Radiation Chemistry vs. Photochemistry Cosmic Synthesis of Prebiotic Molecules

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First Evidence of molecules in space:
Annie Jump Cannon
(Wellesley College Class of 1884)

1. Introduction

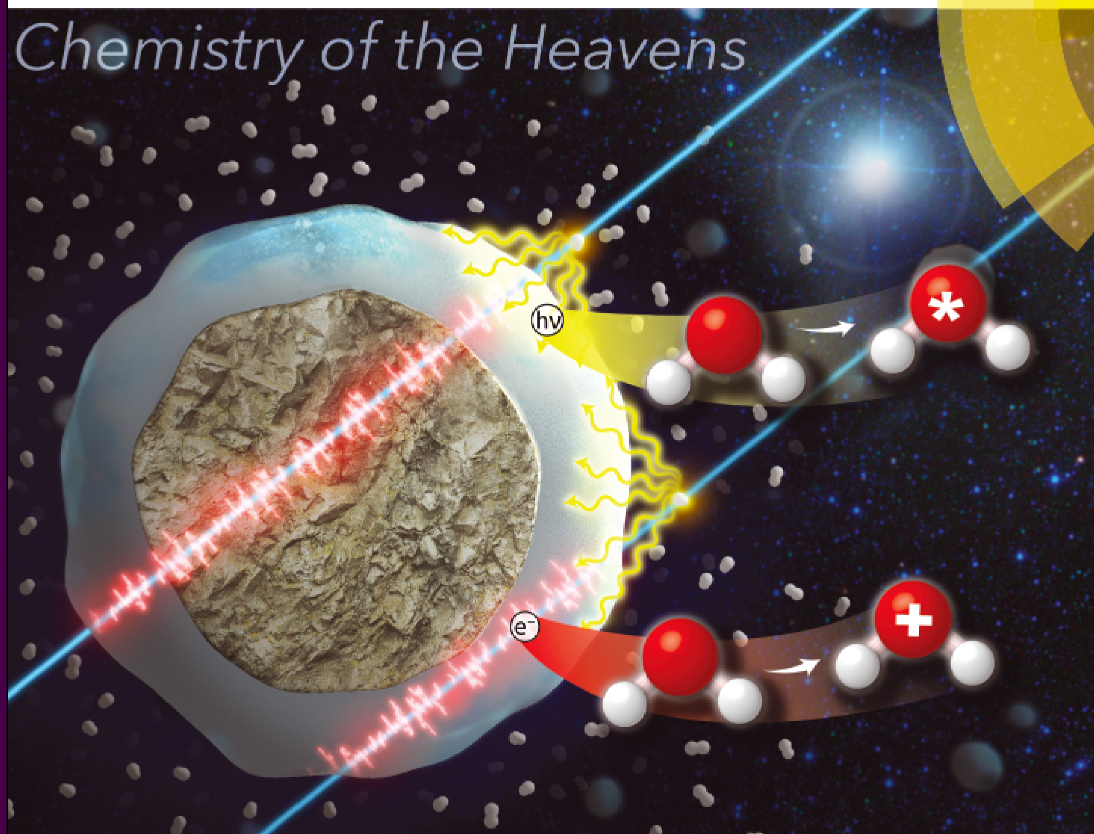
A long-standing question in astronomical spectroscopy has been the identity of the carriers of the diffuse interstellar bands (DIBs). DIBs are broad absorption features, primarily in the visible region, that have been observed in the spectra of numerous stars [1, 2]. After the incidental observation of the strongest DIB at 4430 Å (henceforth referred to as the λ4430 DIB) by Annie Jump Cannon in the early years of stellar spectroscopy [3–5] and reports of the λλ5780 and 5797 DIBs by Mary Heger in 1922 [6, 7], Paul W. Merrill demonstrated in the 1930s that these spectral features arose due to intervening interstellar material [8, 9]. Laboratory spectroscopy and computational modeling have led to a diverse set of hypotheses for the origins of DIBs. Douglas argued for the consideration of long-

