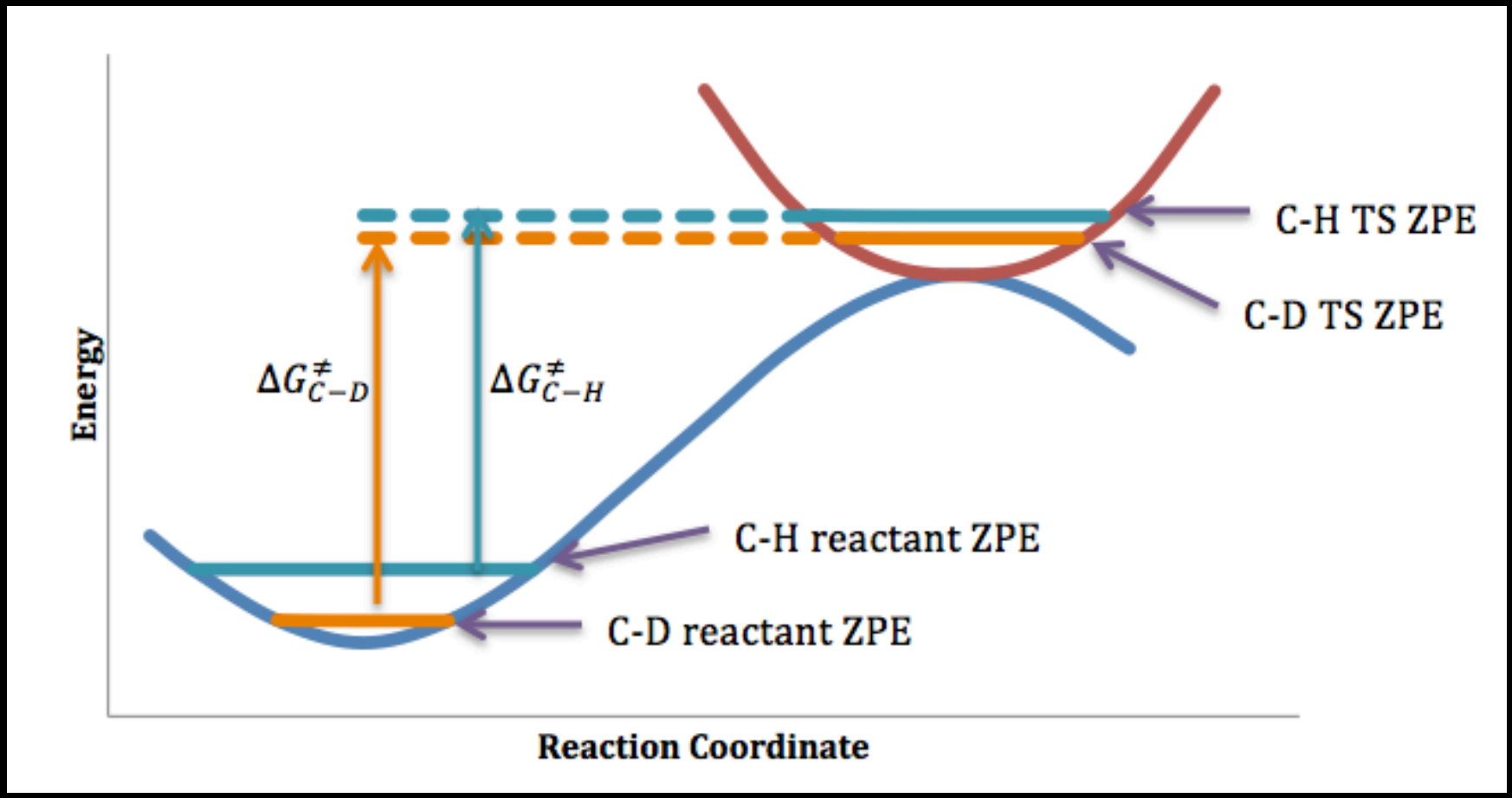
T. J. MILLAR AND A. BENNETT
Department of Mathematics, University of Manchester Institute of Science and Technology
AND
ERIC HERBST
I. Physikalisches Institut, Universität zu Köln, Federal Republic of Germany
Received 1988 May 16; accepted 1988 October 26

For normal exothermic ion-molecule reactions we have assumed that the total rate coefficient is unchanged for deuterium analogs, e.g., $k_1 = k_2 + k_3$, and have also assumed statistical branching ratios, e.g., $k_2 = k_3 = k_1/2$. The first assumption is a reasonable one, since for all exothermic ion-molecule reactions in our model there is no significant activation energy barrier, and only small adjustments in rate due to reduced mass effects exist. The existence of a barrier, however, normally leads to important isotopic differences in rate. The second assumption is made for simplicity and lack of experimental evidence.

Still nowadays, it is common sense to consider gas phase reactions irrelevant in influencing the degree of deuteration of interstellar complex organic molecules.

Kinetic isotope effect

Kinetic isotope effect (KIE) is the change in the reaction rate of a chemical reaction when one of the atoms in the reactants is replaced by one of its isotopes. Formally, it is the ratio of rate constants for the reactions involving the light (k_L) and the heavy (k_H) isotopically substituted reactants (from Wikipedia)



A primary kinetic isotope effect may be found when a bond to the isotopically-labeled atom is being formed or broken; in these cases

$$k_H / k_D >> 1$$

A secondary kinetic isotope effect is observed when no bond to the isotopically-labeled atom in the reactant is broken or formed. Secondary kinetic isotope effects tend to be much smaller than primary kinetic isotope effects; it can be "normal"

$$k_H / k_D > 1$$

or "inverse"

$$k_H / k_D < 1$$

Product branching ratios (BR)

-direct reactions (abstraction mechanism where a new X-H bond is formed) the H-products are favored (because of kinematics)

- indirect reactions (addition/insertion reactions where both an X-H or an X-D bond can be formed) the D-products are favored (the X-D bond is stronger than the X-H bond)

after 30 years from the paper by Millar, Bennet & Herbst it is time to move on

Deuteration of interstellar complex organic molecules in gas-phase chemistry

Case 1: formamide

A&A 590, L6 (2016)
DOI: 10.1051/0004-6361/201628612
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Astronomy & Astrophysics

LETTER TO THE EDITOR

IRAS16293-2422B

The ALMA-PILS survey: First detections of deuterated formamide and deuterated isocyanic acid in the interstellar medium

A. Coutens[1], J. K. Jørgensen[2], M. H. D. van der Wiel[2], H. S. P. Müller[3], J. M. Lykke[2], P. Bjerkeli[2,4], T. L. Bourke[5], H. Calcutt[2], M. N. Drozdovskaya[6], C. Favre[7], E. C. Fayolle[8], R. T. Garrod[9], S. K. Jacobsen[2], N. F. W. Ligterink[6], K. I. Öberg[8], M. V. Persson[6], E. F. van Dishoeck[6,10], and S. F. Wampfler[2]

Assuming that the deuteration of formaldehyde in the region probed by the ALMA observations of formamide is similar to the value derived with single-dish observations (~15%, Loinard et al. 2000), we can discuss the possibility for the gas-phase formation mechanism proposed by Barone et al. (2015), $H_2CO + NH_2 \rightarrow NH_2CHO + H$. According to this reaction, the deuterated form NHDCHO would result from the reaction between NHD and H_2CO, while NH_2CDO would form from NH_2 and HDCO. We would consequently expect a higher deuteration for NH_2CDO, compared to the observations, unless the reaction between NH_2 and HDCO leads more efficiently to NH_2CHO and D, compared to NH_2CDO and H. Theoretical or experimental studies of the branching ratios of these reactions would be needed to rule out this scenario. The determination of the $HDCO/H_2CO$ ratio from the PILS survey is also necessary. Nev-

Case 1: formamide

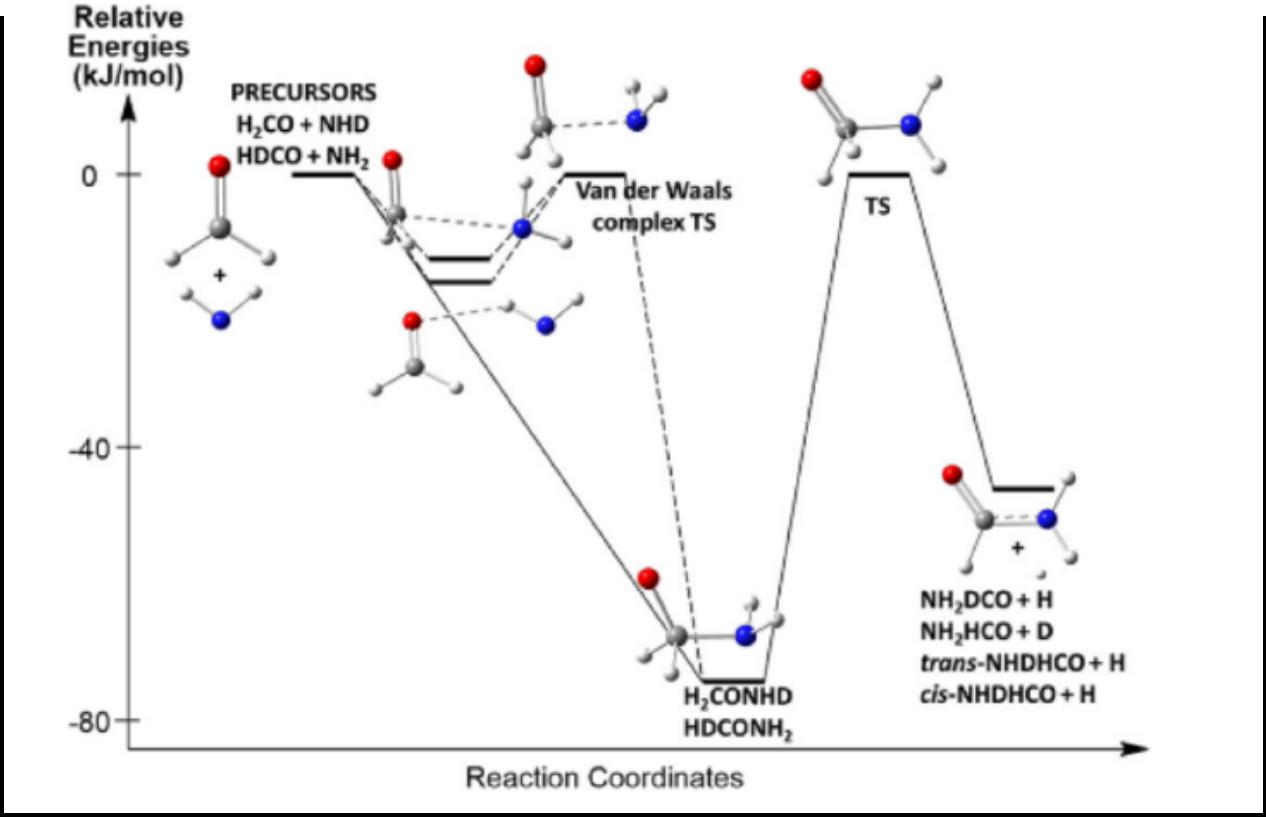
Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

