
# Radiation-Driven Chemistry in Ices in Space

## *Laboratory Simulations and Results*

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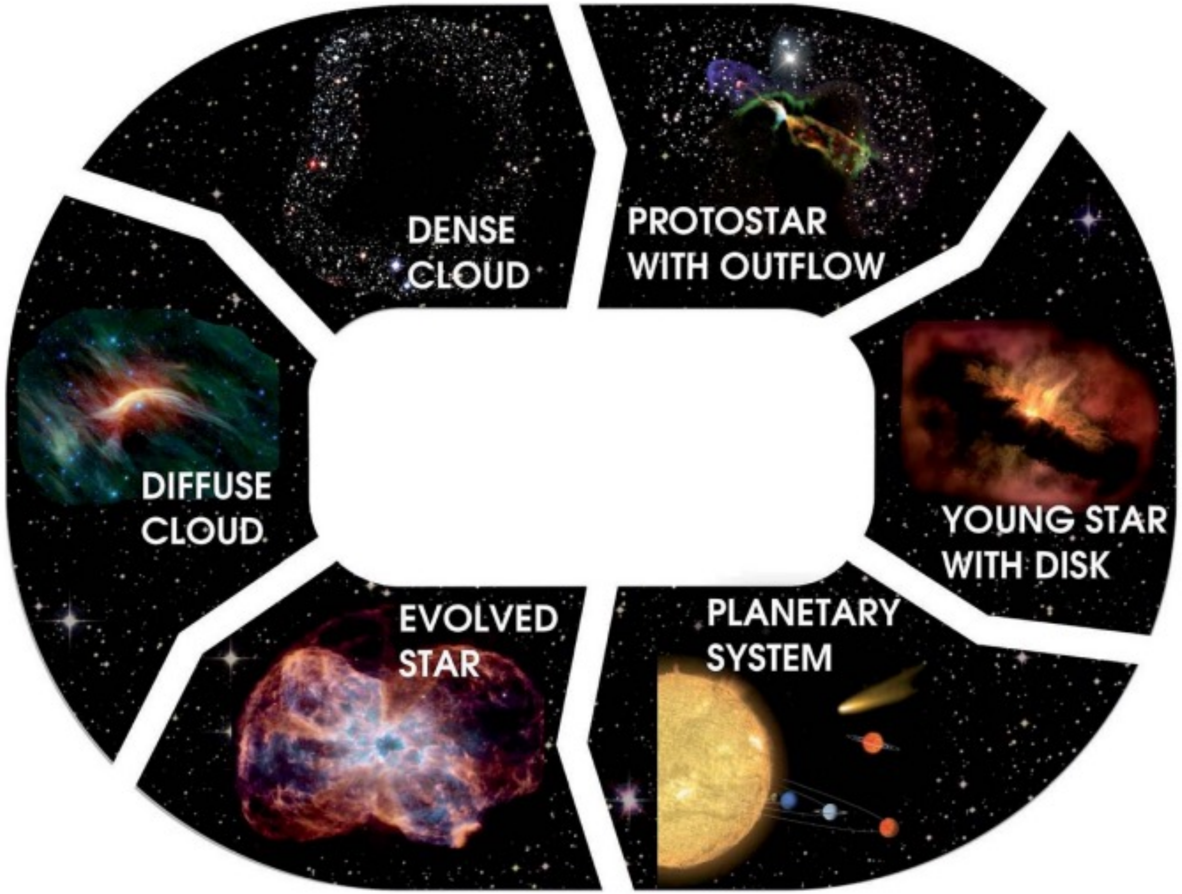
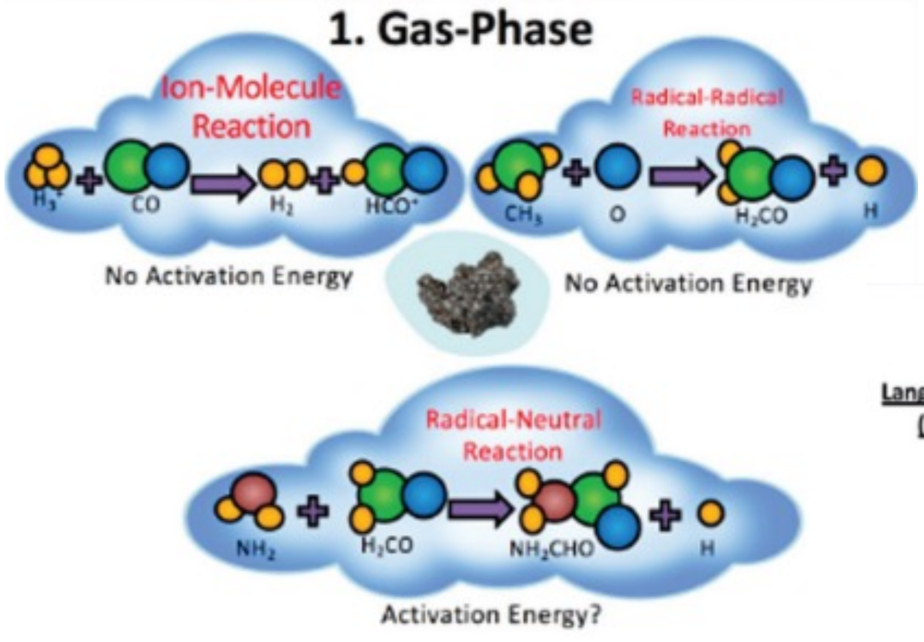
# Astrochemistry and the Cosmic Chemistry Cycle

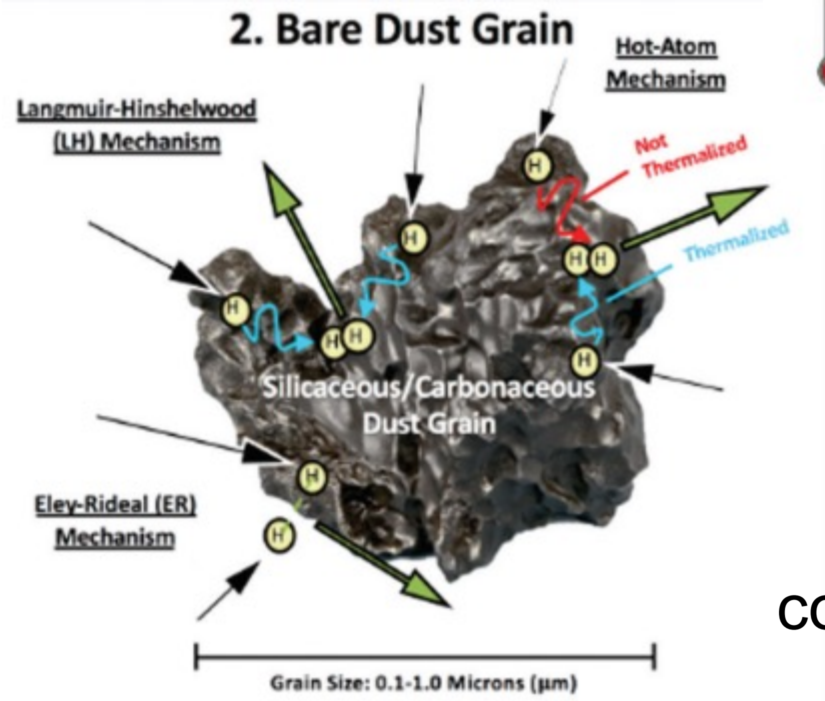
- The interstellar medium is not a homogeneous structure!
- Various environments with different temperature (10-$10^4$ K) conditions.
- Different particle density conditions present.
- Different types of chemistry are dominant in each environment.




van Dishoeck, 2014, *Faraday Discuss.* 168, 9.