Molecular Physics, **2015**,113, 2159-2168

Volume 48 | Number 8 | 21 April 2019 | Pages 2267–2496

Chem Soc Rev

Chemical Society Reviews
rsc.li/chem-soc-rev

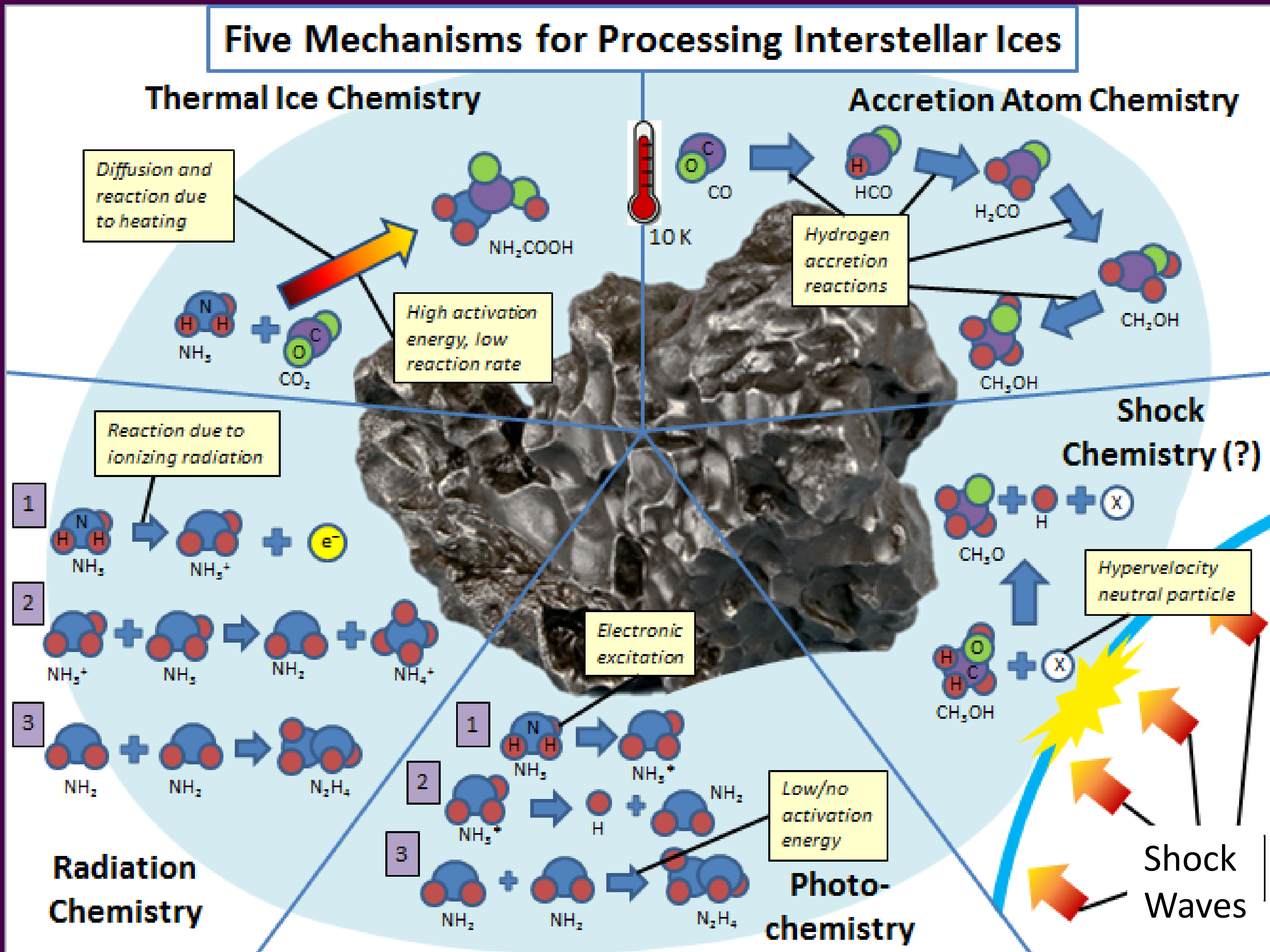


ISSN 0306-0012

ROYAL SOCIETY OF CHEMISTRY | Celebrating IYPT 2019

TUTORIAL REVIEW
Chris R. Arumainayagam *et al.*
Extraterrestrial prebiotic molecules: photochemistry *vs.* radiation chemistry of interstellar ices

Five Mechanisms for Processing Interstellar Ices



Arumainayagam *et. al.*, *Chemical Society Reviews* **2019**, 48, 8, 2267–2496.