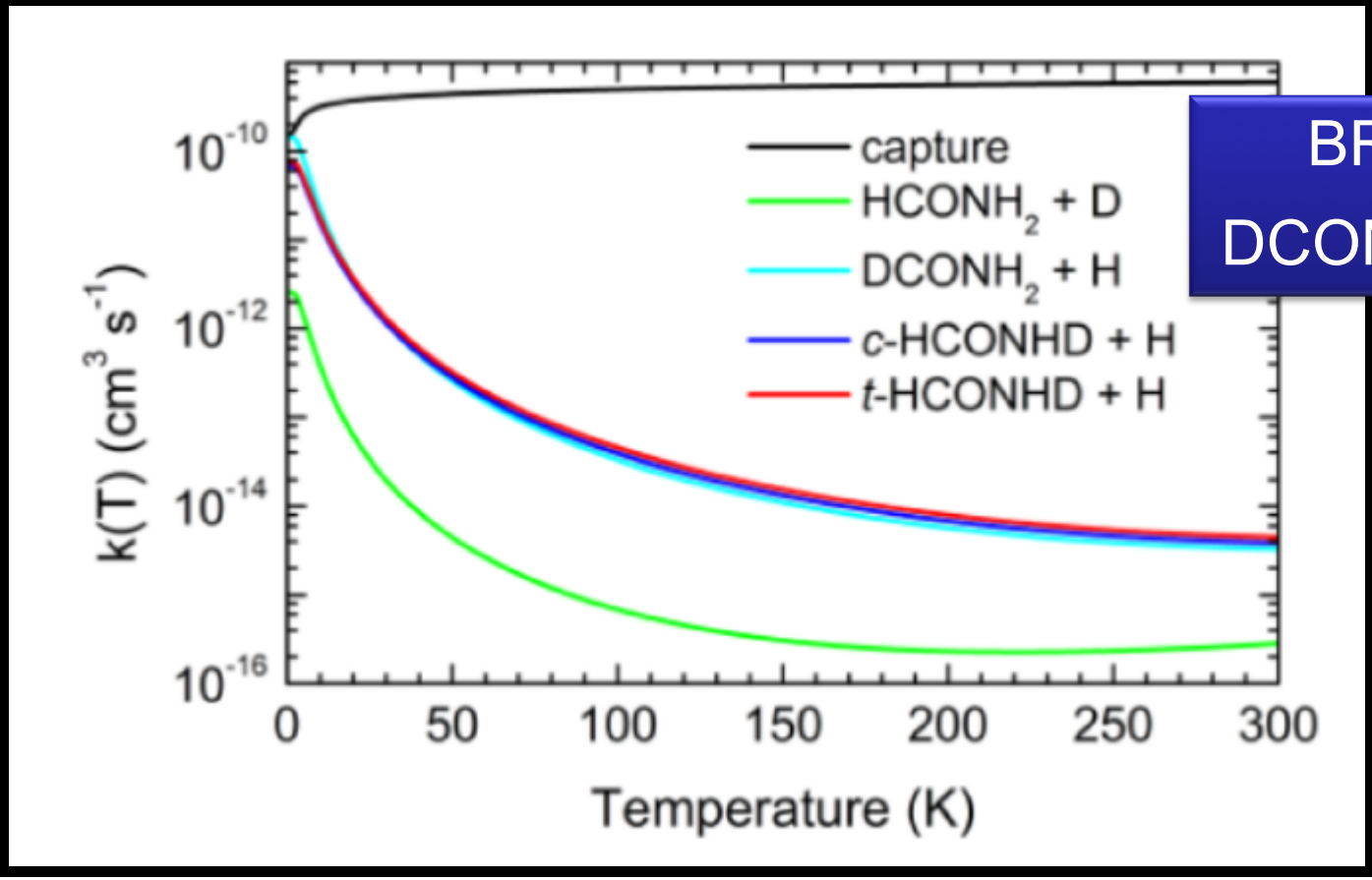
MNRAS **468,** L1–L5 (2017)
Advance Access publication 2017 January 25

doi:10.1093/mnrasl/slx012

New quantum chemical computations of formamide deuteration support gas-phase formation of this prebiotic molecule

D. Skouteris,[1★] F. Vazart,[1★] C. Ceccarelli,[2,3★] N. Balucani,[3,4] C. Puzzarini[3,5] and V. Barone[1]





BR as expected

$DCONH_2$ >> $HCONH_2$

KIE

$k_H/k_D \approx 3$

Reaction	A ($\times 10^{-16}$ cm^{3}s^{-1})	β	γ (K)	k(T = 10 K)	k(T = 60 K) ($\times 10^{-13}$ cm^{3}s^{-1})	k(T = 100 K) ($\times 10^{-13}$ cm^{3}s^{-1})
(1) NH_2 + HDCO → $DCONH_2$ + H	20.7	−2.75	4.34	153	1.60	0.41
(2) NH_2 + HDCO → $HCONH_2$ + D	1.08	−2.15	0.96	1.49	0.03	0.01
(3) NHD + H_2CO → trans-HCONHD + H	30.7	−2.63	5.05	141	1.93	0.52
(4) NHD + H_2CO → cis-HCONHD + H	26.2	−2.64	5.04	126	1.69	0.45
(5) NH_2 + H_2CO → $HCONH_2$ + H	77.9	−2.56	4.88	287	4.41	1.23

Skouteris et al. MNRAS 2017

Our prediction: the deuteration of formamide synthesized in the gas-phase will be 3 times smaller than that of the parent species NH_2 and H_2CO

(i) *$DCONH_2/HCONH_2$ and $HCONHD/HCONH_2$ abundance ratios smaller than $HDCO/H_2CO$.* The values in Table 2 show that there is a factor of 3 difference in the rates of formation of H- against D-formamide. Therefore, the deuteration of formamide synthesized in the gas phase will be three times smaller than that of the mother molecules NH_2 and H_2CO. No observations

A few months later: the best estimate $HDCO/H_2CO$ is 3 times higher than NH_2CDO/NH_2CHO

Astronomy & Astrophysics manuscript no. persson_formaldehyde_v1.9
November 17, 2017
©ESO 2017

The ALMA-PILS survey: Formaldehyde deuteration in warm gas on small scales toward IRAS 16293–2422 B

M. V. Persson[1,2], J. K. Jørgensen[3], H. S. P. Müller[4], A. Coutens[5], E. F. van Dishoeck[2,6], V. Taquet[7], H. Calcutt[2], M. H. D. van der Wiel[8], T. L. Bourke[9], and S. Wampfler[10]

2% assuming a standard $^{12}C/^{13}C$ ratio of 68. Skouteris et al. (2017) also calculated the rate coefficients of the reactions producing deuterated formamide. Consequently, a comparison of the deuteration of formamide and formaldehyde can help determine if this gas phase pathway (for formamide) is possible or if it has to be ruled out in this source. According to the respective rate coefficients determined for NH_2CHO and NH_2CDO by Skouteris et al., the $HDCO/H_2CO$ ratio should be three times higher than the NH_2CDO/NH_2CHO ratio if this gas-phase reaction occurs. At similar spatial scales, the best estimate $HDCO/H_2CO$ ratio is 6.5±1 %, i.e. approximately three times higher than the NH_2CDO/NH_2CHO ratio. Thus, a gas phase formation pathway

A&A 605, L3 (2017)
DOI: 10.1051/0004-6361/201731249
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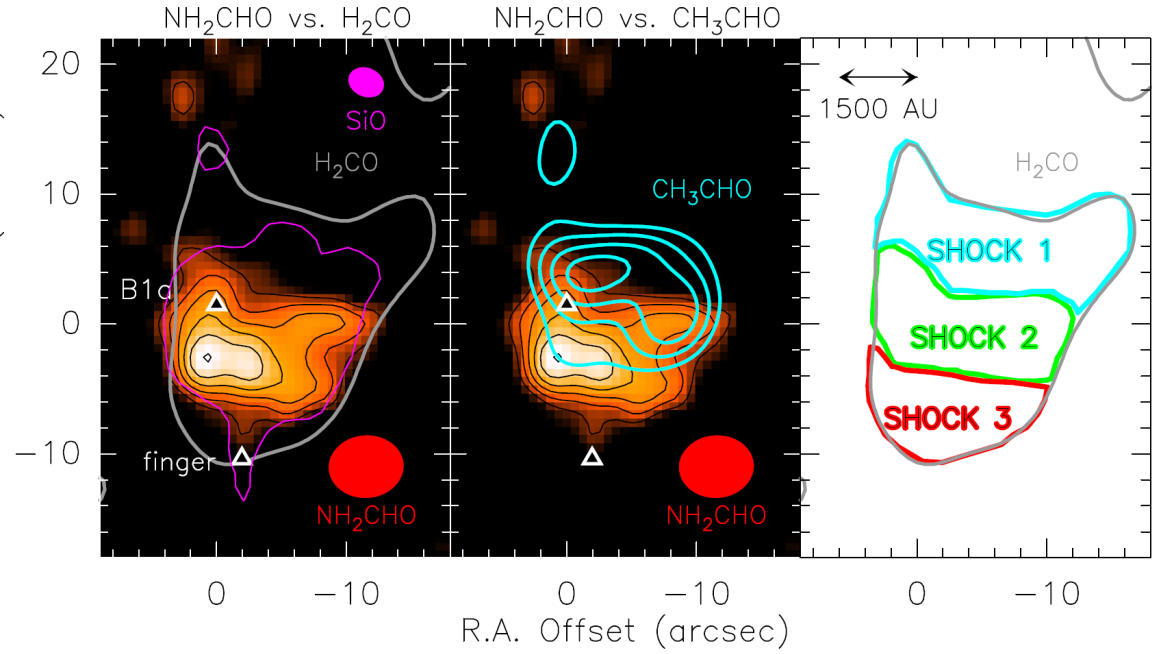
Astronomy & Astrophysics

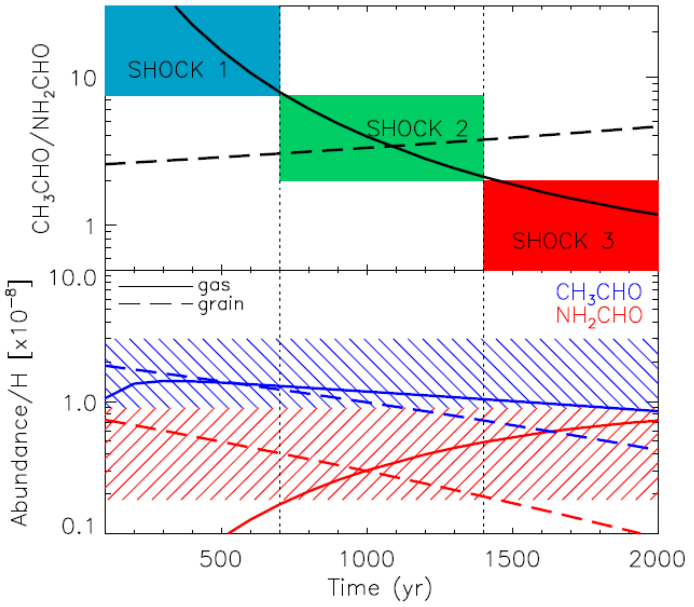
Letter to the Editor

Seeds of Life in Space (SOLIS)