# Different Types of Chemistry



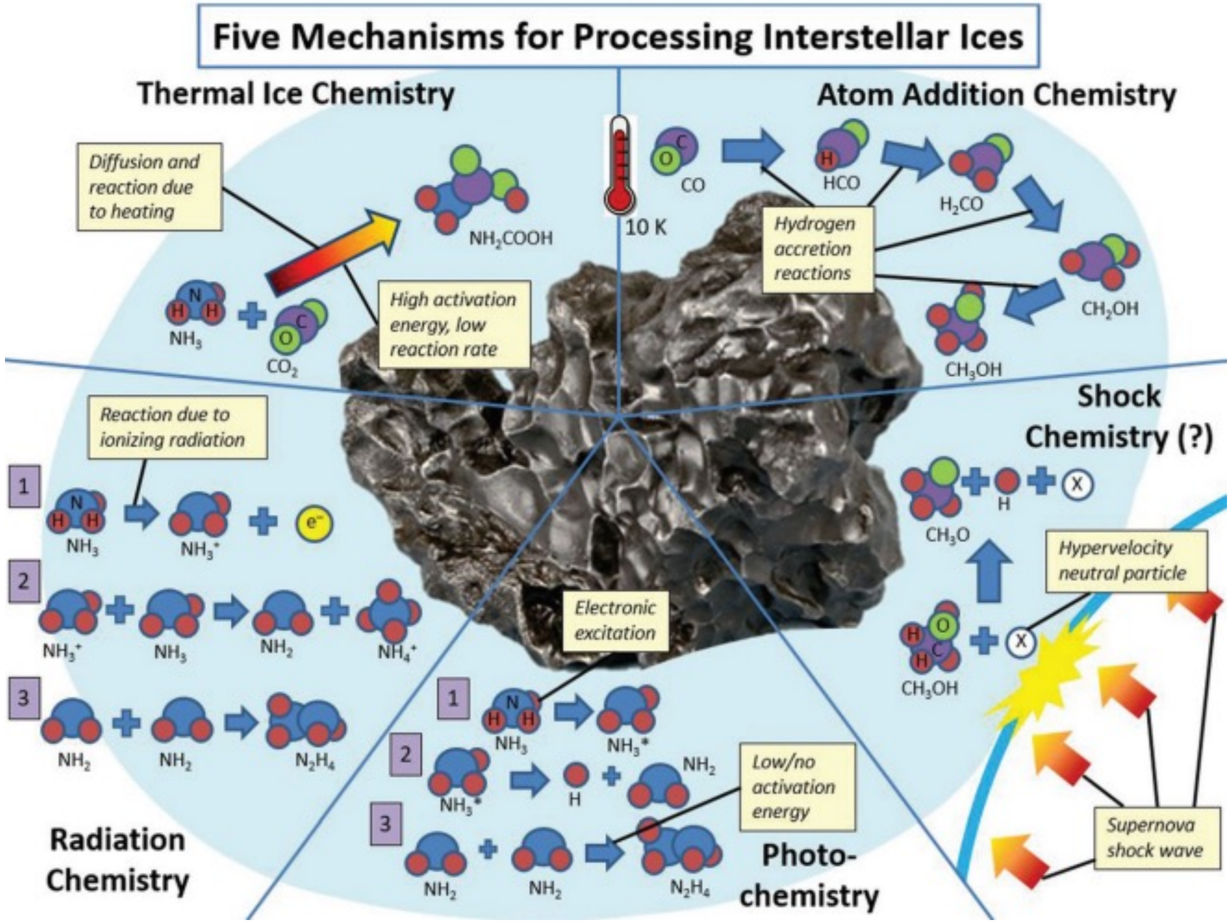


Formation reservoir of complex organic molecules!

**Arumainayagam et al. 2019, *Chem. Soc. Rev.* 48, 2293**

# Mechanisms of Chemistry in Ices

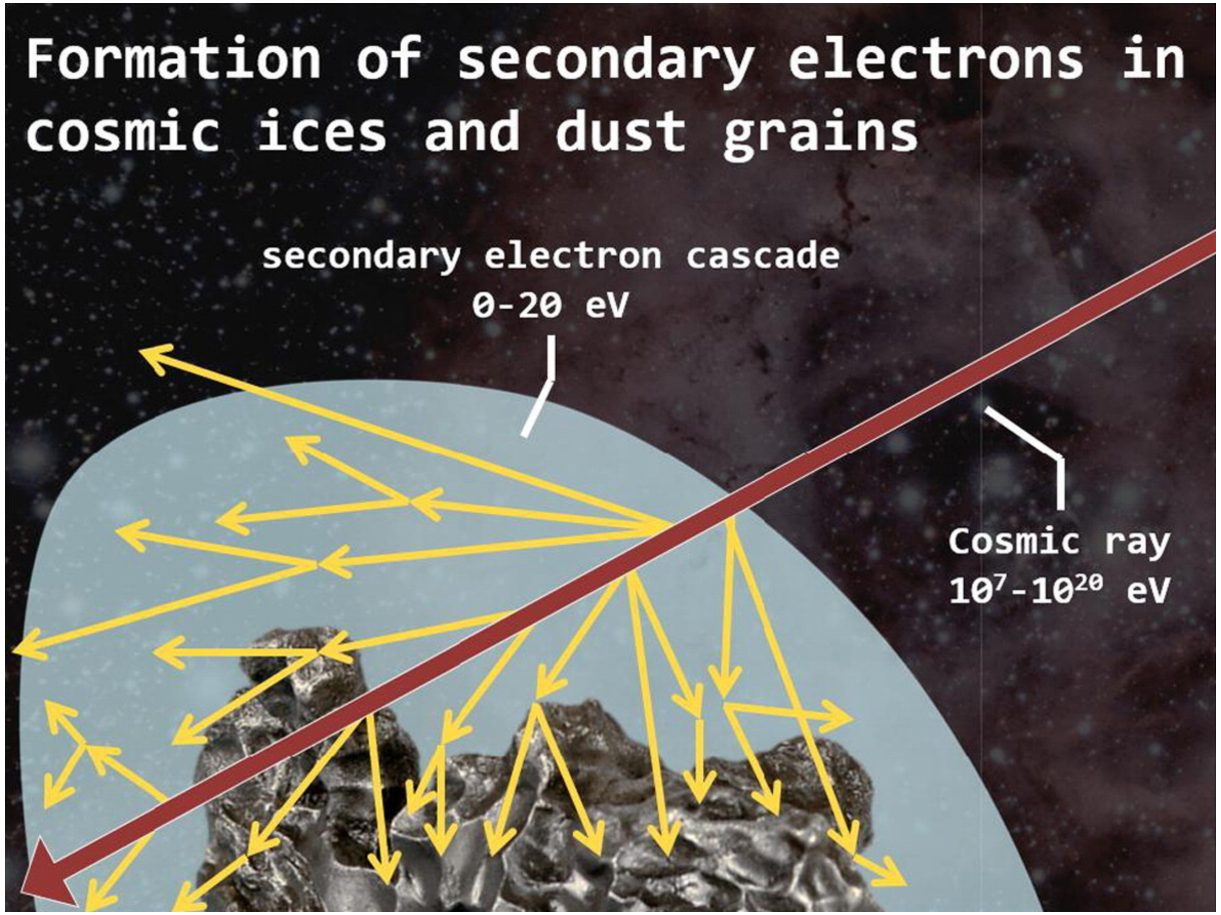
- **Thermal ice chemistry:** reactions occurring at low (<50 K) temperatures.
- **Atom addition reactions:** reactions mediated by radicals and atoms.
- **Shock chemistry:** induced by impacts or supernovae shock waves.
- **Photochemistry:** reactions induced by VUV photons.
- **Radiation chemistry:** reactions induced by cosmic rays or stellar winds.




