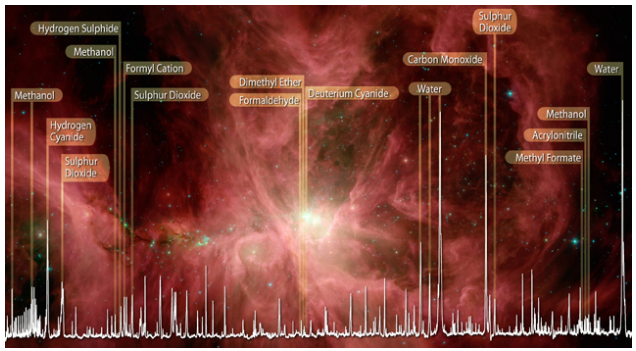
Ion-molecule reactions as a possible synthetic route for the formation of prebiotic molecules in space

Riccardo SPEZIA and Yannick JEANVOINE
LAMBE, CNRS CEA, Université d'Evry, Université Paris-Saclay, Evry, France



Molecules in the interstellar medium

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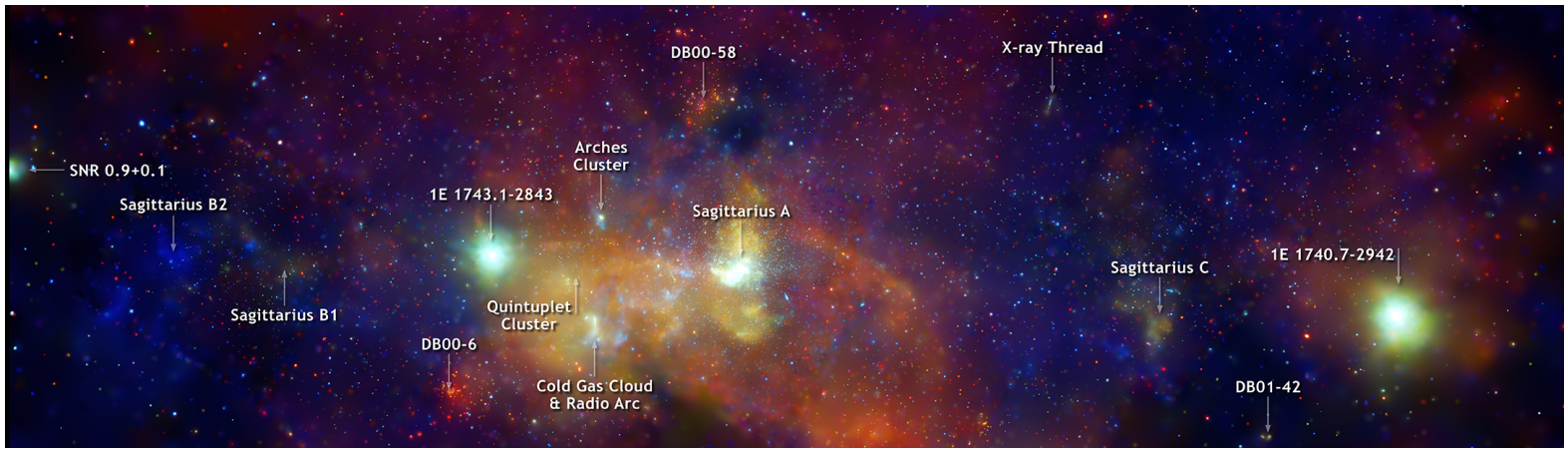
- Observed : Diatomic (43); Triatomic (43); Four atoms (27); Five atoms (23); Six atoms (17); Seven atoms (11); Eight atoms (11); Nine atoms (11); Ten or more atoms (17)



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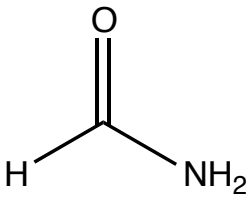

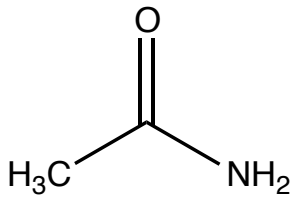

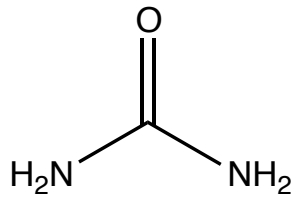

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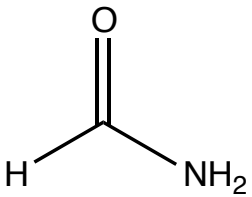

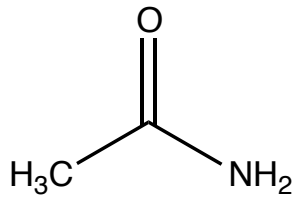

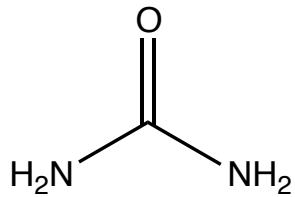

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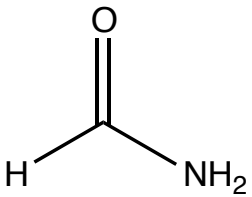

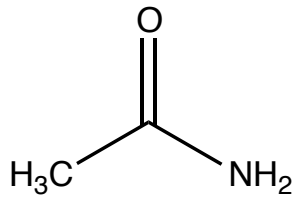

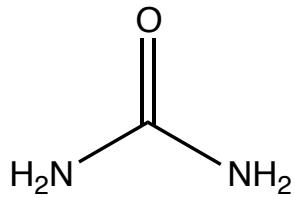

- Extraterrestrial origin of life ...
- *A long trip starts with one step* (Lao Tzu)