II. Formamide in protostellar shocks: Evidence for gas-phase formation★

C. Codella[1], C. Ceccarelli[2,1], P. Caselli[3], N. Balucani[4,1], V. Barone[5], F. Fontani[1], B. Lefloch[2], L. Podio[1], S. Viti[6], S. Feng[3], R. Bachiller[7], E. Bianchi[1,8], F. Dulieu[9], I. Jiménez-Serra[10], J. Holdship[6], R. Neri[11], J. E. Pineda[3], A. Pon[12], I. Sims[13], S. Spezzano[3], A. I. Vasyunin[3,14], F. Alves[3], L. Bizzocchi[3], S. Bottinelli[15,16], E. Caux[15,16], A. Chacón-Tanarro[3], R. Choudhury[3], A. Coutens[6], C. Favre[1,2], P. Hily-Blant[2], C. Kahane[2], A. Jaber Al-Edhari[2,17], J. Laas[3], A. López-Sepulcre[11], J. Ospina[2], Y. Oya[18], A. Punanova[3], C. Puzzarini[19], D. Quenard[10], A. Rimola[20], N. Sakai[21], D. Skouteris[5], V. Taquet[22,1], L. Testi[23,1], P. Theulé[24], P. Ugliengo[25], C. Vastel[15,16], F. Vazart[5], L. Wiesenfeld[2], and S. Yamamoto[18,26]





Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

Case 2: dimethyl ether

MNRAS **482,** 3567–3575 (2019)
Advance Access publication 2018 October 27
doi:10.1093/mnras/sty2903

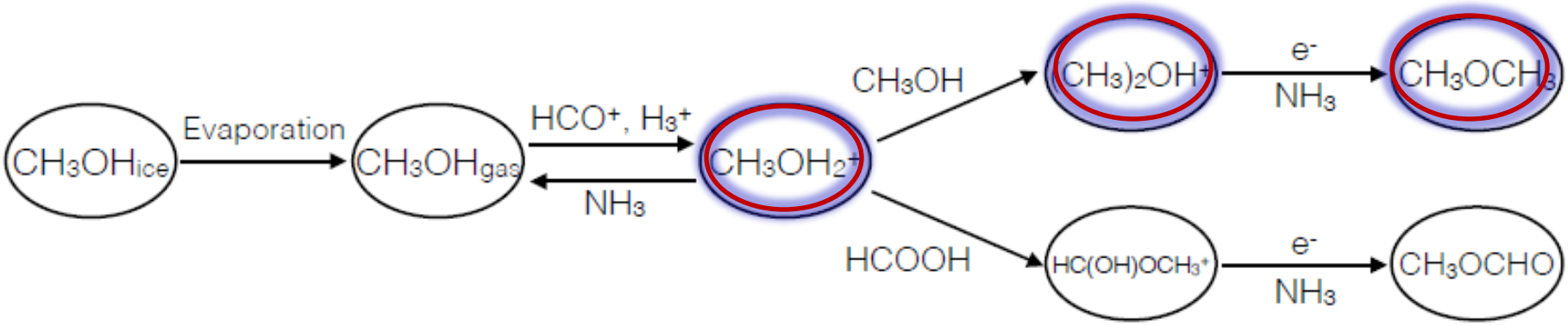
Interstellar dimethyl ether gas-phase formation: a quantum chemistry and kinetics study

Dimitrios Skouteris,[1]★ Nadia Balucani,[2,3,4]† Cecilia Ceccarelli,[3]†
Noelia Faginas Lago,[2] Claudio Codella,[3,4] Stefano Falcinelli[5] and Marzio Rosi[5]†

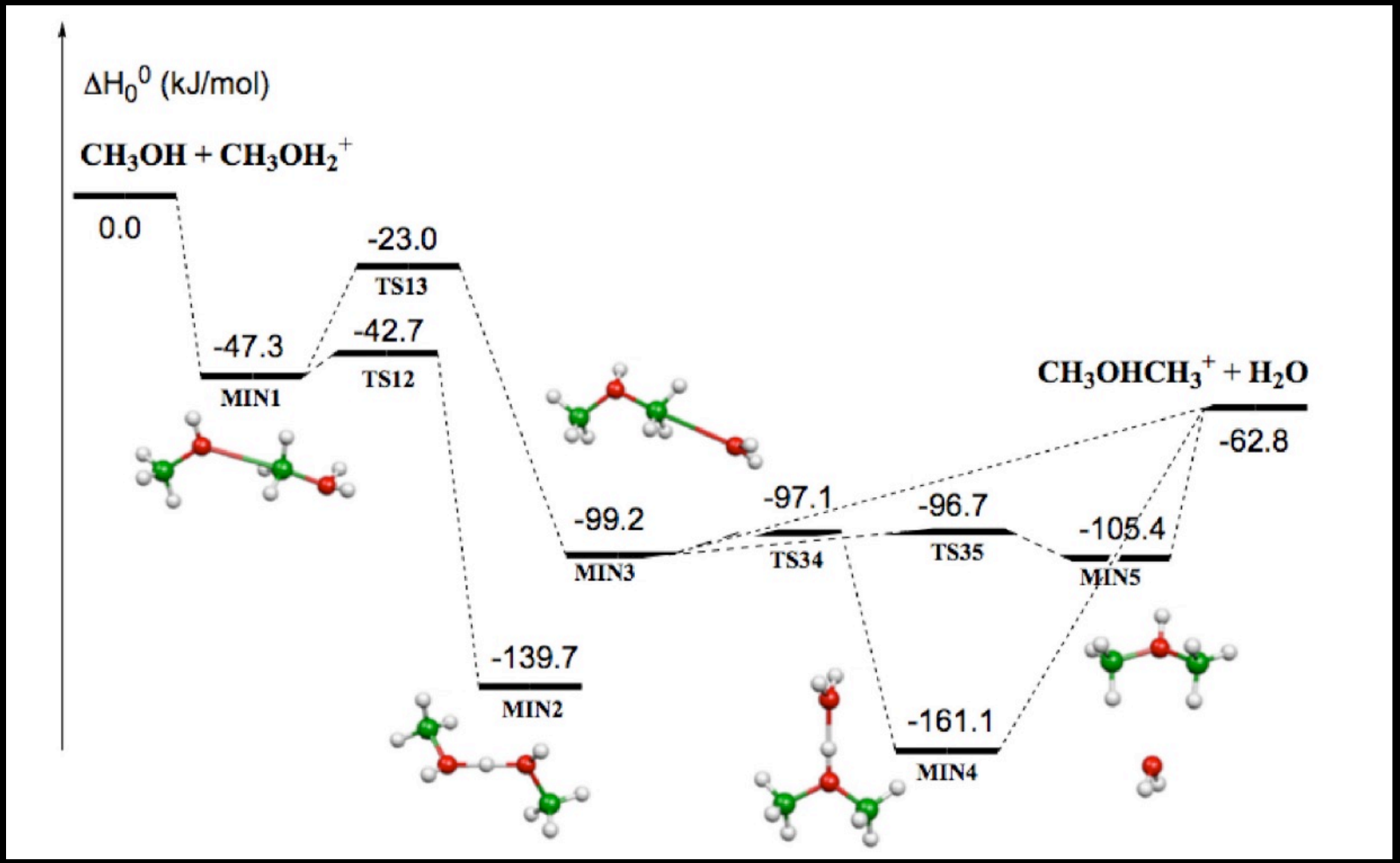
FORMATION AND RECONDENSATION OF COMPLEX ORGANIC MOLECULES DURING PROTOSTELLAR LUMINOSITY OUTBURSTS

VIANNEY TAQUET[1], EVA S. WIRSTRÖM[2] AND STEVEN B. CHARNLEY[3]