Arumainayagam et al. 2019, *Chem. Soc. Rev.* 48, 2293

# Cosmic Rays Are Important!

- Cosmic rays are a primary driver of radiation chemistry in extra-terrestrial ices.
- The interaction of the cosmic ray with the ice leads to the deposition of some energy into the solid.
- This results in a cascade of $>10^5$ low-energy (<20 eV) secondary electrons per ion.




Boyer et al. 2016, *Surf. Sci.* 652, 26

# Why Should We Care About Interstellar Chemistry?

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Article | Published: 15 September 2013

## Shock synthesis of amino acids from impacting cometary and icy planet surface analogues

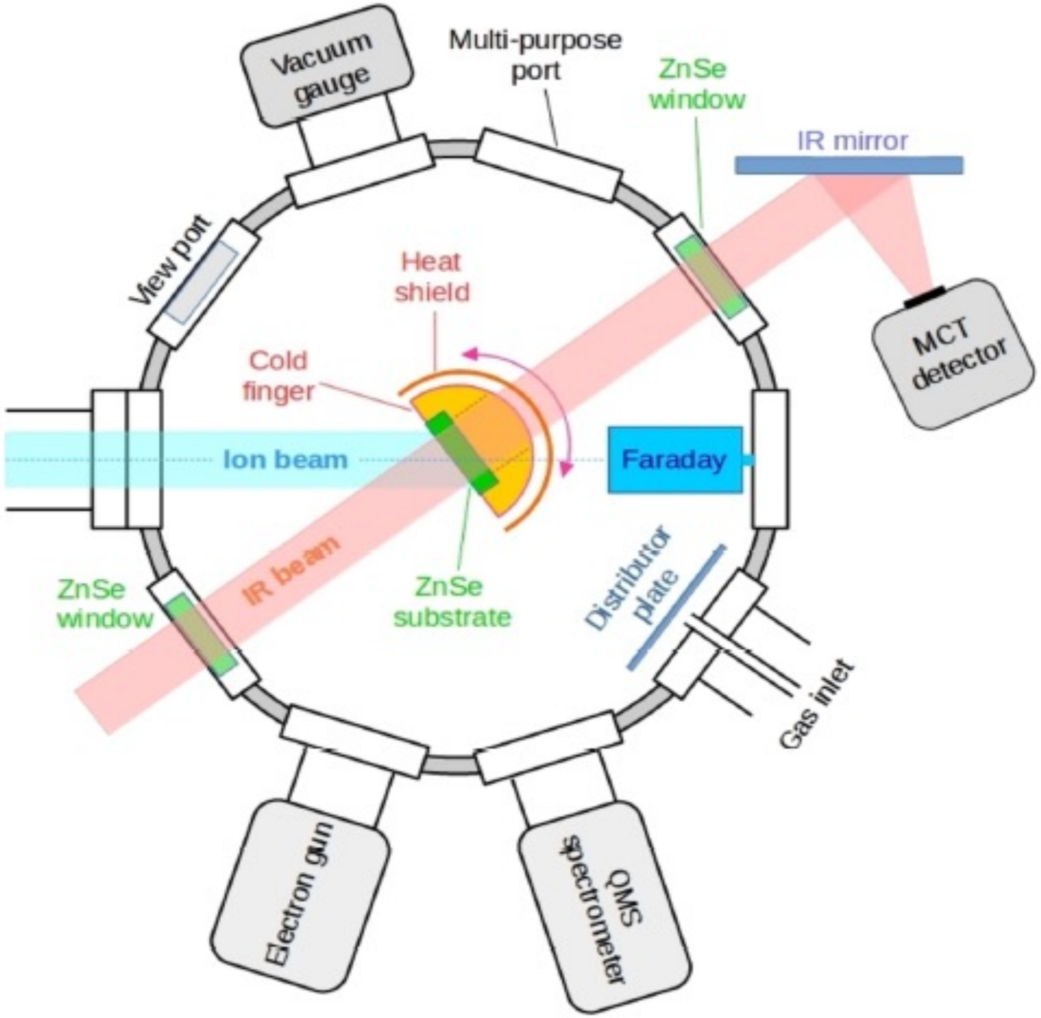
Zita Martins, Mark C. Price, Nir Goldman, Mark A. Sephton & Mark J. Burchell

*Nature Geoscience* **6**, 1045–1049 (2013) | Cite this article

# Questions Asked in this Presentation

- Does the phase of an astrophysical ice have any impact on its radiation-induced decay?
- Does the type of particle used have an effect on the radiation chemistry taking place?
- How does this effect the survivability of complex organic molecules of prebiotic importance in space?

# How We Do Astrochemistry Experiments in Debrecen: The ICA




Herczku et al. 2021, *Rev. Sci. Instrum.* 92, 084501.

# Is it Just a Phase?

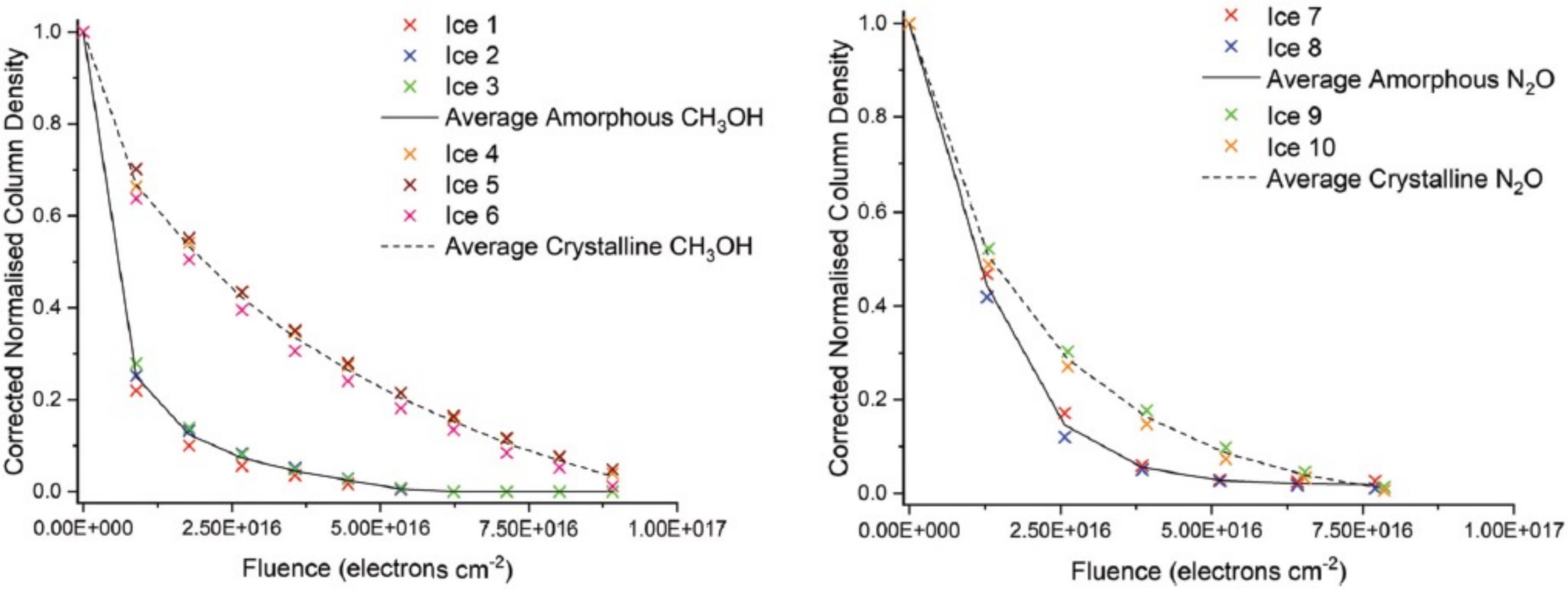
- Ices in space could adopt several phases, including **amorphous structures** or any of a number of **crystalline phases.**

- These phases display vastly different absorption spectra (especially in the IR).