Molecules in the interstellar medium

- The question is: **how are they formed ?**

Molecules in the interstellar medium

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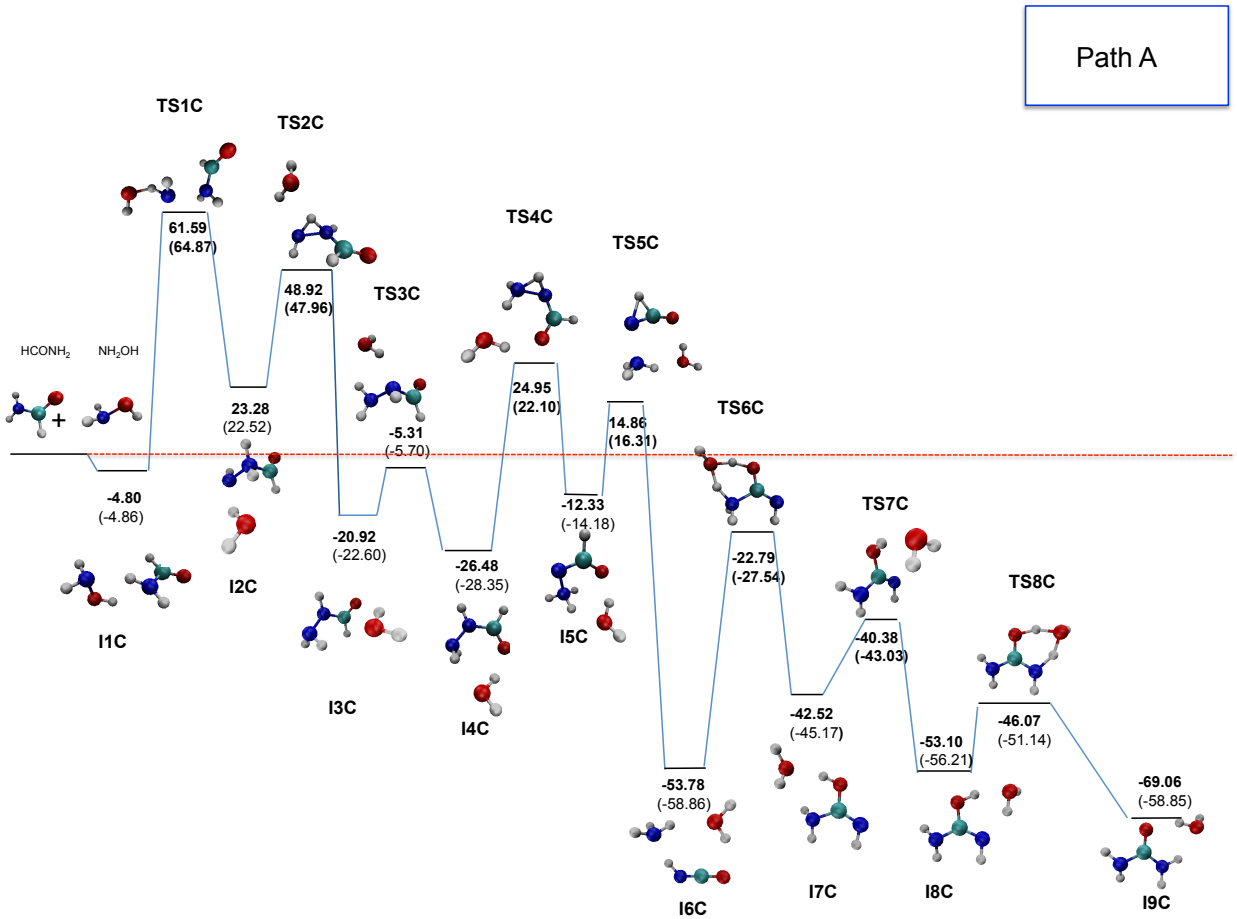
- Problem: they are cold (internally) so activation energy barriers are difficult to be passed



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3. Electromagnetic radiation can trigger reactivity (often in the UV-Vis range)
4. Ion-molecule collisions:
   (a) ion-dipole interaction lows the energy barriers;
   (b) the ions can have some translational energy and they can be accelerated by the presence of a magnetic field

Ion–molecule reactions

Bimolecular collisions in space

- Association process is not favored in the gas phase
  $A^+ + B \rightarrow (A\text{-}B)^+ + h\nu$
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- Experiments: mass spectrometry as a chemical reactor (e.g. Bohme)

Formamide in the ISM

Rubin, et al. 1971, ApJ, 169, L39

The Astrophysical Journal, 743:60 (12pp), 2011 December 10 doi:10.1088/0004-637X/743/1/60

FORMATION OF PEPTIDE BONDS IN SPACE: A COMPREHENSIVE STUDY
OF FORMAMIDE AND ACETAMIDE IN Sgr B2(N)

D. T. Halfen[1,2,3], V. Ilyushin[4], and L. M. Ziurys[1,2,3]
[1] Departments of Chemistry and Astronomy, University of Arizona, Tucson, AZ 85721, USA; halfendt@as.arizona.edu, lziurys@as.arizona.edu
[2] Arizona Radio Observatory, University of Arizona, Tucson, AZ 85721, USA
[3] Steward Observatory, University of Arizona, Tucson, AZ 85721, USA
[4] Institute of Radio Astronomy of the National Academy of Sciences Ukraine, Chervonopraporna 4, 61002 Kharkov, Ukraine
Received 2011 June 29; accepted 2011 August 25; published 2011 November 22

Observed in giant molecular clouds (Orion-KL, Sgr(B2)) but also in dozen of molecular clouds through space

The high abundances of acetamide and formamide in Sgr B2(N) additionally suggest that there might be other plausible synthetic routes to simple peptide polymers that do not involve amino acids.