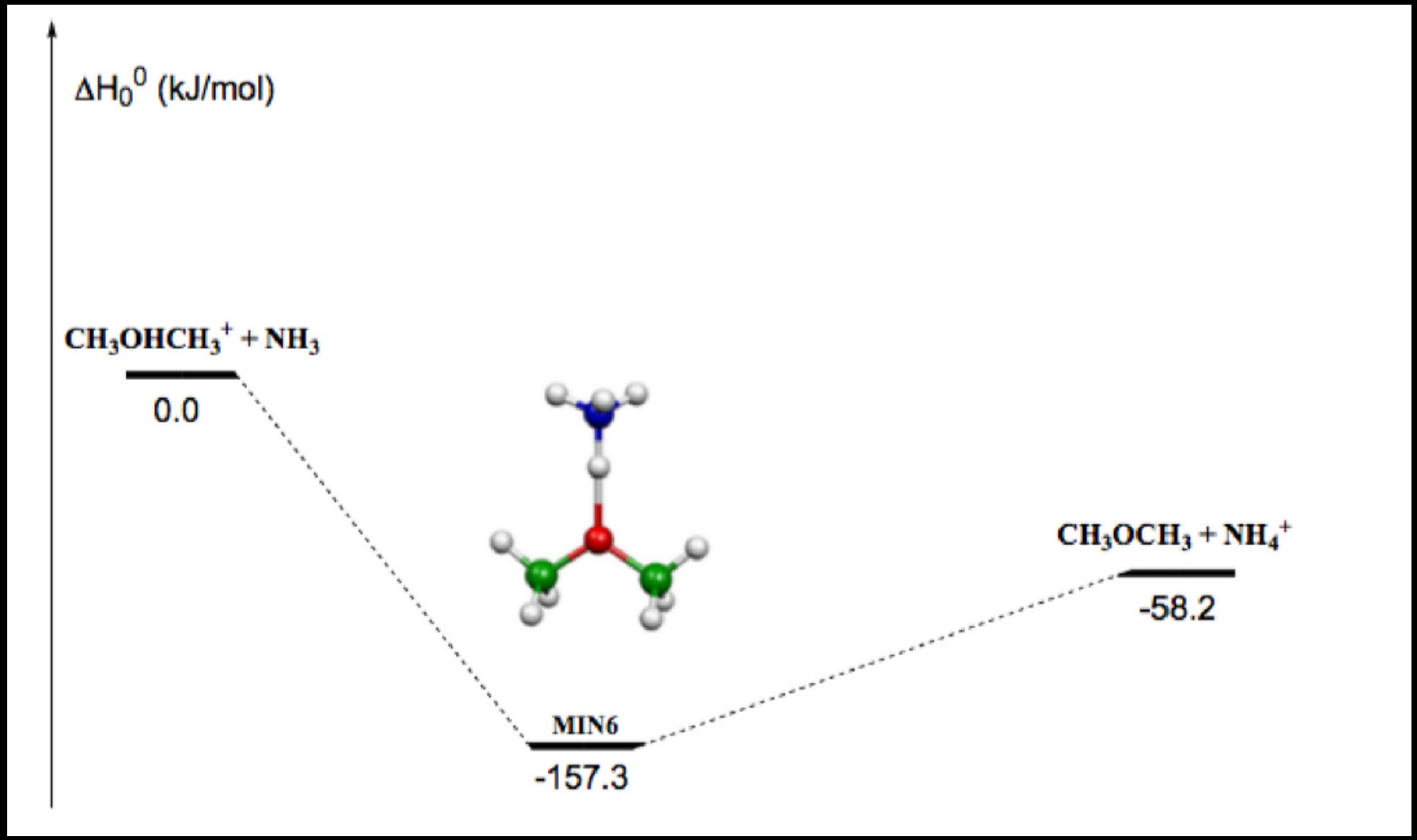
ApJ 2016



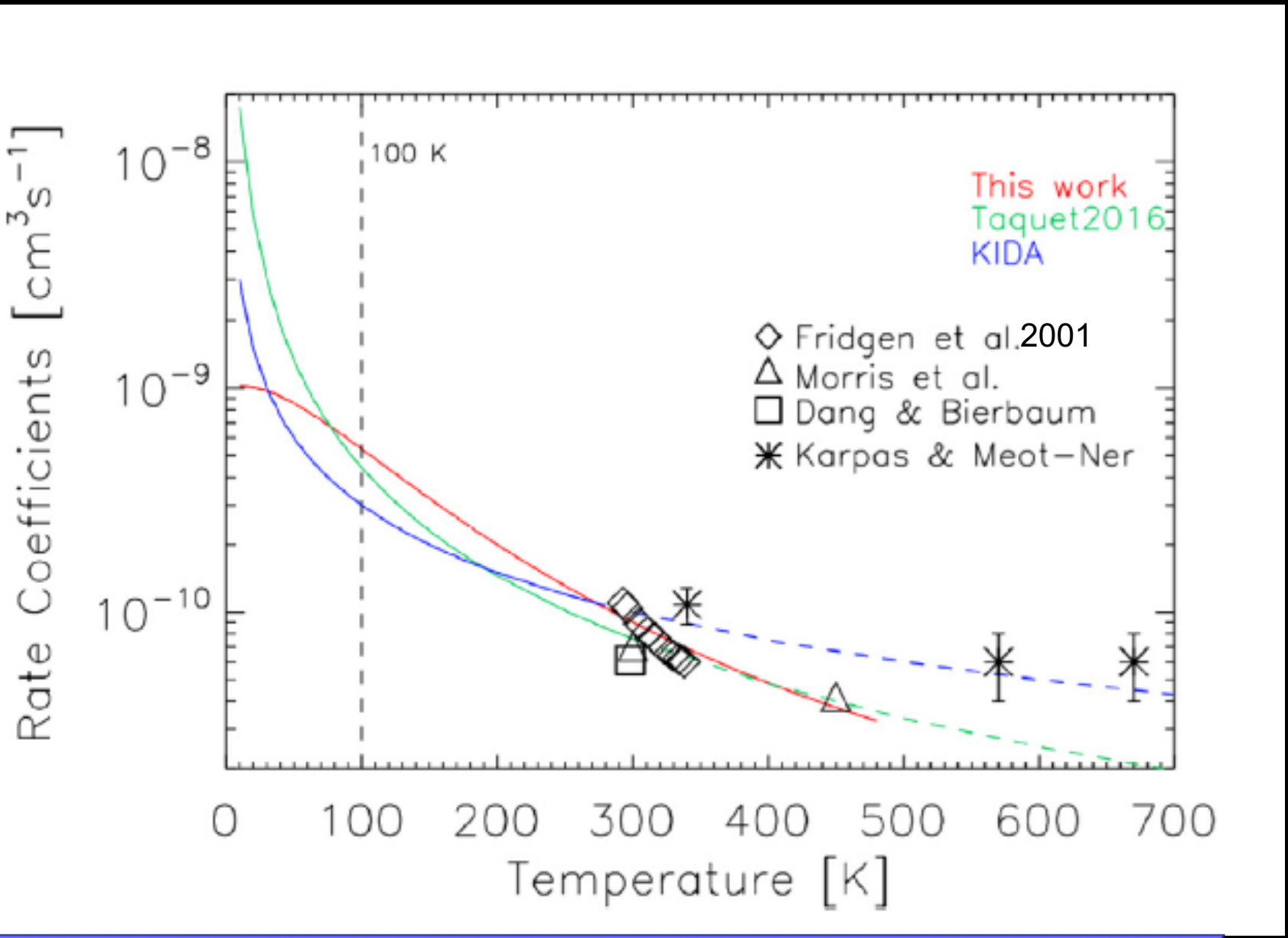
Skouteris et al. MNRAS 2019



Skouteris et al. MNRAS 2019



Skouteris et al. MNRAS 2019



Our results fully validate the mechanism proposed by Taquet et al (2016)

Astronomy & Astrophysics manuscript no. ms
August 28, 2018
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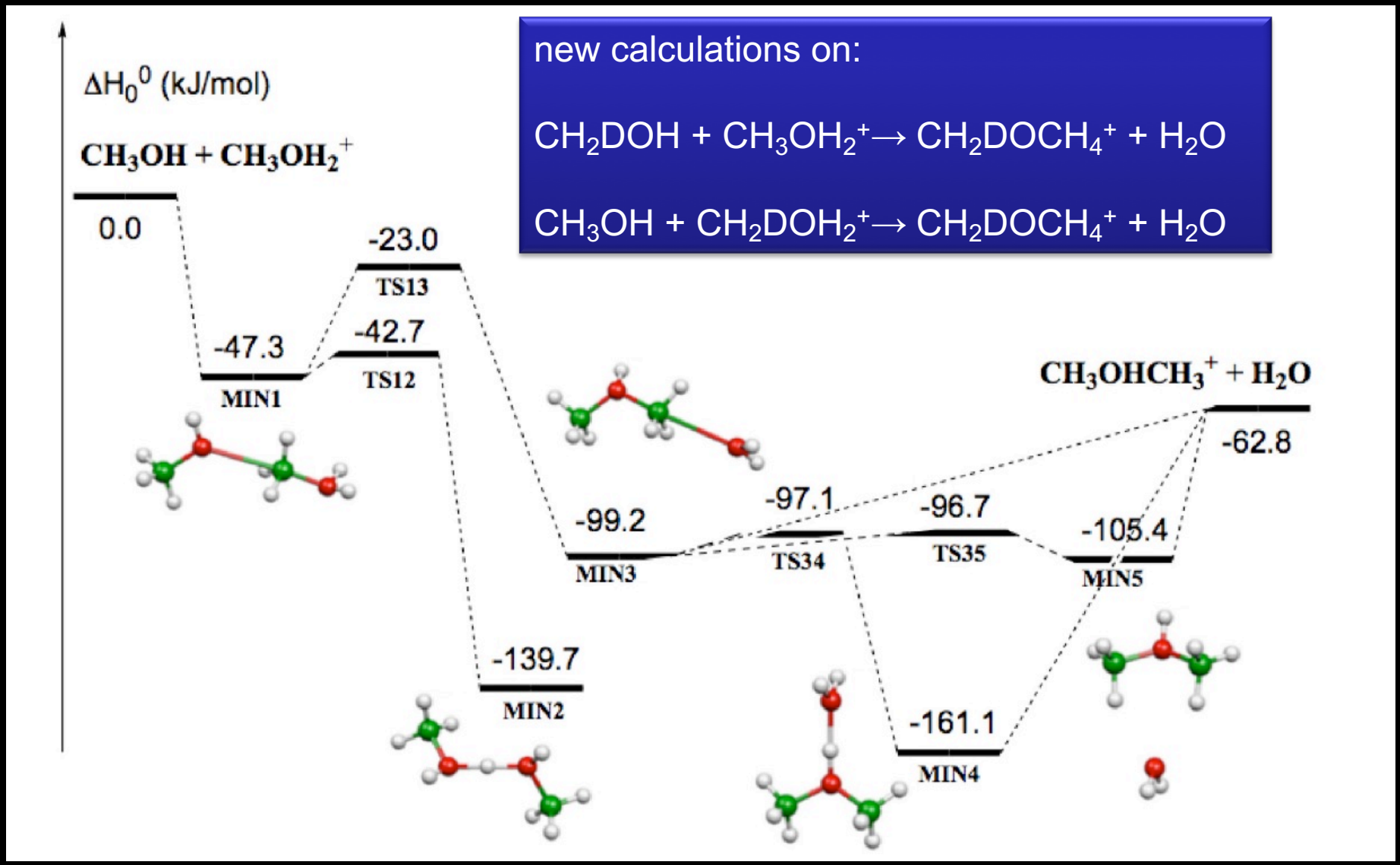
The ALMA-PILS survey: Isotopic composition of oxygen-containing complex organic molecules toward IRAS 16293–2422B

J. K. Jørgensen[1], H. S. P. Müller[2], H. Calcutt[1], A. Coutens[3], M. N. Drozdovskaya[4], K. I. Öberg[5] M. V. Persson[6], V. Taquet[7], E. F. van Dishoeck[8,9], and S. F. Wampfler[4]