- No studies have ever checked to see if radiation chemistry induced in each phase is similar.

- We performed experiments on the amorphous and crystalline phases of a number of pure molecular ices, including $CH_3OH$, $N_2O$, $H_2O$, $H_2S$, and $SO_2$.

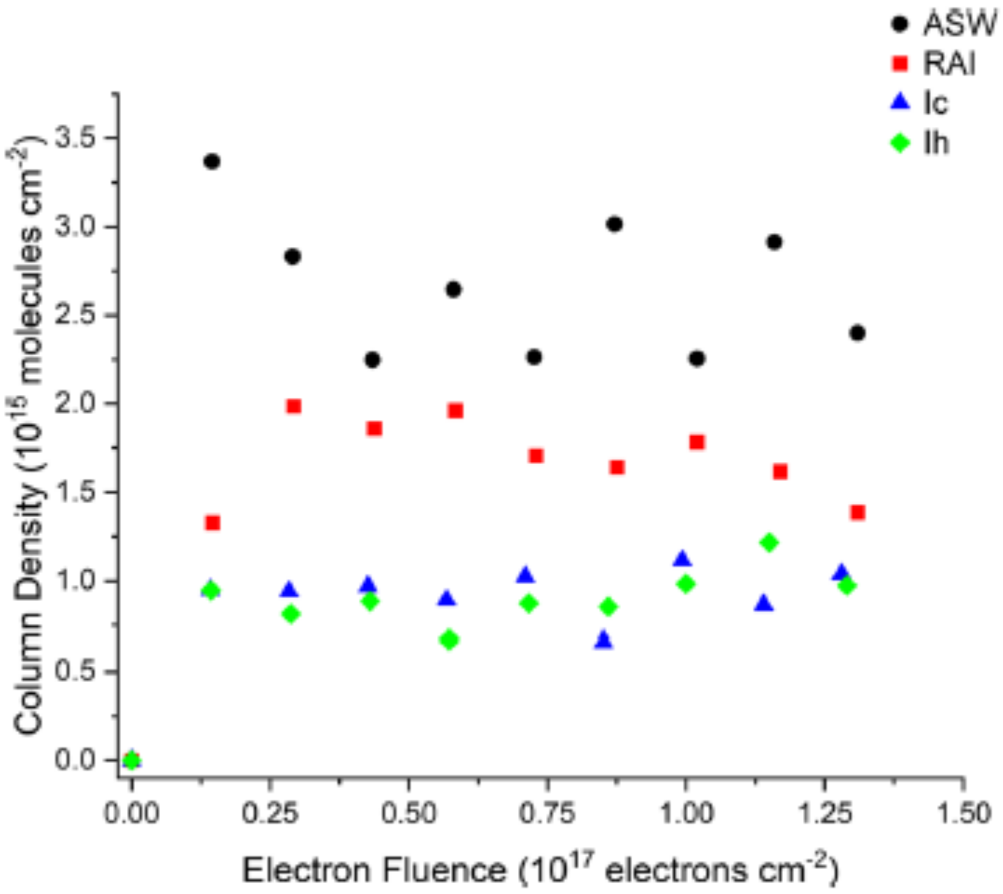
# The Influence of Phase




**Mifsud et al. 2022,** ***Phys. Chem. Chem. Phys.*** **24, 10974.**

# The Influence of Phase

- Crystalline ices are characterised by strong networks of intermolecular forces of attraction, which require more energy to be overcome.
- Crystalline ices decay more slowly when exposed to ionising radiation compared to amorphous ices.
- Products are also formed in greater abundances if amorphous ices are irradiated.

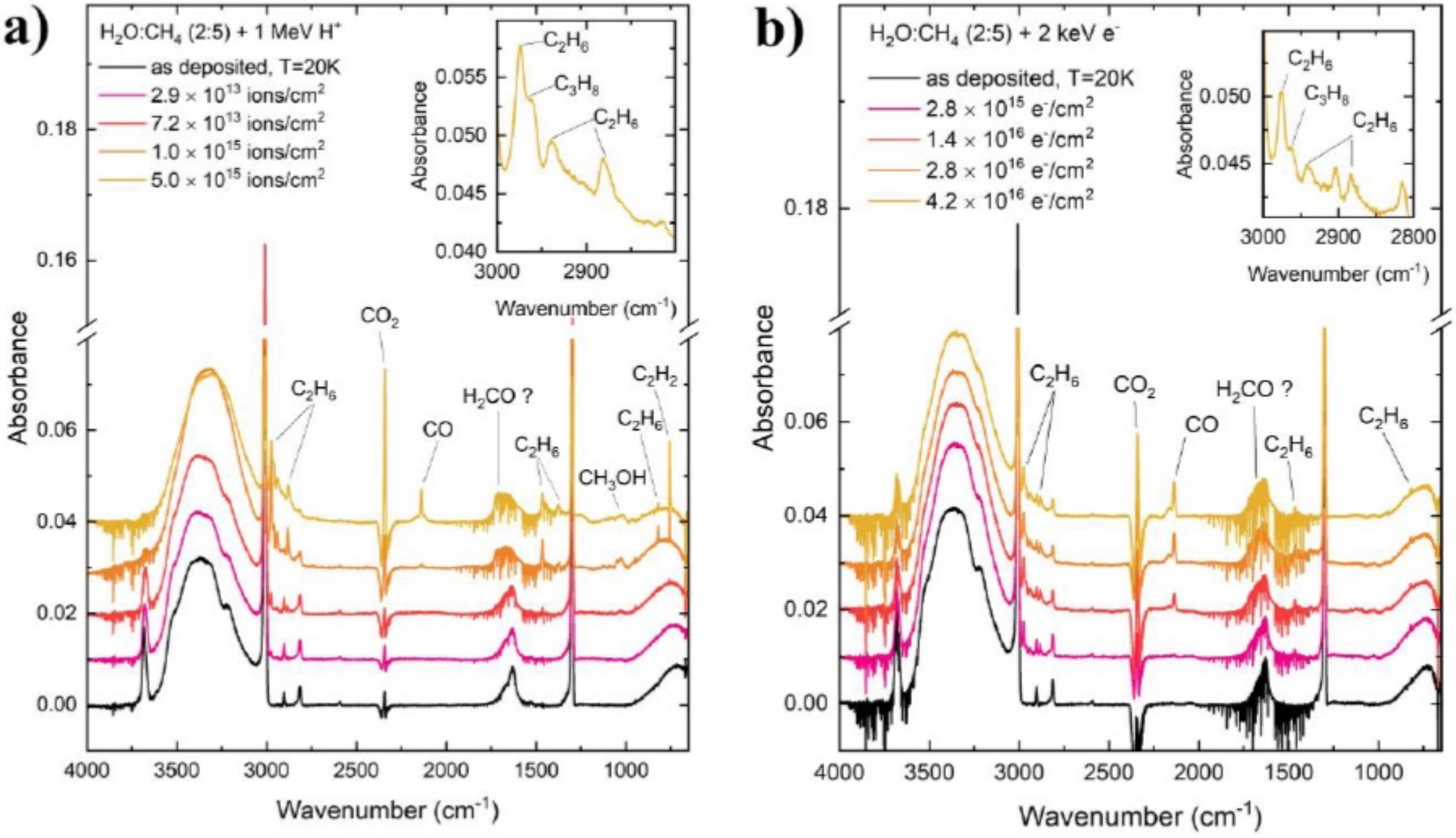



Mifsud et al. 2022, *Eur. Phys. J. D* 76, 87.