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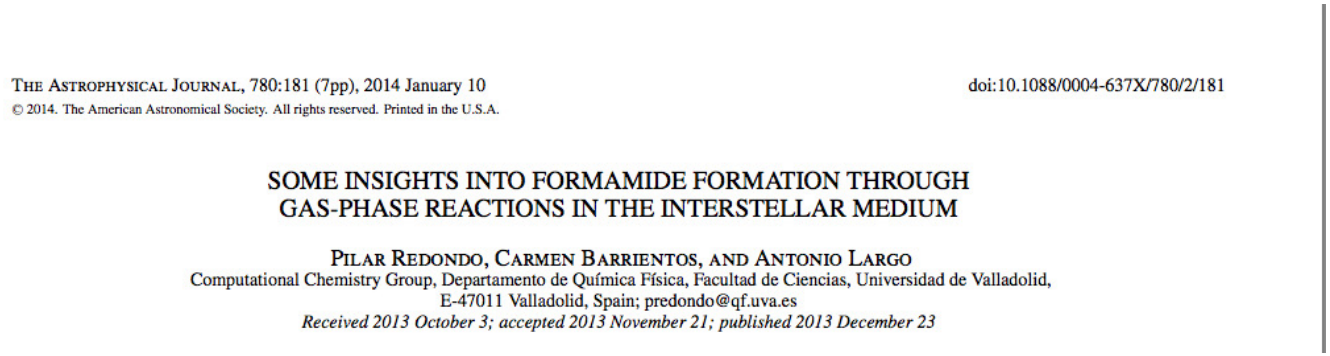

THE ASTROPHYSICAL JOURNAL, 780:181 (7pp), 2014 January 10 doi:10.1088/0004-637X/780/2/181

SOME INSIGHTS INTO FORMAMIDE FORMATION THROUGH GAS-PHASE REACTIONS IN THE INTERSTELLAR MEDIUM

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Computational Chemistry Group, Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain; predondo@qf.uva.es
Received 2013 October 3; accepted 2013 November 21; published 2013 December 23

- Ion-molecule reaction with the smallest barrier (0.12 eV) is: $NH_2OH_2^+ + H_2CO \rightarrow NH_2CHOH^+ + H_2O$

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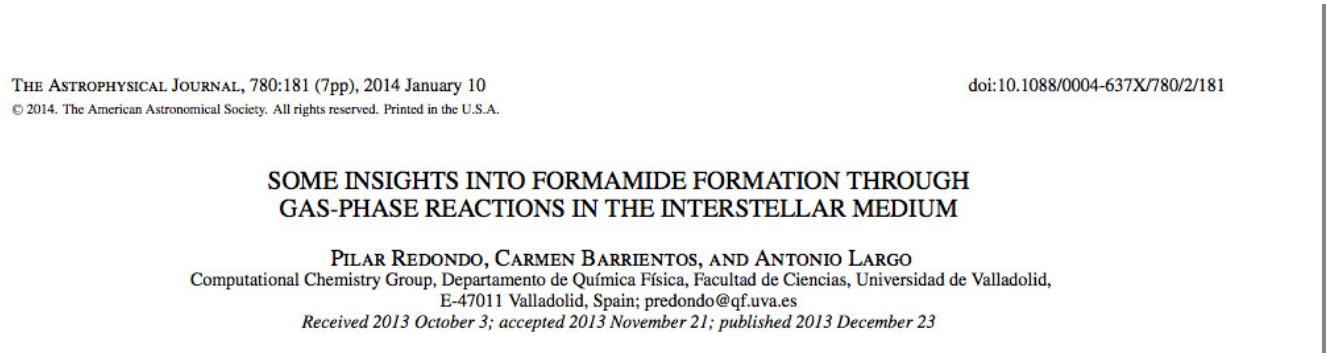

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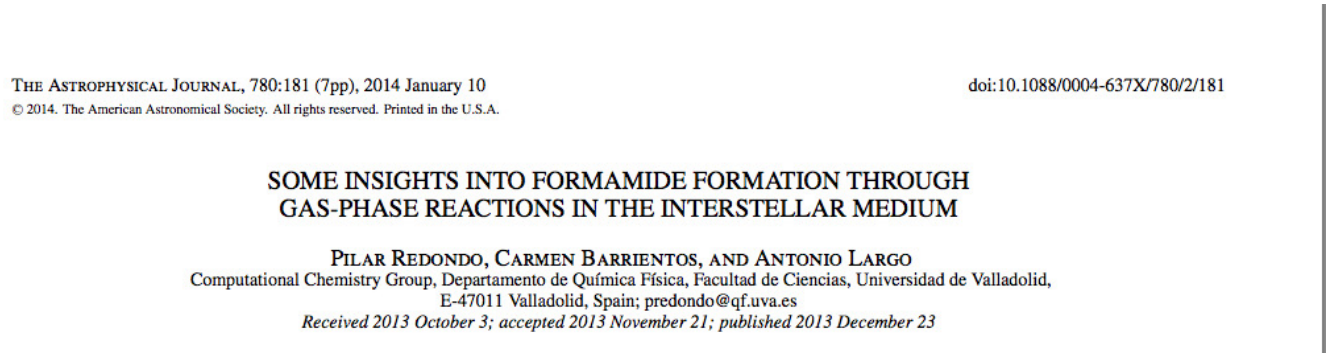