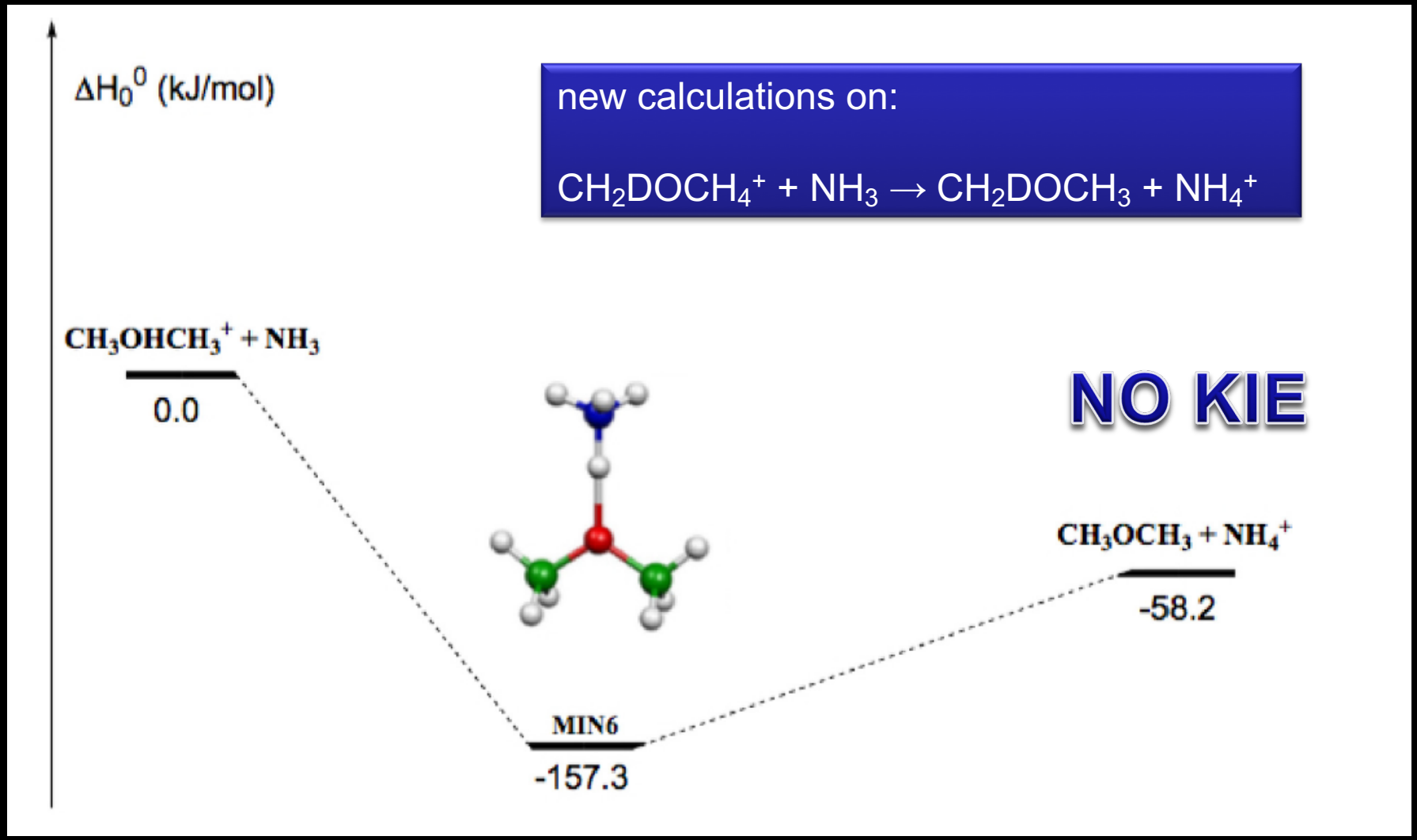
Species		[X/CH_3OH]	[D/H] ratios			
			Single-dish (~ 1000 AU)	Interferometric (~ 50 AU)	Model (Taquet et al. 2014) 1.1×10^5 yr	Model (Taquet et al. 2014) 2.0×10^5 yr
Formaldehyde	H_2CO	19%	7.5%[f]	3%[a]	2.1%	0.21%
Methanol	CH_3OH	—	1.8–5.9%[f,g]	2%[b]	3.5–1.8%	0.28–0.17%
Ethanol	CH_3CH_2OH	2.3%	...	5%[b]	0.63–9.7%[m]	0.090%–0.12%[m]
Dimethyl ether	CH_3OCH_3	2.4%	3%[j]	4%[b]	3.7%	0.10%
Glycolaldehyde	CH_2OHCHO	0.34%	...	5%[c]	6.5–13%	0.22–0.38%
Methyl formate	CH_3OCHO	2.6%	6%[h]	6%[b]	7–9%	0.25–0.22%
Acetaldehyde	CH_3CHO	1.2%	...	8%[b]	9.2%[l]	0.068%[l]
Ketene	CH_2CO	0.48%	...	2%[b]	0.25%	0.015%
Formic acid	HCOOH	0.56%	...	2%[b]	2.3–1.0%[k]	0.58–0.66%[k]
Isocyanic acid	HNCO	0.27%	...	1%[d]	...	...
Formamide	NH_2CHO	0.10%	...	2%[d]	...	...
Water	H_2O	...	0.25%[i]	0.046%[e]	1.2%	0.33%

Skouteris et al. MNRAS 2019



Balucani, Ceccarelli, Skouteris, Rosi (to be submitted)

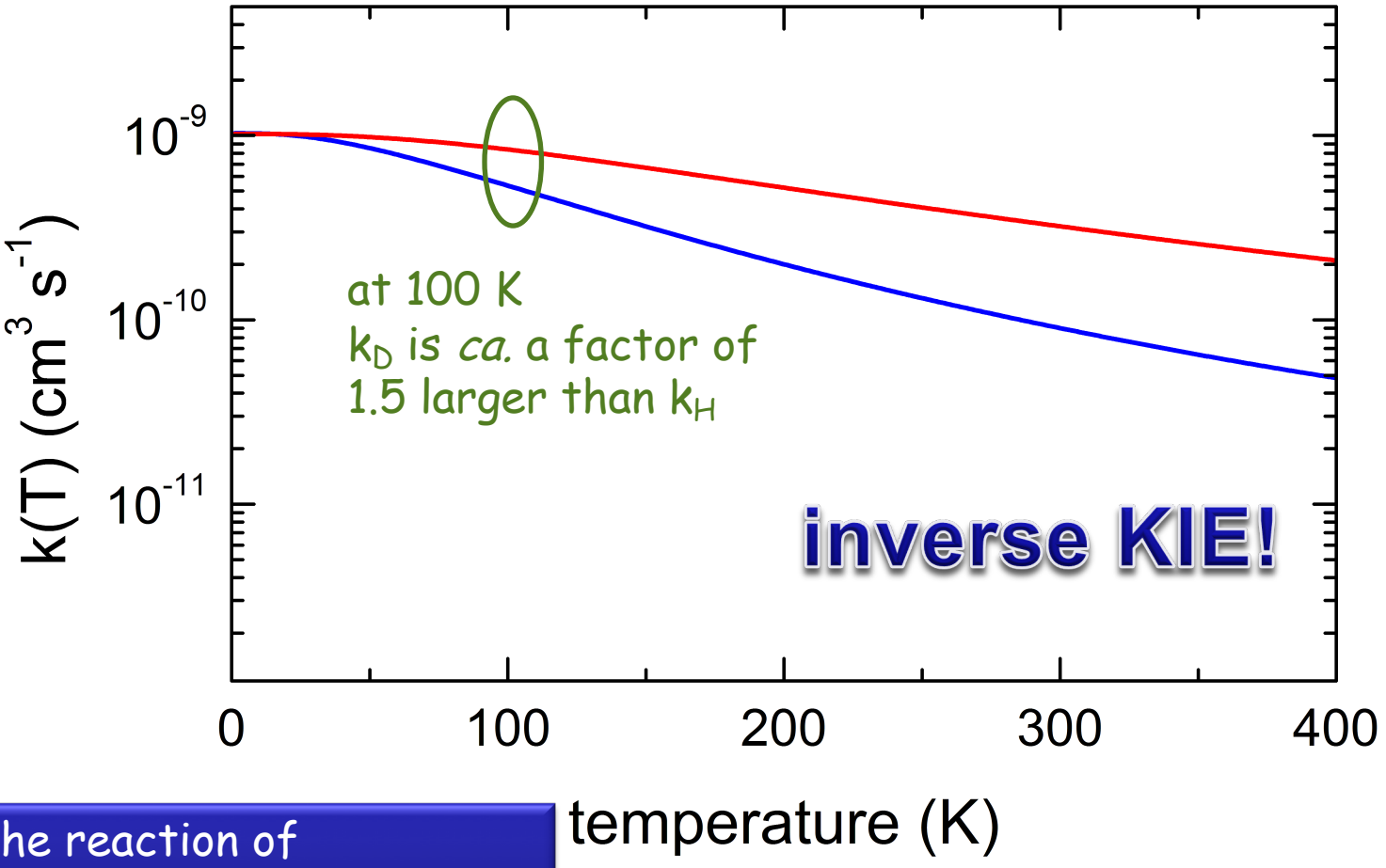
Skouteris et al. MNRAS 2019



Balucani, Ceccarelli, Skouteris, Rosi (to be submitted)

$CH_3OH + CH_3OH_2^+ \rightarrow CH_3OCH_4^+ + H_2O$

$CH_2DOH + CH_3OH_2^+ / CH_3OH + CH_2DOH_2^+ \rightarrow CH_2DOCH_4^+ + H_2O$



This time, the reaction of deuterated species are faster than those involving all protium reactants!

Balucani, Ceccarelli, Skouteris, Rosi (to be submitted)

$$\frac{v_{CH_2DOCH_3}}{v_{CH_3OCH_3}} = \frac{\frac{d[CH_2DOCH_3]}{dt}}{\frac{d[CH_3OCH_3]}{dt}} = \frac{k'_D[CH_2DOH][CH_3OH_2^+] + k''_D[CH_3OH][CH_2DOH_2^+]}{k_H[CH_3OH][CH_3OH_2^+]}$$

$$k'_D \cong k''_D \quad (= k_D)$$

$$[CH_2DOH] \approx 0.071[CH_3OH]$$

PILS 2018

$$[CH_2DOH_2^+] \approx 0.071[CH_3OH_2^+]$$

$$\frac{v_{CH_2DOCH_3}}{v_{CH_3OCH_3}} = \frac{k_D 0.071[CH_3OH][CH_3OH_2^+] + k_D[CH_3OH]0.071[CH_3OH_2^+]}{k_H[CH_3OH][CH_3OH_2^+]} = \frac{k_D \times 0.142}{k_H}$$

with no KIE

$k_D = k_H$

$[CH_2DOCH_3]$ 14% of $[CH_3OCH_3]$ at all T

$$\frac{v_{CH_2DOCH_3}}{v_{CH_3OCH_3}} = \frac{\frac{d[CH_2DOCH_3]}{dt}}{\frac{d[CH_3OCH_3]}{dt}} = \frac{k'_D[CH_2DOH][CH_3OH_2^+] + k''_D[CH_3OH][CH_2DOH_2^+]}{k_H[CH_3OH][CH_3OH_2^+]}$$

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PILS 2018

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with no KIE

$k_D = k_H$

$[CH_2DOCH_3]$ 14% of $[CH_3OCH_3]$ at all T

with KIE

T (K)	k_D/k_H	$[CH_2DOCH_3] / [CH_3OCH_3]$
50	1.1	0.16
70	1.3	0.18
100	1.6	0.22
125	1.8	0.26
150	2.1	0.30
200	2.6	0.36

Astronomy & Astrophysics manuscript no. ms
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The ALMA-PILS survey: Isotopic composition of oxygen-containing complex organic molecules toward IRAS 16293–2422B

J. K. Jørgensen[1], H. S. P. Müller[2], H. Calcutt[1], A. Coutens[3], M. N. Drozdovskaya[4], K. I. Öberg[5] M. V. Persson[6], V. Taquet[7], E. F. van Dishoeck[8,9], and S. F. Wampfler[4]

Species	N [cm^{-2}]	$N/N_{\rm main}$[a]	$N_{\rm corr}/N_{\rm main}$[a]
	Methanol		
CH_3OH[b]	1.0×10^{19}	...	...
CH_2DOH	7.1×10^{17}	0.071	0.024
CH_3OD	1.8×10^{17}	0.018	0.018

Astronomy & Astrophysics manuscript no. ms
August 28, 2018
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The ALMA-PILS survey: Isotopic composition of oxygen-containing complex organic molecules toward IRAS 16293–2422B

J. K. Jørgensen[1], H. S. P. Müller[2], H. Calcutt[1], A. Coutens[3], M. N. Drozdovskaya[4], K. I. Öberg[5] M. V. Persson[6], V. Taquet[7], E. F. van Dishoeck[8,9], and S. F. Wampfler[4]

Species	N [cm^{-2}]	$N/N_{\rm main}$[a]	$N_{\rm corr}/N_{\rm main}$[a]
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CH_2DOH	7.1×10^{17}	0.071	0.024
CH_3OD	1.8×10^{17}	0.018	0.018
	Dimethyl ether		
CH_3OCH_3	2.4×10^{17}	...	...
$^{13}CH_3OCH_3$	1.4×10^{16}	0.029 (1/34)[d]	
asym-CH_2DOCH_3	4.1×10^{16}	0.17	0.043
sym-CH_2DOCH_3	1.2×10^{16}	0.050	0.025

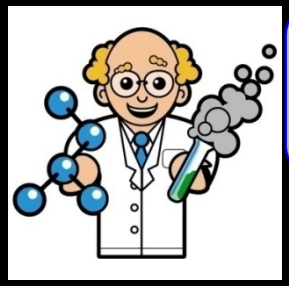
tot=0.22 in excellent agreement with our predictions at 100-125 K

two successful examples where gas-phase formation routes are totally in line with the abundances of the partially deuterated isotopologues

we are now applying this method to the case of the ethanol tree, dimethyl ether/methyl formate, acetaldehyde
(F. Vazart, stay tuned)

KIE in ice chemistry? Sure, J. Enrique-Romero is working on it

The chemical evolution of the interstellar medium: how do we study it?