# What About the Irradiating Particle?

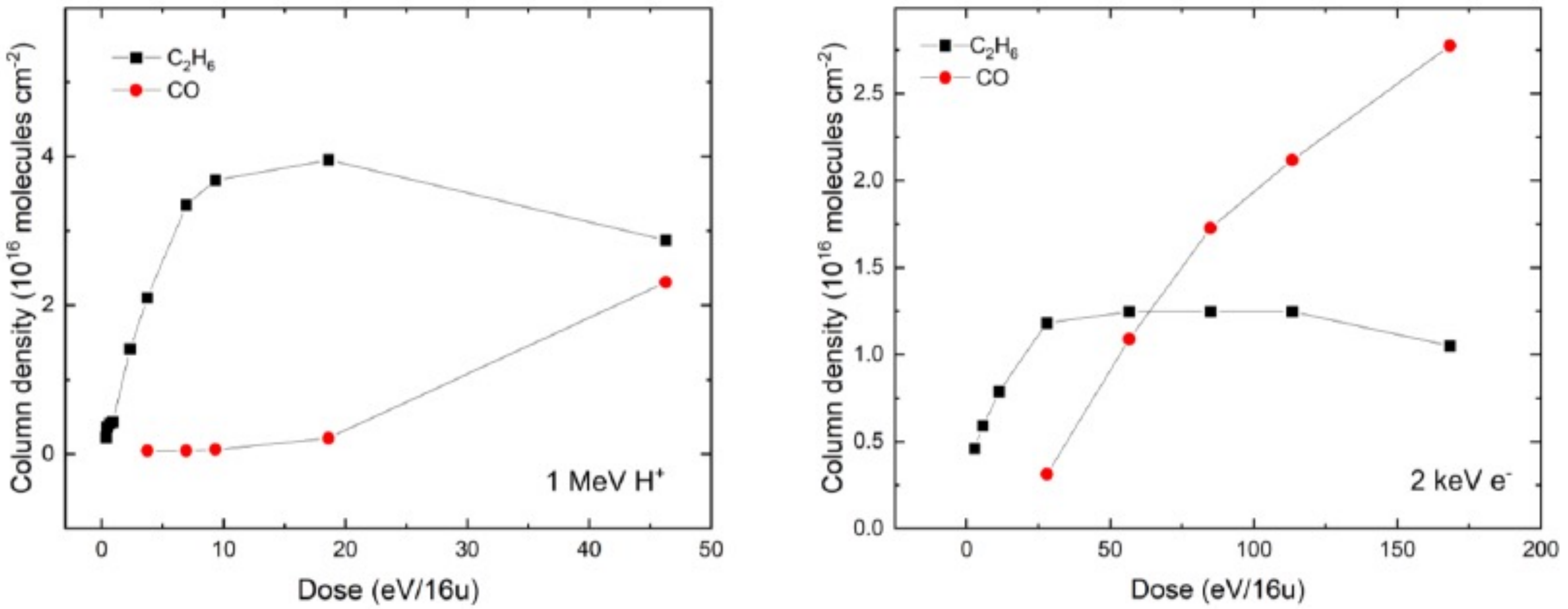
- Radiation in space is very complex and can be composed of ions, electrons, and VUV photons across a wide energy spectrum.
- Each particle can have different effects on ices depending on its mass, charge, energy, etc.
- It is important to quantify these differing effects so that they may be incorporated into models.

# Comparative $H^+$ and $e^-$ Irradiation of $CH_4$:$H_2O$ (5:2) at 20 K




Mifsud et al. 2023, *Atoms* 11, 19.

# Comparative $H^+$ and $e^-$ Irradiation of $CH_4:H_2O$ (5:2) at 20 K




Mifsud et al. 2023, *Atoms* 11, 19.

# What About the Irradiating Particle?

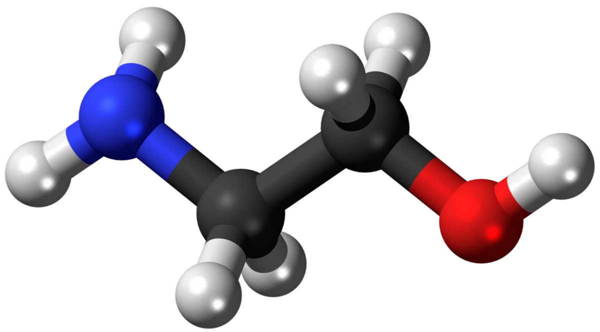
- Although the results of the 1 MeV $H^+$ and 2 keV $e^-$ irradiations are qualitatively similar, there are quantitative differences.
- Product abundances are significantly higher during $H^+$ irradiation, likely due to higher cross-sections.
- Moreover, trends are shifted to lower doses in the case of the $H^+$ irradiation.
- Interestingly, the dose at which CO and $C_2H_6$ abundances were equal was the same in both irradiated ices (~63 eV/16u).

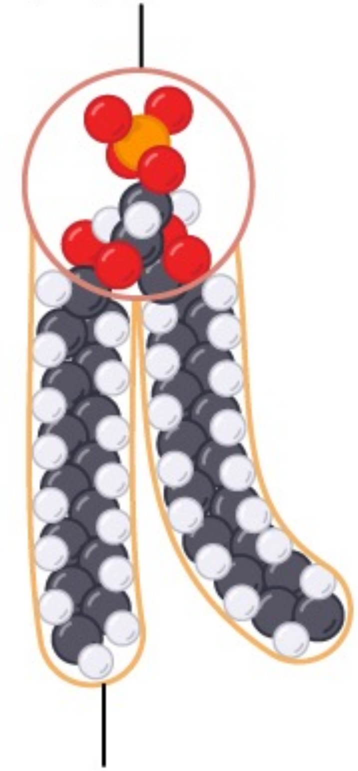
# Let’s Apply All This to a Recently Discovered Interstellar Biomolecule!

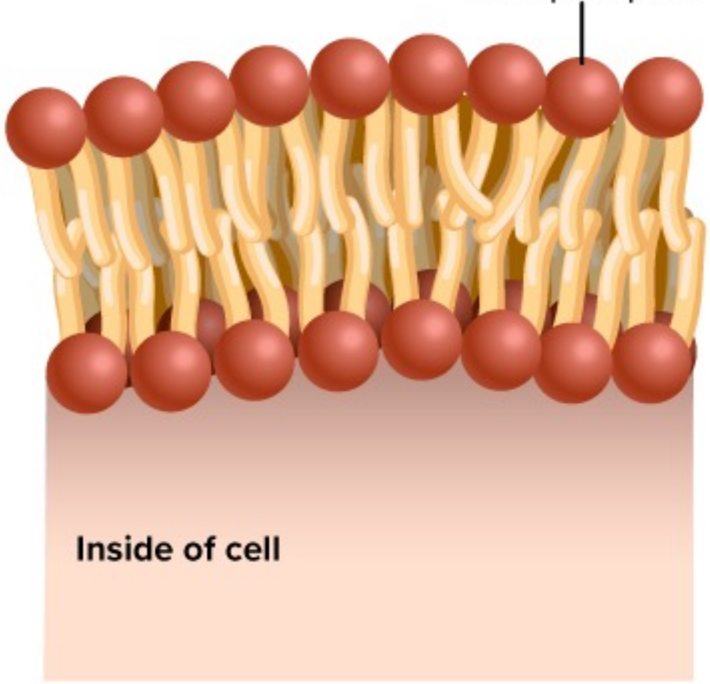
## Discovery in space of ethanolamine, the simplest phospholipid head group

Víctor M. Rivilla[a,b,1], Izaskun Jiménez-Serra[a], Jesús Martín-Pintado[a], Carlos Briones[a], Lucas F. Rodríguez-Almeida[a], Fernando Rico-Villas[a], Belén Tercero[c], Shaoshan Zeng[d], Laura Colzi[a,b], Pablo de Vicente[c], Sergio Martín[e,f], and Miguel A. Requena-Torres[g,h]