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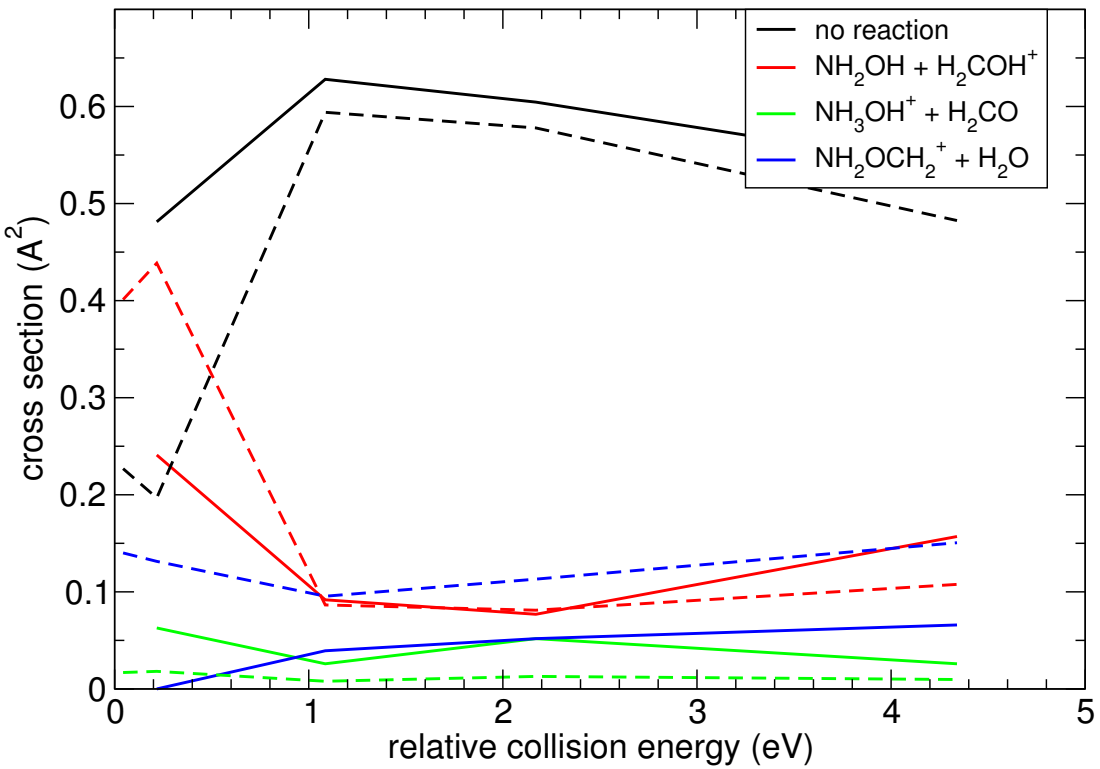
- The other reaction has a high barrier (1.2 eV) : $NH_3OH^+ + H_2CO \rightarrow NH_2CHOH^+ + H_2O$
- Chemical dynamics: investigate this hypothesis as a function of collision energy (in the 0.04 to 4.3 eV range) and test also other possible reactions

Formamide synthesis

Cross section

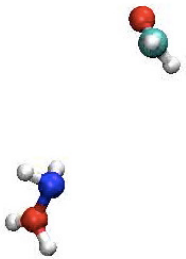
$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O \ (\Delta E = \text{-}0.9 \text{ eV})$$



Formamide synthesis

Mechanism

$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O$$



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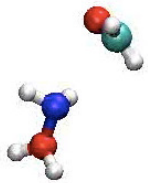

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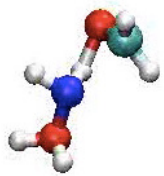

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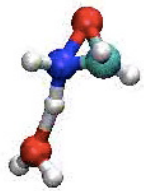