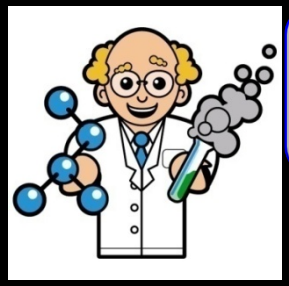
Laboratory experiments

+ quantum calculations

modelling

observations

The chemical evolution of the interstellar medium: how do we study it?



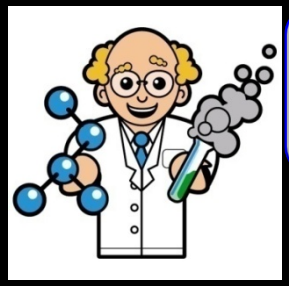
Laboratory experiments

+ quantum calculations

observations

so far, we have seen what chemistry can do for astronomy

The chemical evolution of the interstellar medium: how do we study it?



Laboratory experiments

+ quantum calculations

but can astronomy do something for chemistry?

observations

let's go back to the OH + CH_3OH reaction

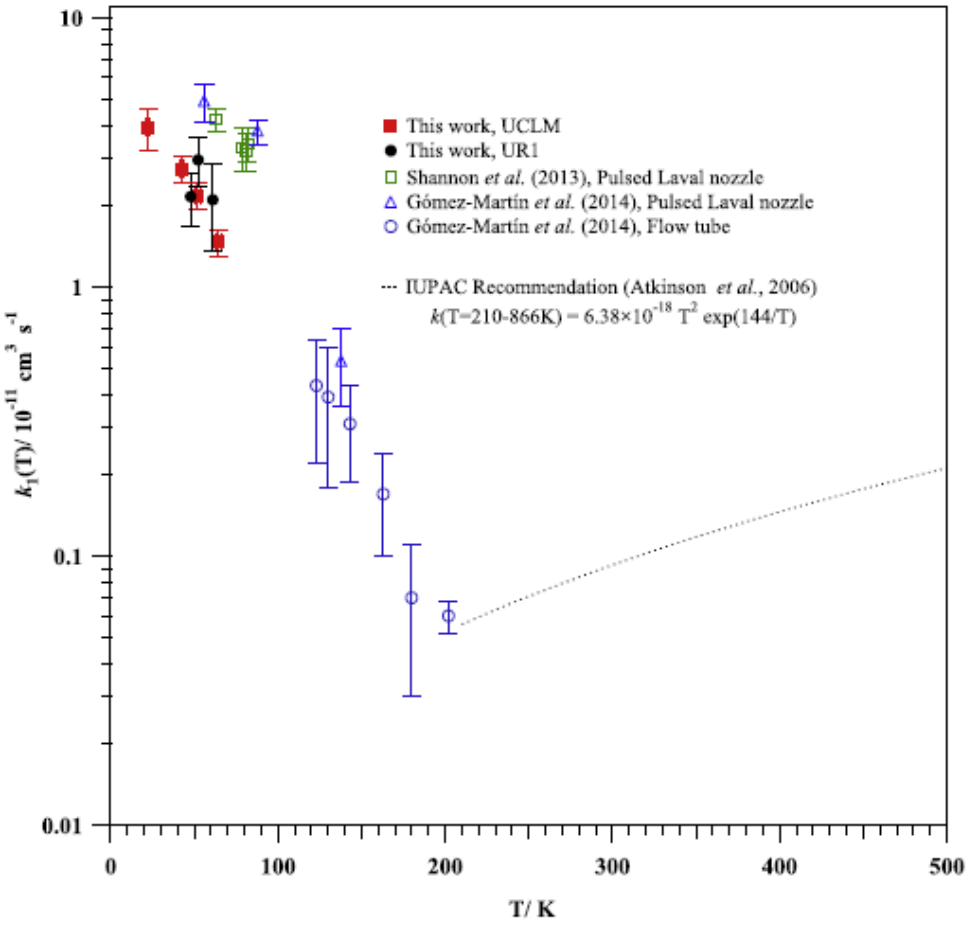


Figure 3. Rate coefficients for the reaction of OH with CH_3OH as a function of temperature. Filled symbols are kinetic data presented in this work and empty symbols are values reported in the literature.

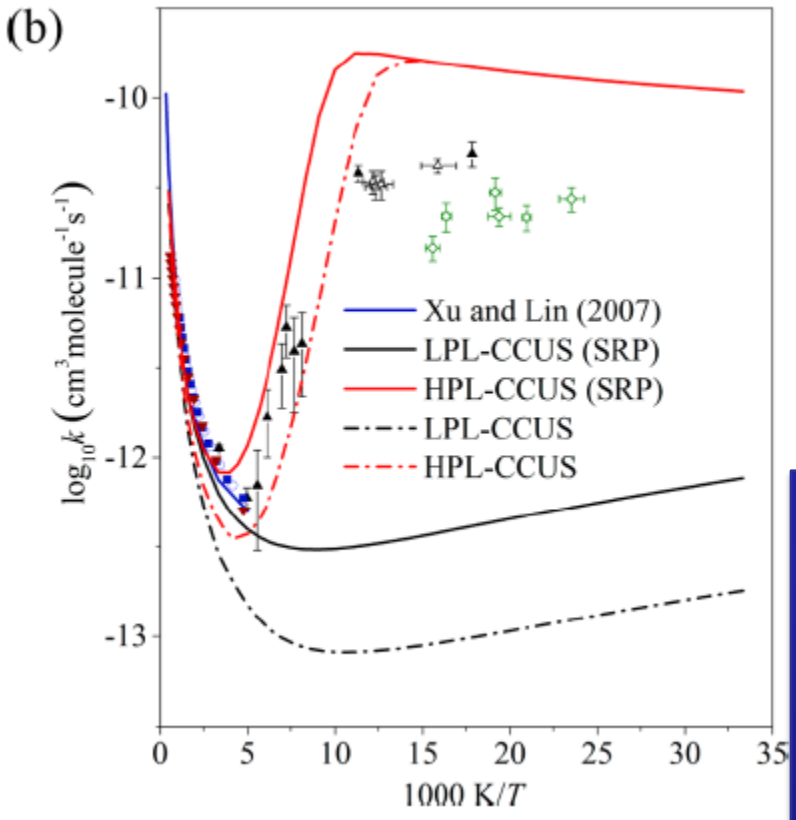
according to the CRESU experiments the effect of the prereactive complex below 200 K is huge

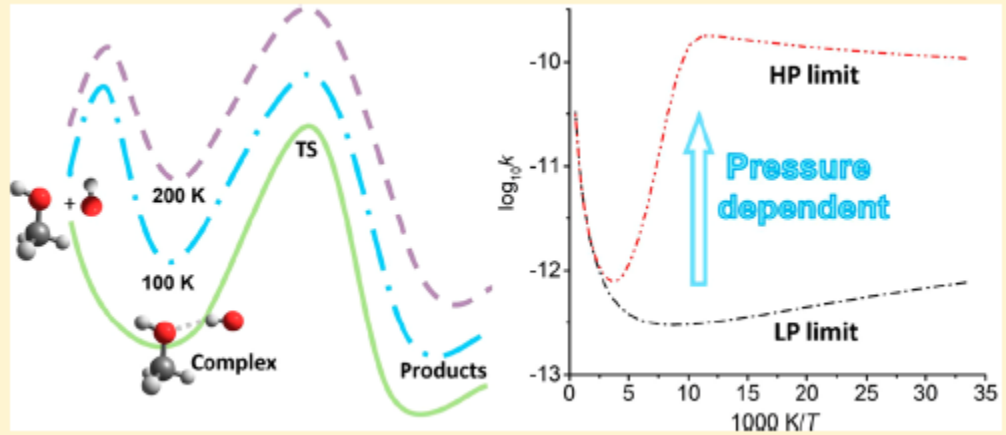
maybe too much..?!

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
Cite This: J. Am. Chem. Soc. 2018, 140, 2906−2918
pubs.acs.org/JACS

Kinetics of the Methanol Reaction with OH at Interstellar, Atmospheric, and Combustion Temperatures

Lu Gem Gao,[†] Jingjing Zheng,[‡] Antonio Fernández-Ramos,[∥] Donald G. Truhlar,[*,§] and Xuefei Xu[*,†]





a recent and accurate theoretical study confirmed the effect of tunneling at low T, but it is less important than what experiments suggest (some collisional stabilization has been invoked)

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Cite this: *Phys. Chem. Chem. Phys.*, 2019, 21, 6942

Gas-phase reactivity of CH_3OH toward OH at interstellar temperatures (11.7–177.5 K): experimental and theoretical study†

Antonio J. Ocaña, [a] Sergio Blázquez, [a] Alexey Potapov, [b] Bernabé Ballesteros, [ac] André Canosa, [d] María Antiñolo, [c] Luc Vereecken, [*e] José Albaladejo [ac] and Elena Jiménez [*ac]

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Cite this: *Phys. Chem. Chem. Phys.*, 2018, 20, 25951