[a]Centro de Astrobiología, Consejo Superior de Investigaciones Científicas–Instituto Nacional de Técnica Aeroespacial “Esteban Terradas”, 28850 Madrid, Spain; [b]Osservatorio Astrofisico di Arcetri, Istituto Nazionale de Astrofisica, 50125 Florence, Italy; [c]Observatorio Astronómico Nacional, Instituto Geográfico Nacional, 28014 Madrid, Spain; [d]Star and Planet Formation Laboratory, Cluster for Pioneering Research, RIKEN, Wako 351-0198, Japan; [e]ALMA Department of Science, European Southern Observatory, Santiago 763-0355, Chile; [f]Department of Science Operations, Joint Atacama Large Millimeter/Submillimeter Array Observatory, Santiago 763-0355, Chile; [g]Department of Astronomy, University of Maryland, College Park, MD 20742; and [h]Department of Physics, Astronomy and Geosciences, Towson University, Towson, MD 21252





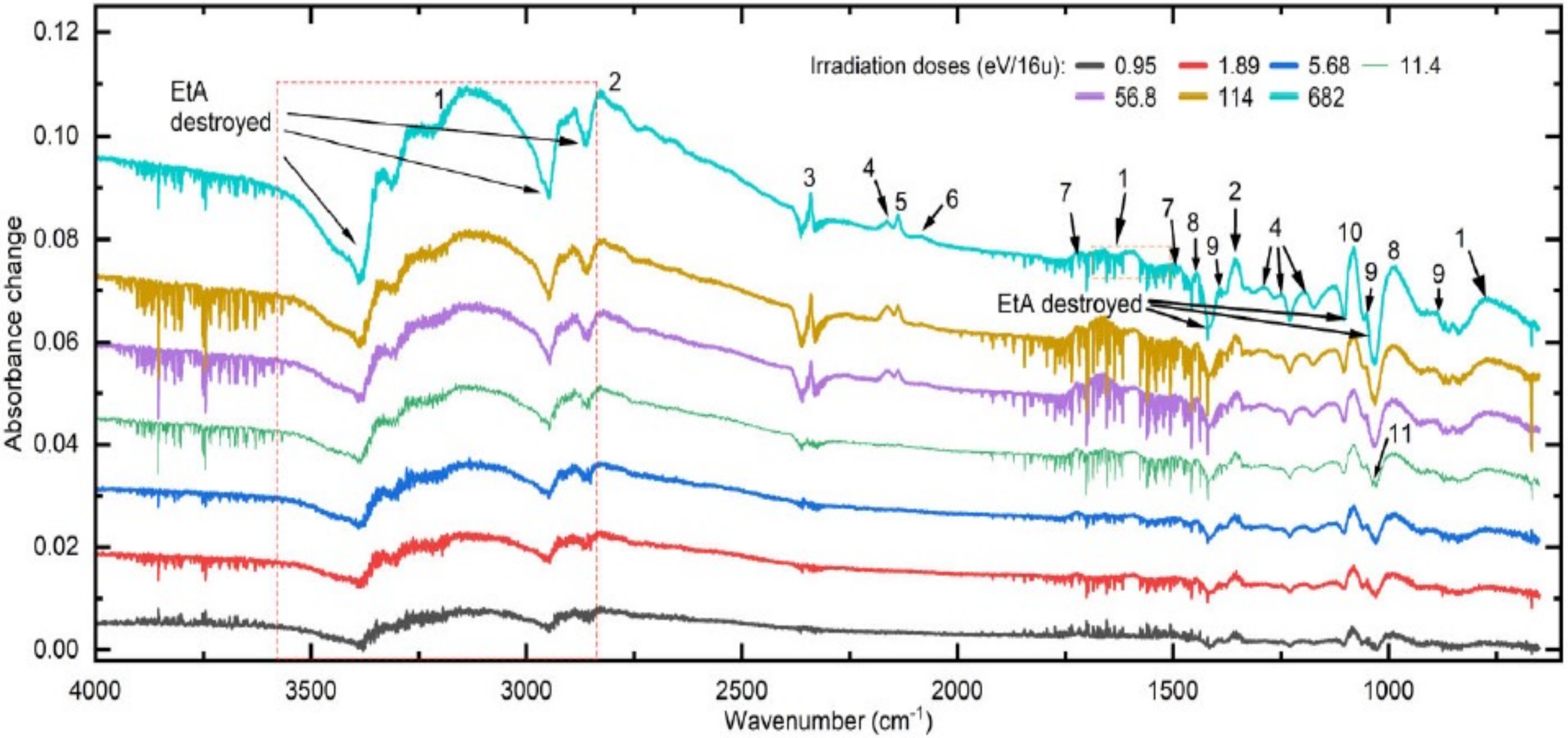



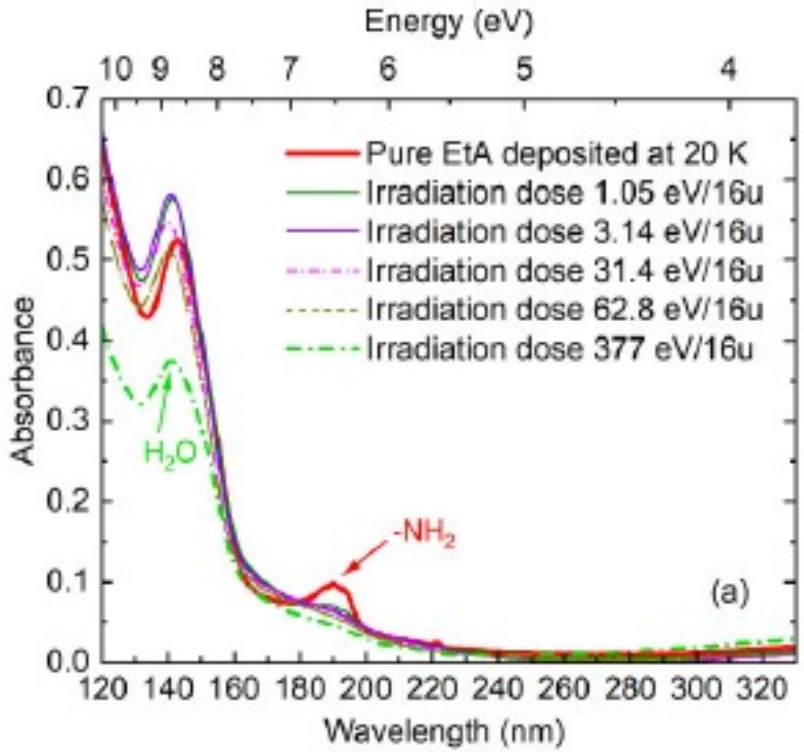
# We Have Performed Several Experiments

| Ice Sample | 1† | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Composition | Pure EtA | Pure EtA | Pure EtA | $H_2O$:EtA (50:1) | $H_2O$:EtA (20:1) | $H_2O$:EtA (50:1) |
| Temperature (K) | 20-225 | 20 | 20 | 20 | 20 | 20 |
| Thickness (μm) | 0.33 | 0.34 | 0.04 | 1.90 | 0.03 | 1.40 |
| Projectile | – | 1 keV $e^-$ | 1 keV $e^-$ | 1 keV $e^-$ | 1 keV $e^-$ | 1 MeV $He^+$ |
| Penetration depth (μm) | – | 0.045 | 0.045 | 0.050 | 0.050 | 5.6 |
| Stopping power (eV $Å^{-1}$) | – | 2.22 | 1.98 | 2.00 | 2.00 | 25.13 |
| Mass stopping power ($\times10^{-15}$ eV $cm^2$/16u) | – | 5.88 | 5.23 | 5.69 | 5.69 | 71.40 |
| Spectroscopic analysis | IR | IR | VUV | IR | VUV | IR |
| Facility | Atomki | Atomki | ASTRID2 | Atomki | ASTRID2 | Atomki |

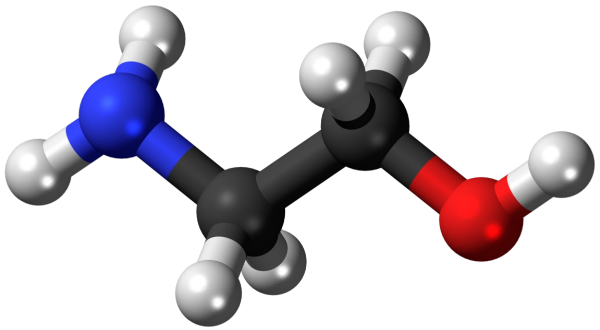
*Note.* † Non-irradiative heating experiment.