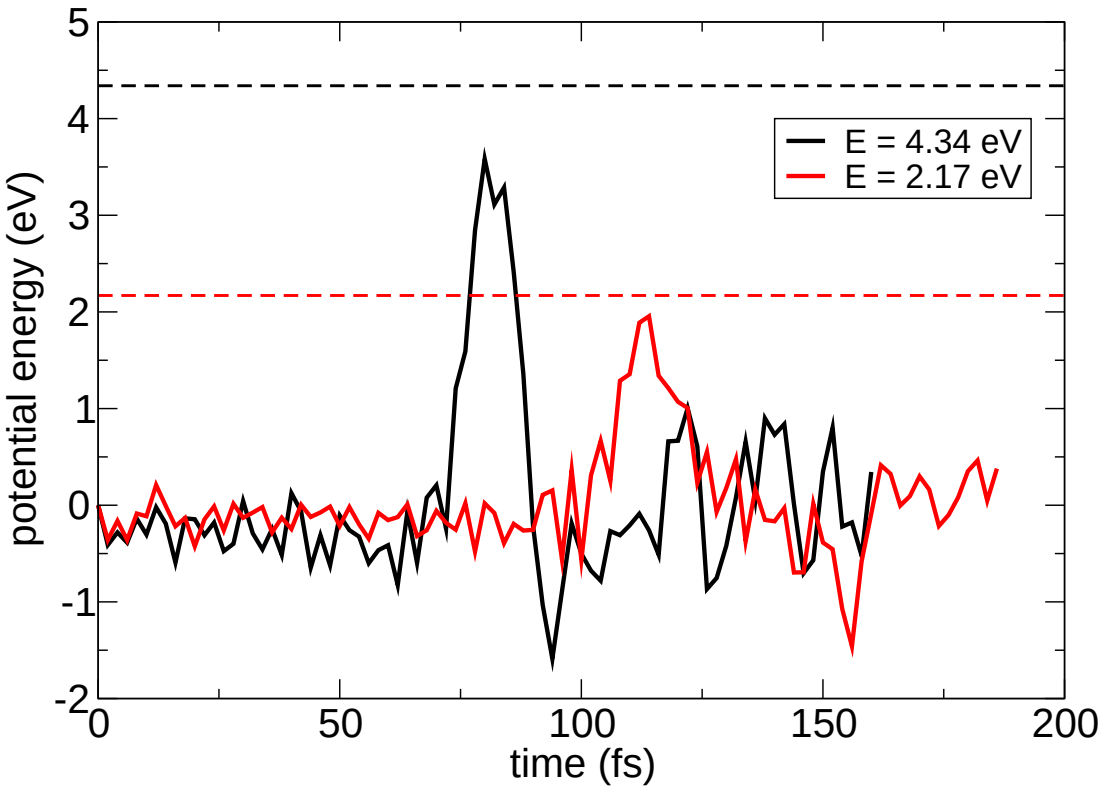
t = 100 fs

t = 120 fs

Formamide synthesis

Energetics

$$NH_2OH_2^+ + H_2CO \rightarrow NH_2OCH_2^+ + H_2O$$

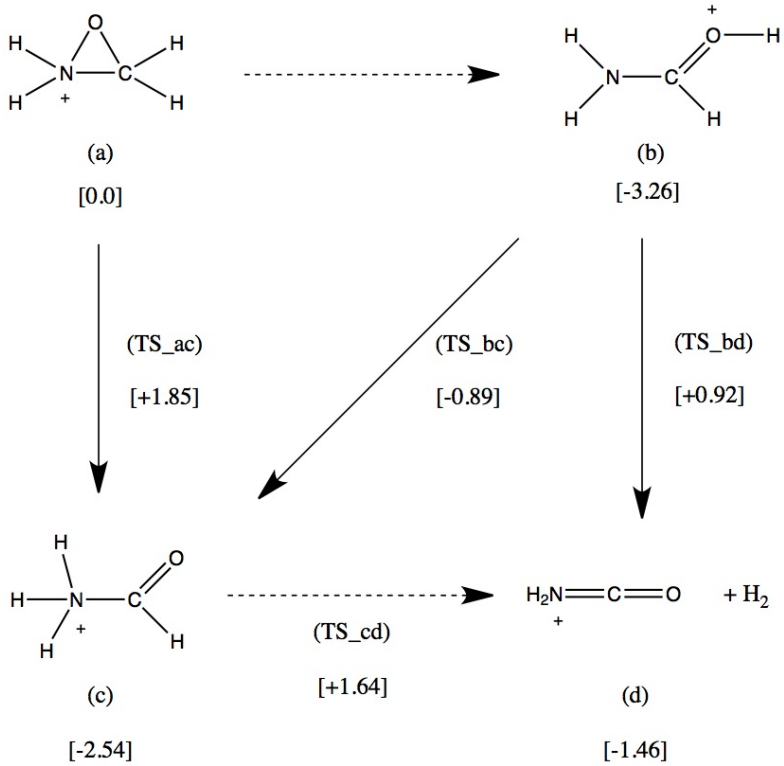


Formamide synthesis

Isomerization vs dissociative recombination (MP2/CCSD(T))

Isomerization and fragmentation

For $E_{int} \geq 1.85$ eV



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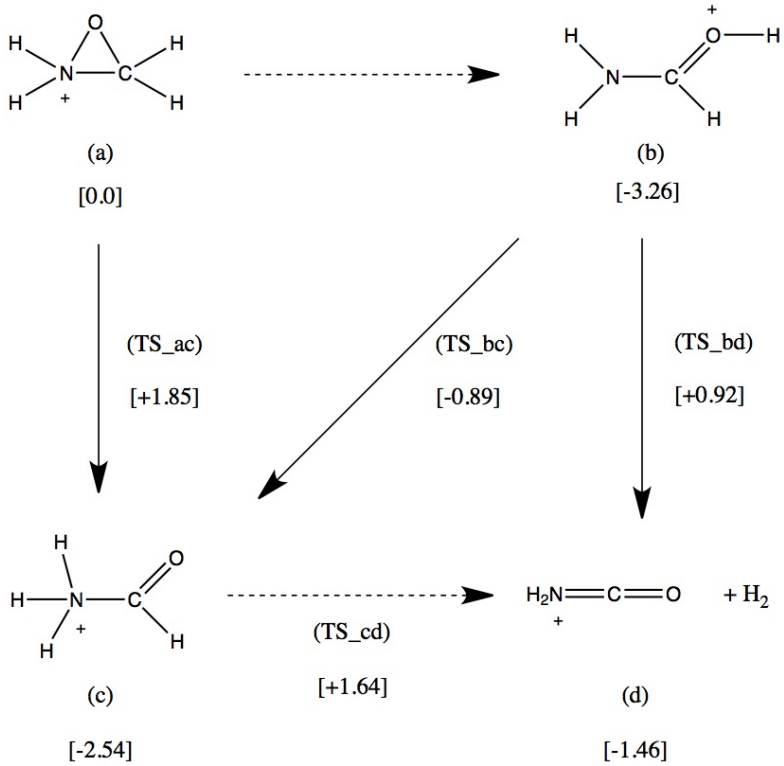