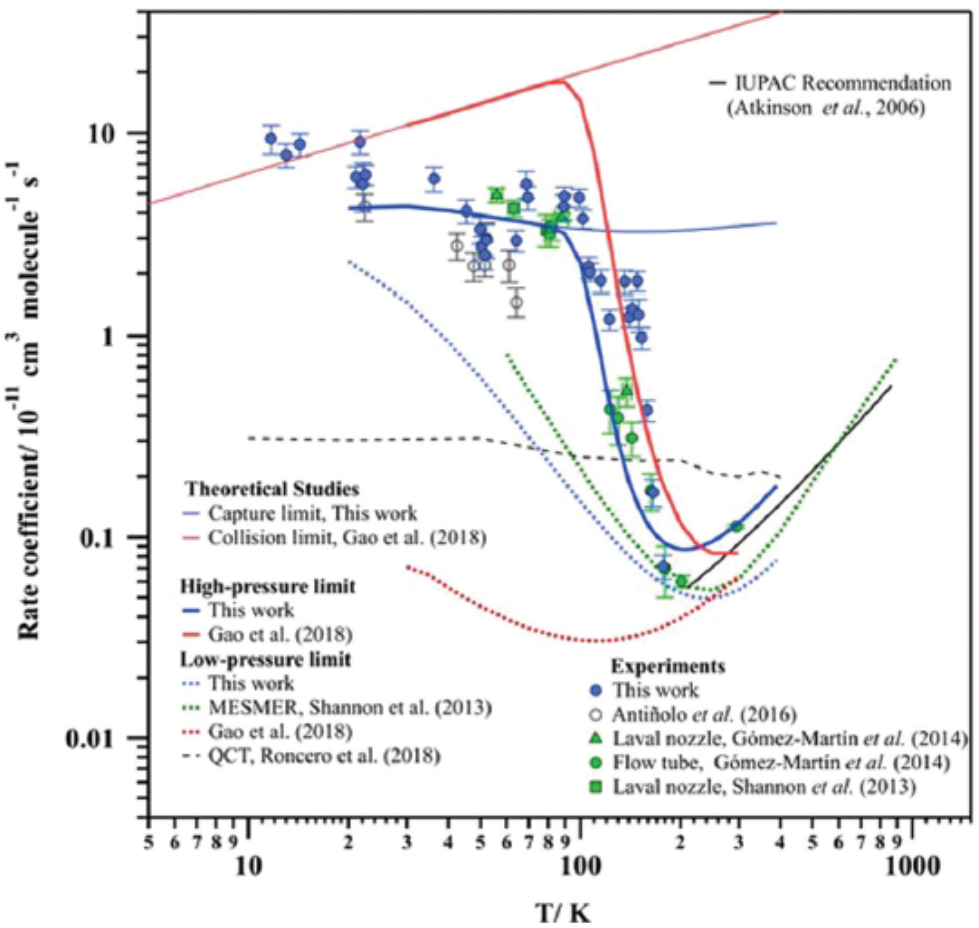
Low temperature reaction dynamics for CH_3OH + OH collisions on a new full dimensional potential energy surface†

Octavio Roncero, [*a] Alexandre Zanchet‡ [b] and Alfredo Aguado [c]

A master equation simulation for the $^{\bullet}OH$ + CH_3OH reaction

Cite as: J. Chem. Phys. 150, 084105 (2019); https://doi.org/10.1063/1.5081827
Submitted: 16 November 2018 . Accepted: 01 February 2019 . Published Online: 25 February 2019

Thanh Lam Nguyen, Branko Ruscic, and John F. Stanton



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Quantum Roaming in the Complex-Forming Mechanism of the Reactions of OH with Formaldehyde and Methanol at Low Temperature and Zero Pressure: A Ring Polymer Molecular Dynamics Approach

Pablo del Mazo-Sevillano, Alfredo Aguado, Elena Jiménez, Yury V. Suleimanov and Octavio Roncero*

Cite This: *J. Phys. Chem. Lett.* 2019, 10, 8, 1900-1907
Publication Date: April 2, 2019
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Zero- and High-Pressure Mechanisms in the Complex Forming Reactions of OH with Methanol and Formaldehyde at Low Temperatures

Fedor Naumkin, Pablo del Mazo-Sevillano, Alfredo Aguado, Yury V. Suleimanov and Octavio Roncero*

Cite This: *ACS Earth Space Chem.* 2019, 3, 7, 1158-1169
Publication Date: May 14, 2019
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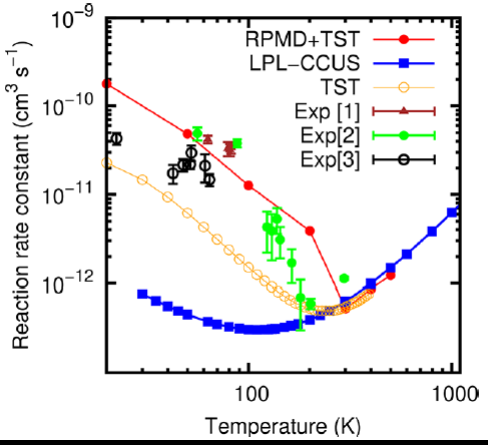
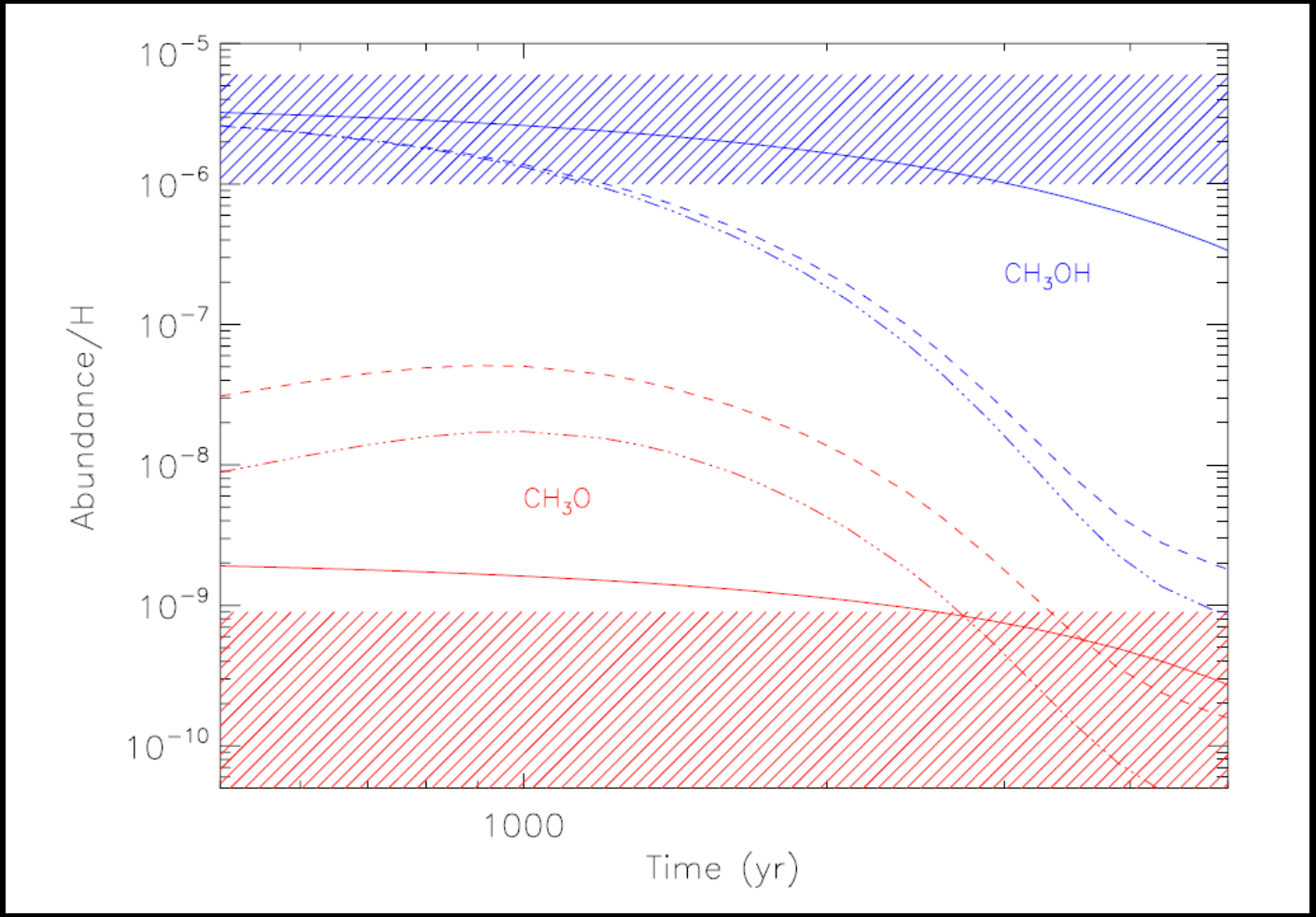


modeling L1157-B1

Balucani, Ceccarelli, Vazart et al. (SOLIS paper, to be submitted)

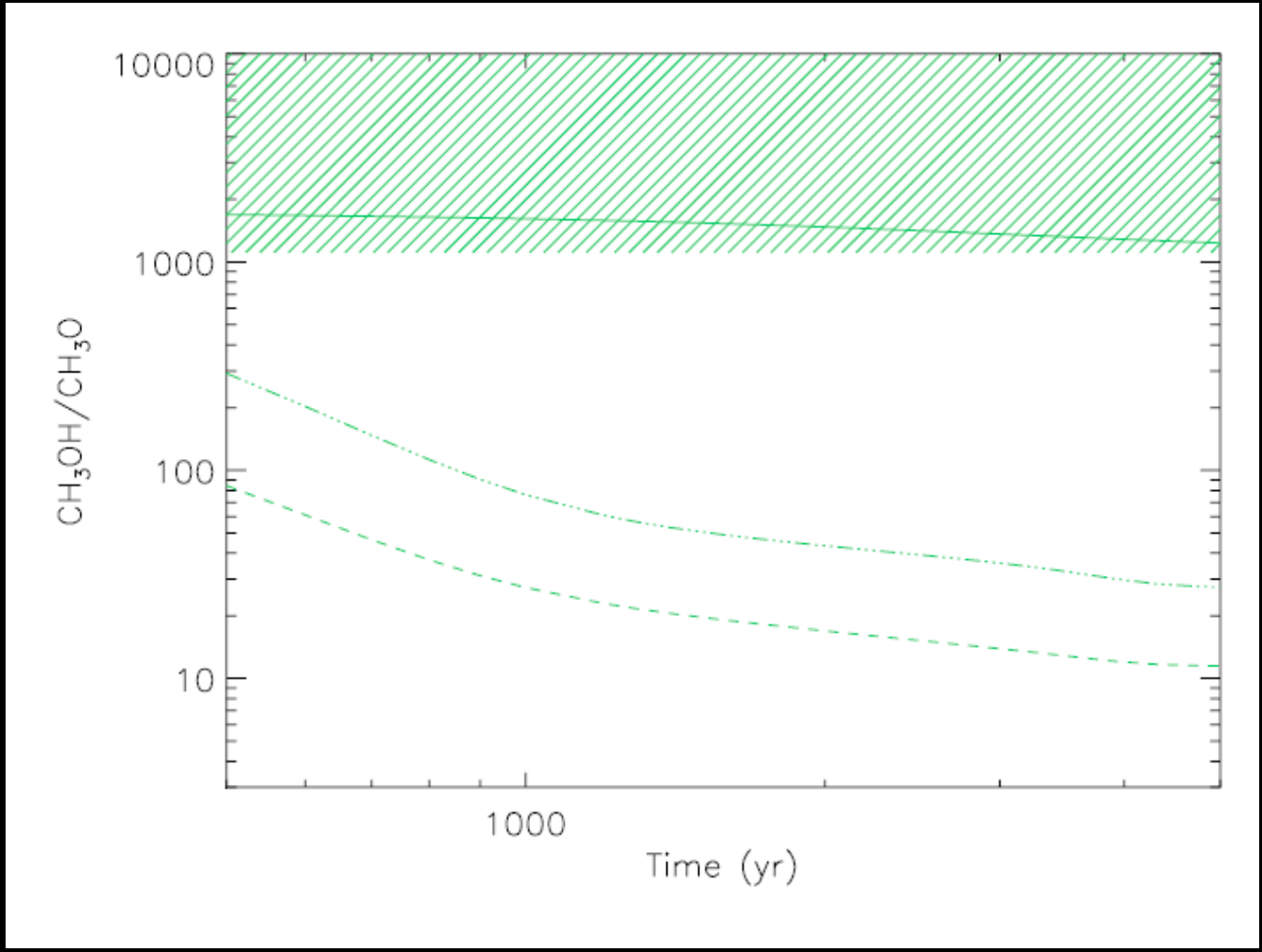


continuous line: using the OH+CH_3OH rate coefficient of Gao et al.
broken lines: using the CRESU rate coefficients

modeling L1157-B1

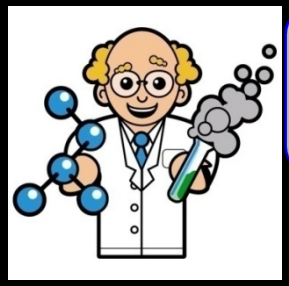
the rate coefficients derived by Gao et al. seem to reproduce much better the observed relative abundances of CH_3OH/CH_3O

Balucani, Ceccarelli, Vazart et al. (SOLIS paper, to be submitted)



continuous line: using the $OH+CH_3OH$ rate coefficient of Gao et al.
broken lines: using the CRESU rate coefficients

The chemical evolution of the interstellar medium: how do we study it?