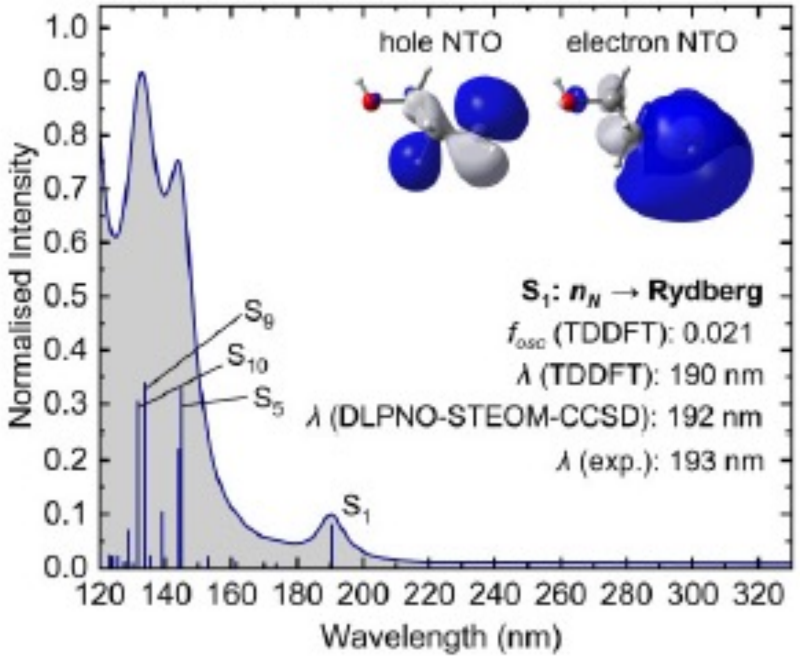
Zhang et al. 2024, *Mon. Not. R. Astron. Soc.* 533, 826.



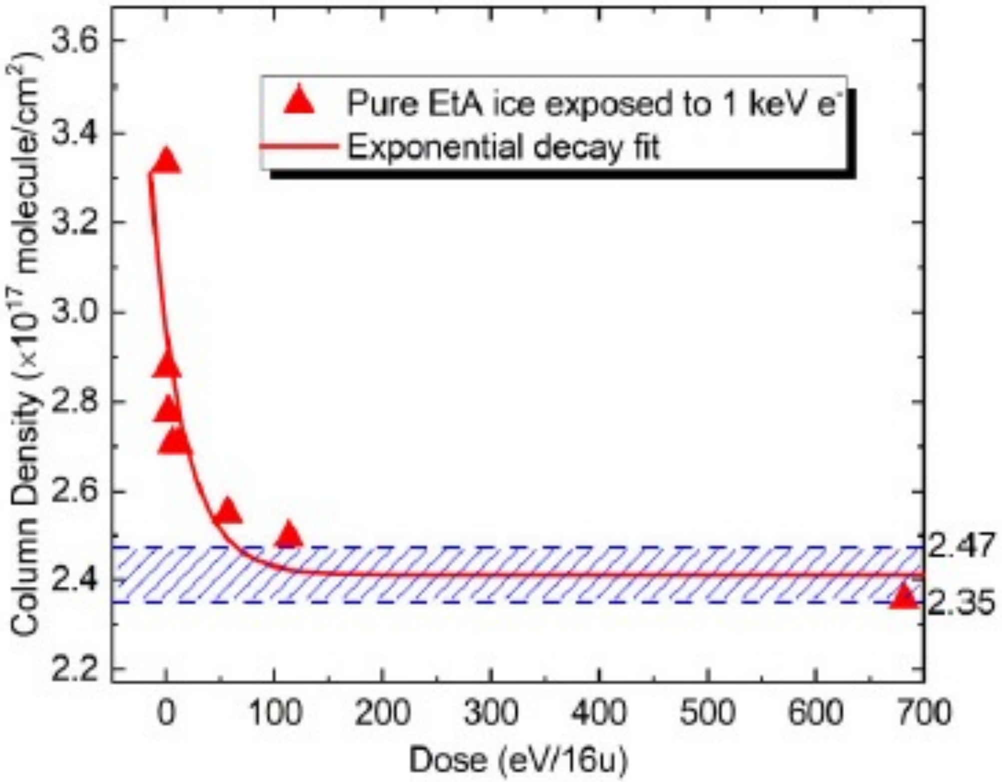



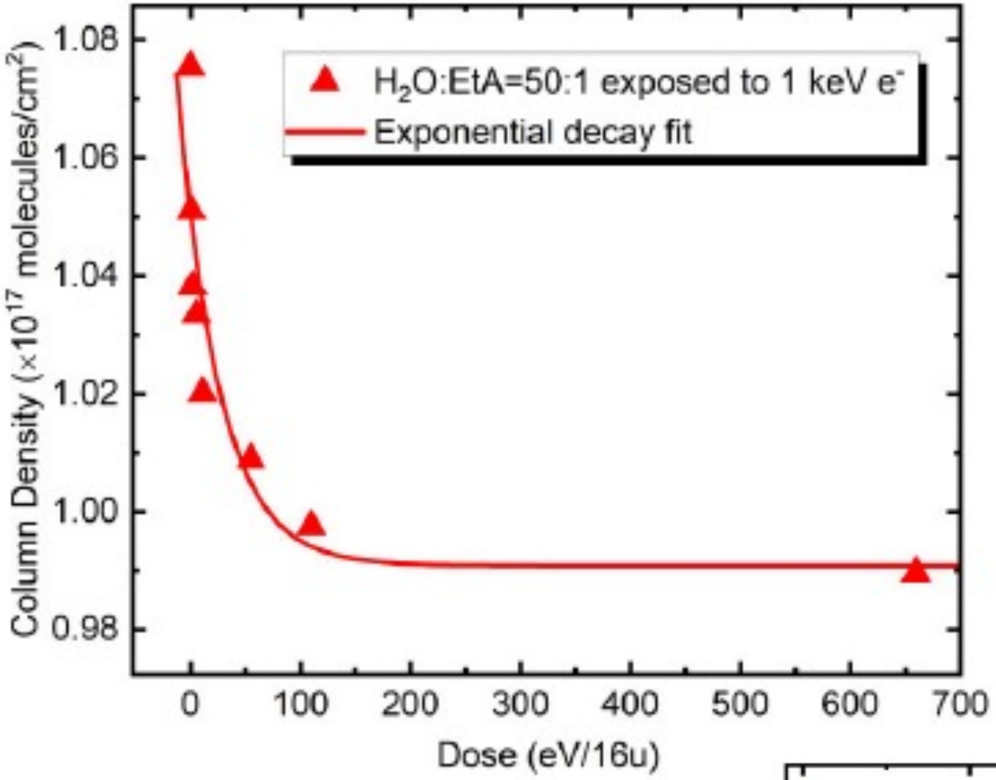

| Band No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Wavenumber (cm$^{-1}$) | 3200 | 2830 | 2340 | 2160 | 2140 | 2080 |
| | 1650 | 1350 | | 1295 | | |
| | 770 | | | 1250 | | |
| | | | | 1195 | | |
| Product | $H_2O$ | $H_2O_2$ | $CO_2$ | $OCN^-$ | CO | $CN^-$ |
| References | *a* | *b* | *c*, *d* | *e* | *f* | *g*, *h* |
| Band No. | 7 | 8 | 9 | 10 | 11 | |
| Wavenumber (cm$^{-1}$) | 1720 | 1445 | 1390 | 1080 | 1030 | |
| | 1490 | 985 | 1050 | | | |
| | | | 885 | | | |
| Product | HCHO | $C_2H_4$ | $C_2H_5OH$ | $NH_3$ | $CH_3OH$ | |
| References | *i* | *j* | *k* | *l* | *m*, *n* | |