Dissociative recombination

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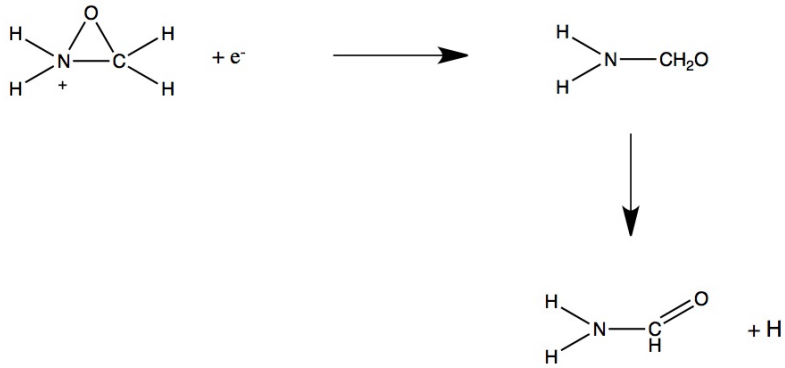
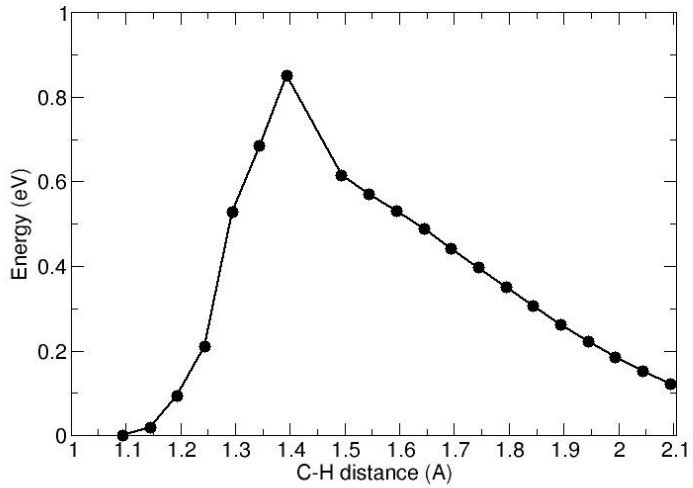




Other products

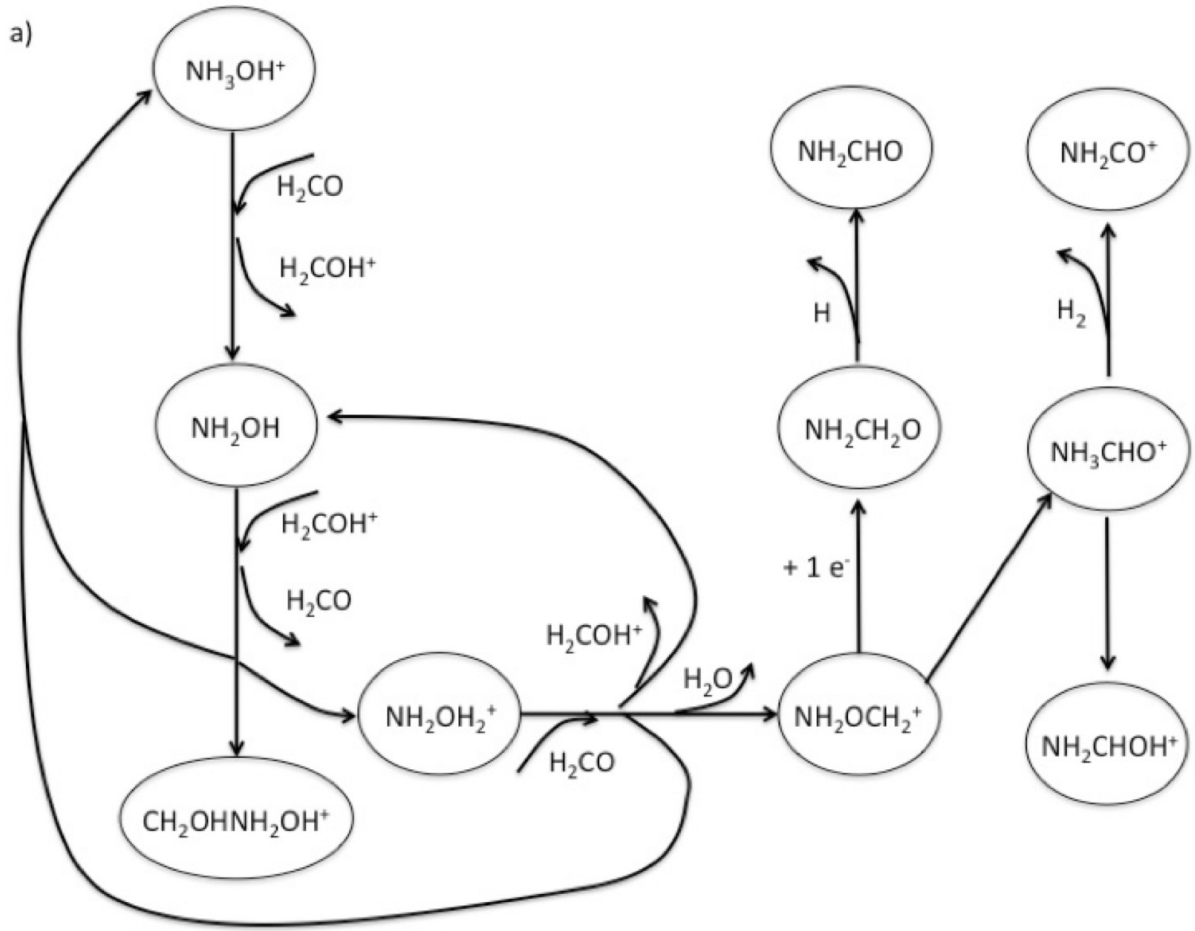
$NH_3 + H_2COH^+$

$NH_3 + H_2COH^+ \rightarrow NH_2CH_2^+ + H_2O$: ΔE = -1.6 eV
$NH_2CH_2^+$ has not yet been observed in the ISM.
But it can further react :

1. Dissociative recombination $NH_2CH_2^+ + e^- \rightarrow NH_2CH + H$
   NH_2CH was observed in 1973
2. Radiative association $NH_2CH_2^+ + CN^- \rightarrow NH_2CH_2CN + h\nu$:
   ΔE = -7.2 eV
   NH_2CH_2CN was observed in 2008. The radiative association can go through vibrational relaxation ($k_r = 29\ s^{-1}$) but also through excited states (S_1 is at about 6 eV).