Laboratory experiments

+ quantum calculations

observations

but can astronomy do something for chemistry?

YES, we can use observations to constrain chemical parameters (at least in some extreme, favorable cases)

A&A 625, A72 (2019)
https://doi.org/10.1051/0004-6361/201834585
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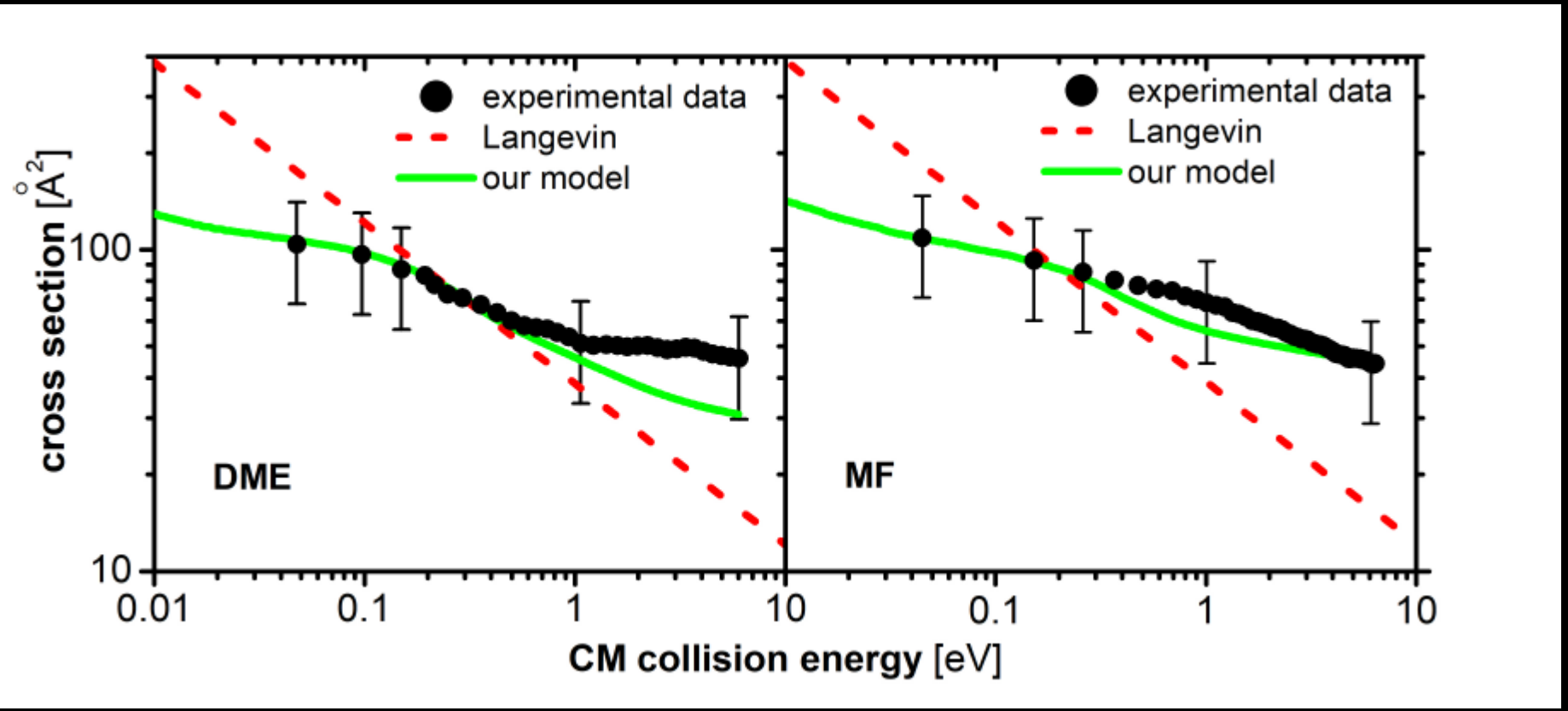
Astronomy & Astrophysics

Destruction of dimethyl ether and methyl formate by collisions with He^+

Daniela Ascenzi[1], Andrea Cernuto[1], Nadia Balucani[2,3,4], Paolo Tosi[1], Cecilia Ceccarelli[3,4], Luca Matteo Martini[1], and Fernando Pirani[2]



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MNRAS **484,** 659–664 (2019)
Advance Access publication 2019 January 2

doi:10.1093/mnras/sty3514

Dissociative recombination of $CH_2NH_2^+$: a crucial link with interstellar methanimine and Titan ammonia

C. H. Yuen,[1] M. A. Ayouz,[2] N. Balucani,[3,4] C. Ceccarelli,[4] I. F. Schneider[5,6] and V. Kokoouline[1]★

MNRAS **000**, 1–7 (2019) Preprint 7 August 2019 Compiled using MNRAS LATEX style file v3.0

Dissociative electron recombination of NH_2CHOH^+ and implications for interstellar formamide abundance

M. A. Ayouz[1], C. H. Yuen[2], N. Balucani[3,4], C. Ceccarelli[4], I. F. Schneider[5,6], V. Kokoouline[2] ⋆

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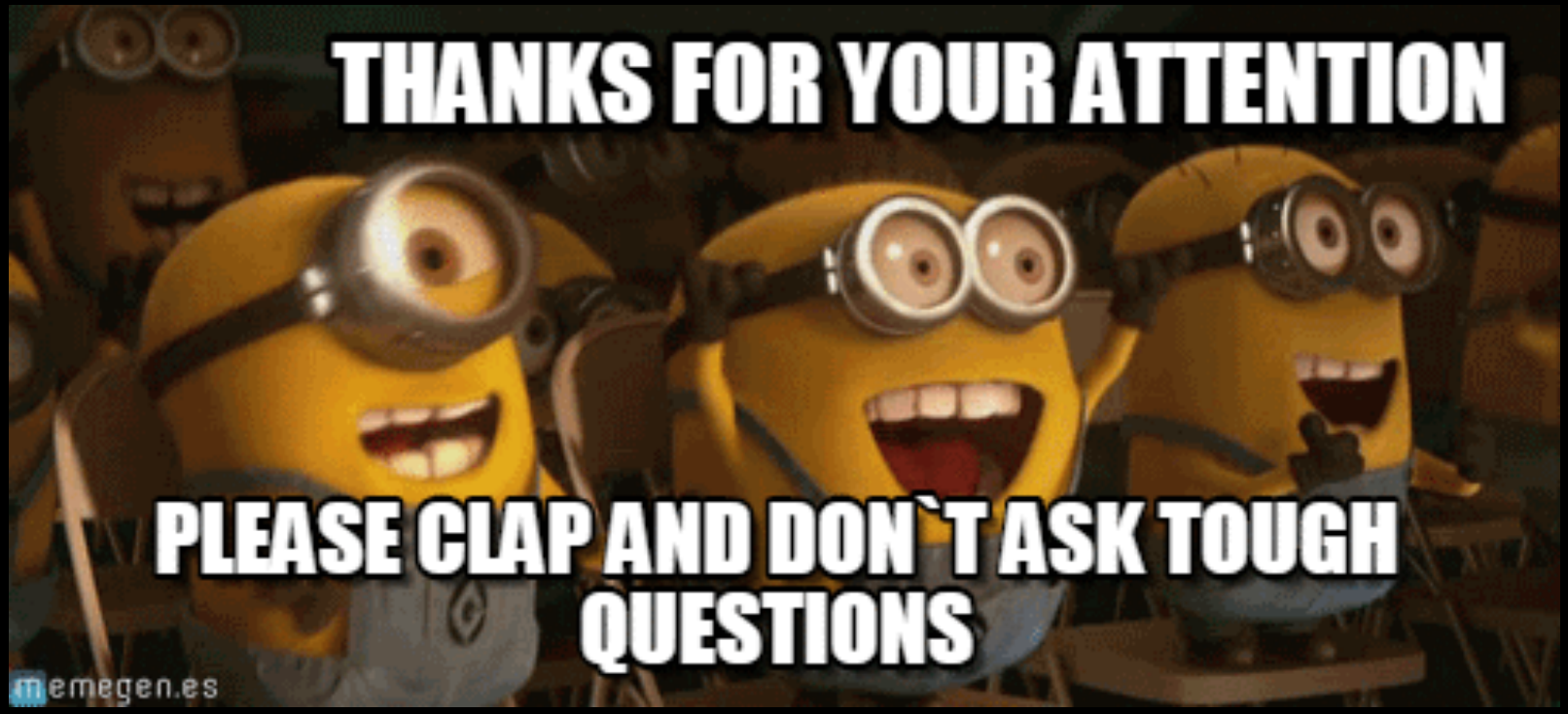
IPAG Grenoble (F): C. Ceccarelli, F. Vazart, B. Lefloch, J. Enrique Romero

C. Codella (INAF Arcetri, I), P. Ugliengo (Univ Torino, I), A. Rimola (Autonoma Barcelona, E), D. Ascenzi & P. Tosi (Univ Trento, I), I. Schneider (Université du Havre, F), V. Kokoouline (University of Central Florida, USA)

~~€€€€€€~~

- PRIN 2015 STARS in the CAOS
- ERC Advanced Grant DOC "The Dawn of Organic Chemistry", PI C. Ceccarelli
- PRIN-INAF 2016 The Cradle of Life-GENESIS-SKA, PI C. Codella
-Seeds Of Life In Space (SOLIS), a Large Project using the IRAM-NOEMA interferometer, PIs C. Ceccarelli & P. Caselli

Future:

EU H2020-MSCA-ITN-2018 "AstroChemical Origin", PI C. Ceccarelli (from May 2019)