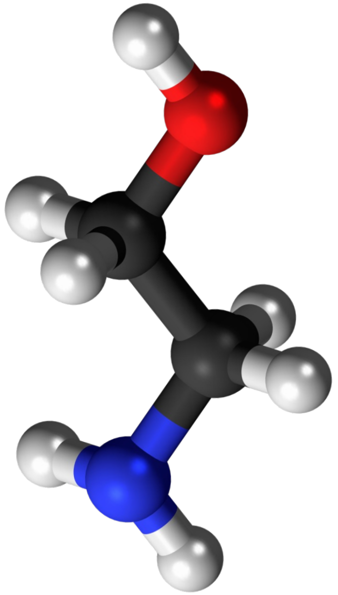




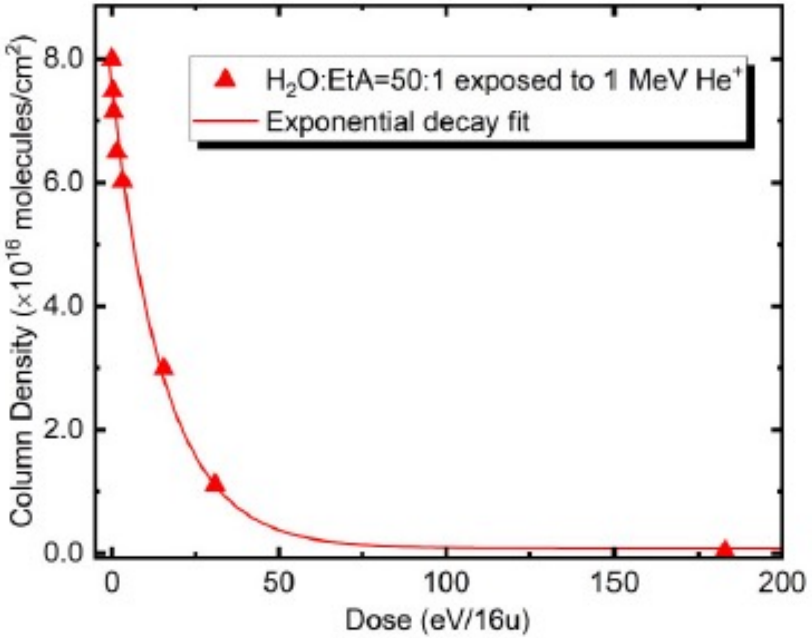

Zhang et al. 2024,
*Mon. Not. R. Astron. Soc.* 533, 826.



| Irradiation Experiment | Amount of Ethanolamine Destroyed (half-life dose) |
|---|---|
| Pure ethanolamine (1 keV e$^-$) | 29% (20.8 eV/16u) |
| Ethanolamine:Water (1 keV e$^-$) | 8% (26.3 eV/16u) |
| Ethanolamine:Water (1 MeV He$^+$ ions) | 99.6% (10.8 eV/16u) |




**Zhang et al. 2024, *Mon. Not. R. Astron. Soc.* 533, 826.**

# So What is the Survivability of Ethanolamine in Space Radiation Environments?

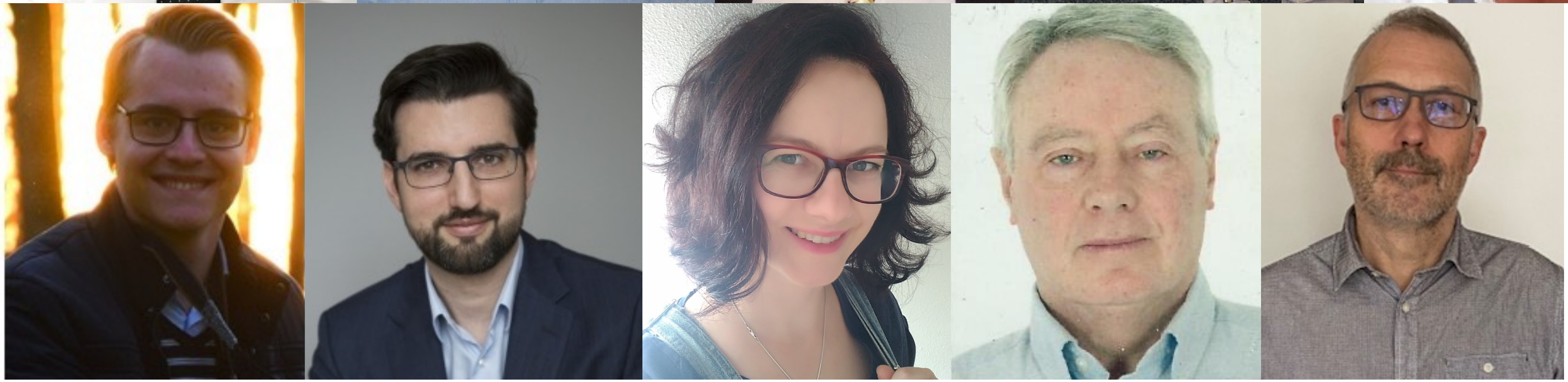
| Location of ice | Ice lifetime (yr) | Dose rate (eV· molecule$^{-1}$ yr$^{-1}$) | Half-life of EtA (yr) |
|---|---|---|---|
| Cold dense cloud | $10^7$ | $3\times10^{-7}$ [a] | $(3.6 \pm 0.4) \times 10^7$ |
| KBO (depth: $<1\times10^{-6}$ cm) | $4.6\times10^9$ | $5.6\times10^{-3}$ [b] | $(1.9 \pm 0.2) \times 10^3$ |
| KBO (depth: $1\times10^{-3}$ cm) | $4.6\times10^9$ | $1.6\times10^{-8}$ [c] | $(6.8 \pm 0.8) \times 10^8$ |

*Notes.* † We consider similar environments to Maté et al. (2018).
[a] Moore, Hudson & Gerakines (2001).
[b] Cooper et al. (2003). We consider a CR dose rate for surface ices of thickness $< 1 \times 10^{-6}$ cm.
[c] Strazzulla et al. (2003). We consider a CR dose rate for ices at depths of $1 \times 10^{-3}$ cm.

Zhang et al. 2024, *Mon. Not. R. Astron. Soc.* 533, 826.

# So What Does This Mean?

- Ethanolamine in interstellar ices can survive the collapse of the cold dense cores.
- In outer Solar System ices, ethanolamine is efficiently destroyed if it is located at the surface of the icy object.
- However, it can be efficiently preserved within the ice if it is buried under $10^{-3}$ cm.



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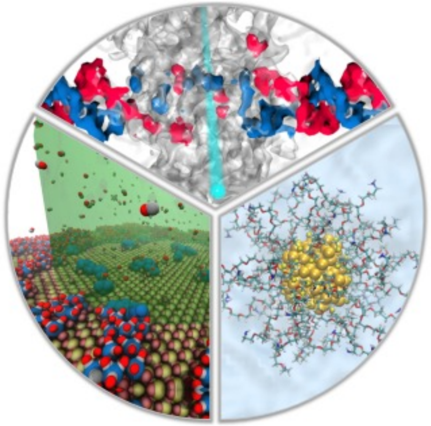

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# Thank you for your attention!

Any Questions?