Formamide synthesis

Summary of reaction mechanisms



NH_2CHO: observed in 1971 ; NH_2CO^+: observed in 2013;

Spezia et al. Astrophy. J. 826, 107 (2016)

Glycine synthesis

Detection in comet and Bohme experiments

RESEARCH ARTICLE

SPACE SCIENCES

Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko

10.1126/sciadv.1600285

Kathrin Altwegg,[1,2]* Hans Balsiger,[1] Akiva Bar-Nun,[3] Jean-Jacques Berthelier,[4] Andre Bieler,[1,5] Peter Bochsler,[1] Christelle Briois,[6] Ursina Calmonte,[1] Michael R. Combi,[5] Hervé Cottin,[7] Johan De Keyser,[8] Frederik Dhooghe,[8] Bjorn Fiethe,[9] Stephen A. Fuselier,[10] Sébastien Gasc,[1] Tamas I. Gombosi,[5] Kenneth C. Hansen,[5] Myrtha Haessig,[1,10] Annette Jäckel,[1] Ernest Kopp,[1] Axel Korth,[11] Lena Le Roy,[2] Urs Mall,[11] Bernard Marty,[12] Olivier Mousis,[13] Tobias Owen,[14] Henri Rème,[15,16] Martin Rubin,[1] Thierry Sémon,[1] Chia-Yu Tzou,[1] James Hunter Waite,[10] Peter Wurz[1]

The importance of comets for the origin of life on Earth has been advocated for many decades. Amino acids are key ingredients in chemistry, leading to life as we know it. Many primitive meteorites contain amino acids, and it is generally believed that these are formed by aqueous alterations. In the collector aerogel and foil samples of the Stardust mission after the flyby at comet Wild 2, the simplest form of amino acids, glycine, has been found together with precursor molecules methylamine and ethylamine. Because of contamination issues of the samples, a cometary origin was deduced from the ^{13}C isotopic signature. We report the presence of volatile glycine accompanied by methylamine and ethylamine in the coma of 67P/Churyumov-Gerasimenko measured by the ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) mass spectrometer, confirming the Stardust results. Together with the detection of phosphorus and a multitude of organic molecules, this result demonstrates that comets could have played a crucial role in the emergence of life on Earth.

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ARTICLES
Published on Web 07/25/2007

Gas-Phase Ionic Syntheses of Amino Acids: β versus α

Jamie L. Snow,† Galina Orlova,*,† Voislav Blagojevic,‡ and Diethard K. Bohme*,‡

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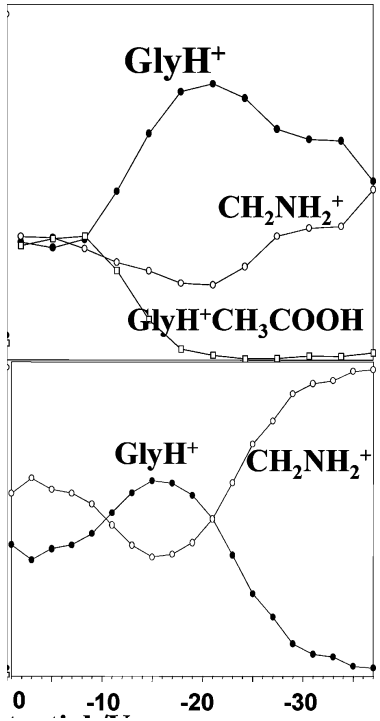
Received December 5, 2006; E-mail: gorlova@stfx.ca; dkbohme@yorku.ca

Glycine synthesis

Bohme experiments

$NH_3OH^+ + CH_3COOH \rightarrow NH_3CH_2COOH^+ + H_2O$

Ion with *m/z 76* was obtained in laboratory by ion-molecule reaction at T = 300 K



J. Am. Chem. Soc., **129**, 9911 (2007)

Glycine synthesis

Ion-molecule simulations at room temperature

Explicit collisions simulations form:

(1) $NH_3OH^+ + CH_3COOH \rightarrow m/z\ 76 + H_2O$

(2) $NH_2OH_2^+ + CH_3COOH \rightarrow m/z\ 76 + H_2O$

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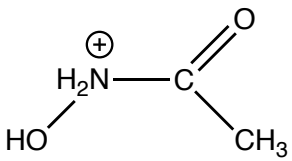
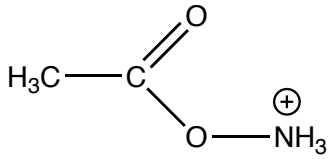
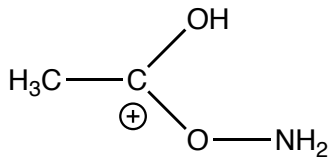
We obtained different isomers of $GlyH^+$, the most abundant are:



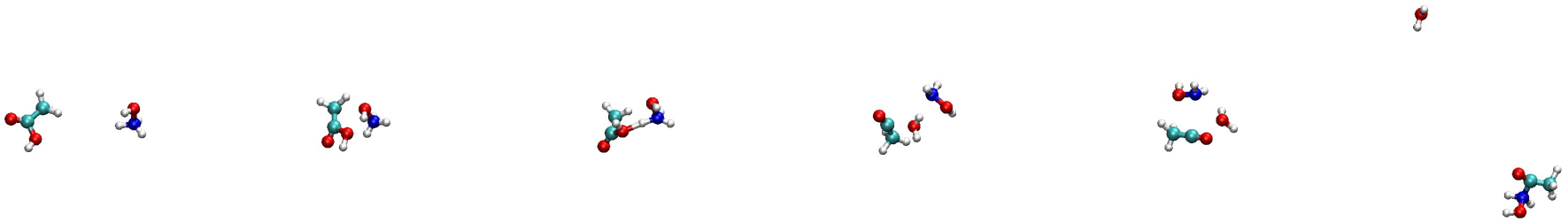




Jeanvoine et al. to be submitted

Glycine synthesis

Ion-molecule simulations at room temperature



t = 0 t = 188 fs t = 925 fs t = 1081 fs t = 1845 fs t = 10 ps

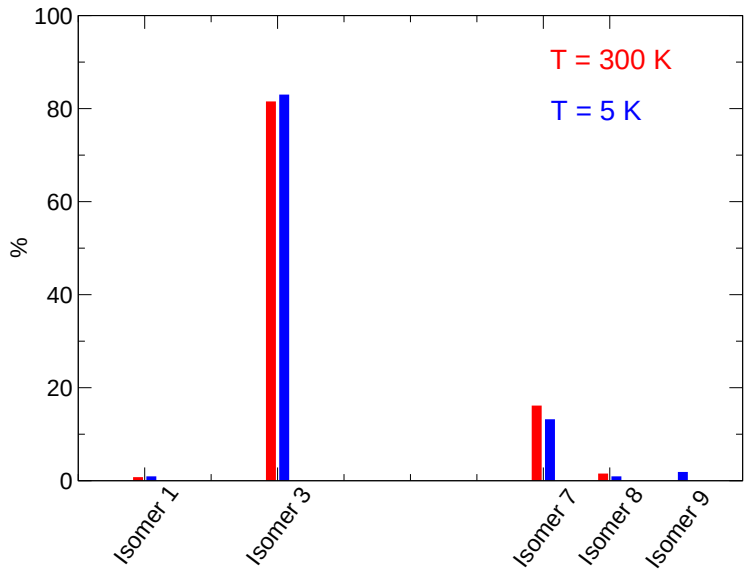
Glycine synthesis

Ion-molecule simulations at low temperature

$NH_3OH^+ + CH_3COOH \rightarrow GlyH^+$ isomers

Collisions with $E_{coll} = 0.2$ eV and impact parameter equal to zero.

Comparing T = 300 K with T = 5 K.



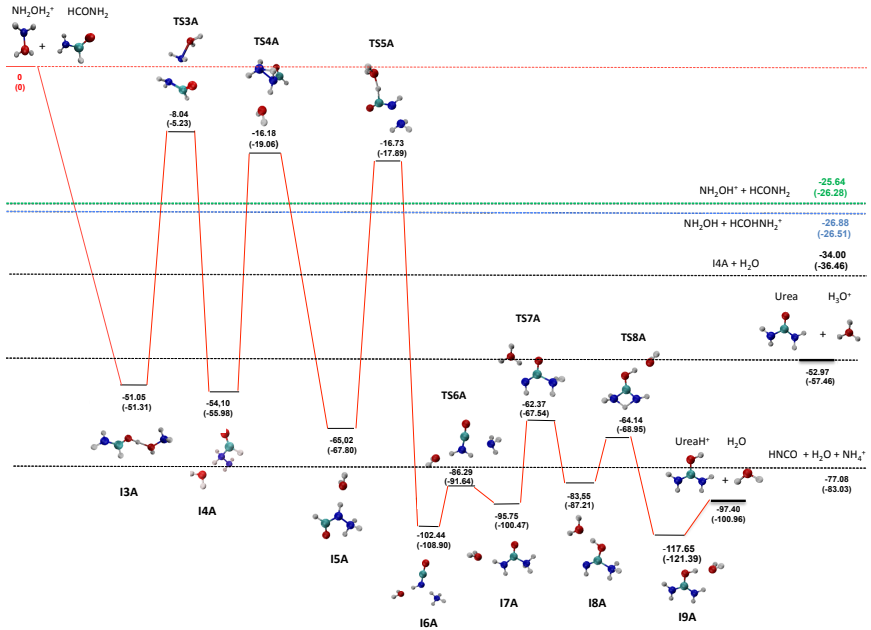
Internal temperature has no effect on product distribution. Gas phase experiments done at room conditions can be a good model.

Urea synthesis

Static calculations

By studying the potential energy surface of many ion-molecule, neutral-neutral and neutral-radical reactions, we found one which has not an activation energy (differently from previous ones):

$$NH_2OH_2^+ + HCONH_2 \rightarrow UreaH^+ + H_2O$$



A&A submitted

Conclusions and perspectives

- *Give us insights not numbers* (C.Coulson)
- Ion-molecule collisions can form interesting prebiotic molecules, given that some translational energy is given. In this case also cold molecules can react.
- Direct formation of N–CO bonds seems to be preferred than forming directly amino-acids. They can then evolve to biological molecules.
- Ion-chemistry in space (ISM, but not only) can be a source of "fuel" for life. First step of life can be extraterrestrial !
- Studying the formation of other molecules and coupling with other activation modes (light, surface, etc . . .)
- Doing new experiments with better product characterization (collaboration with D.Scuderi at CLIO, Orsay)

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