What is the difference between radiation chemistry and photochemistry?

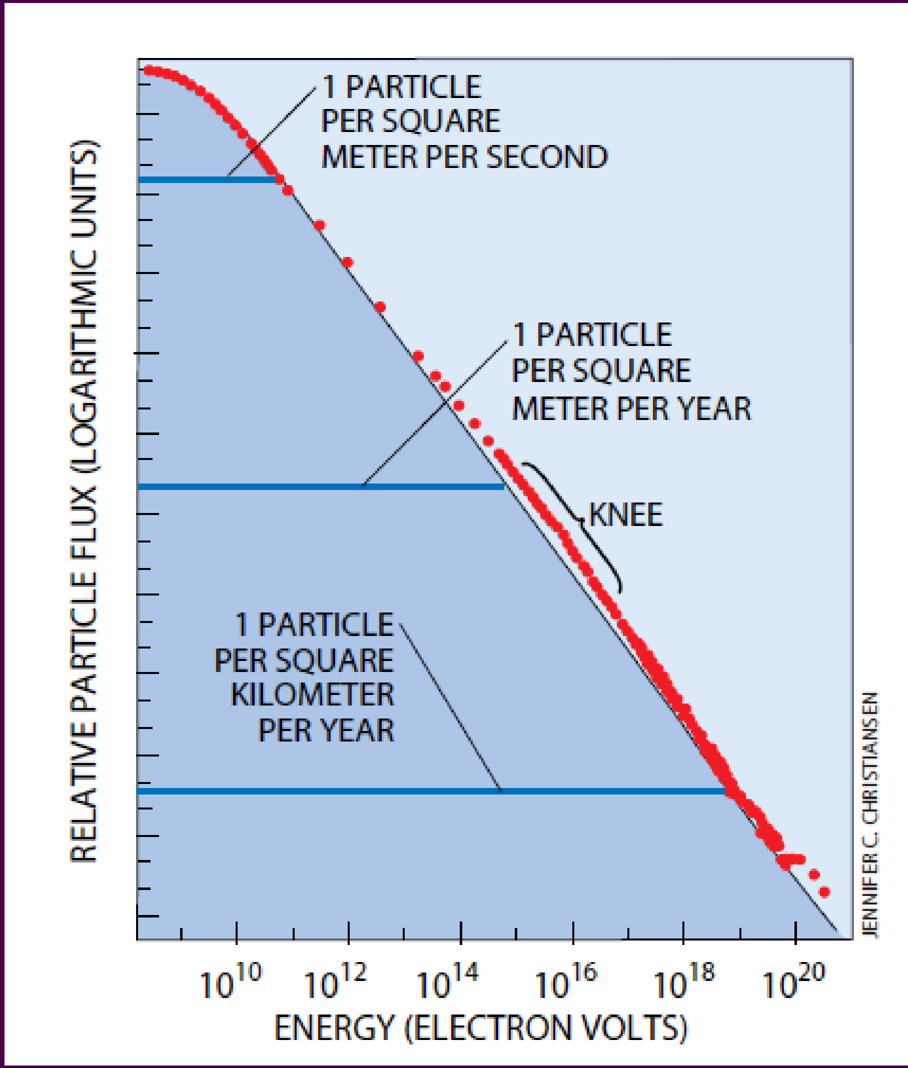
Radiation Chemistry

Radiation chemistry is the “study of the chemical changes produced by the absorption of radiation of sufficiently high energy to produce ionization.”

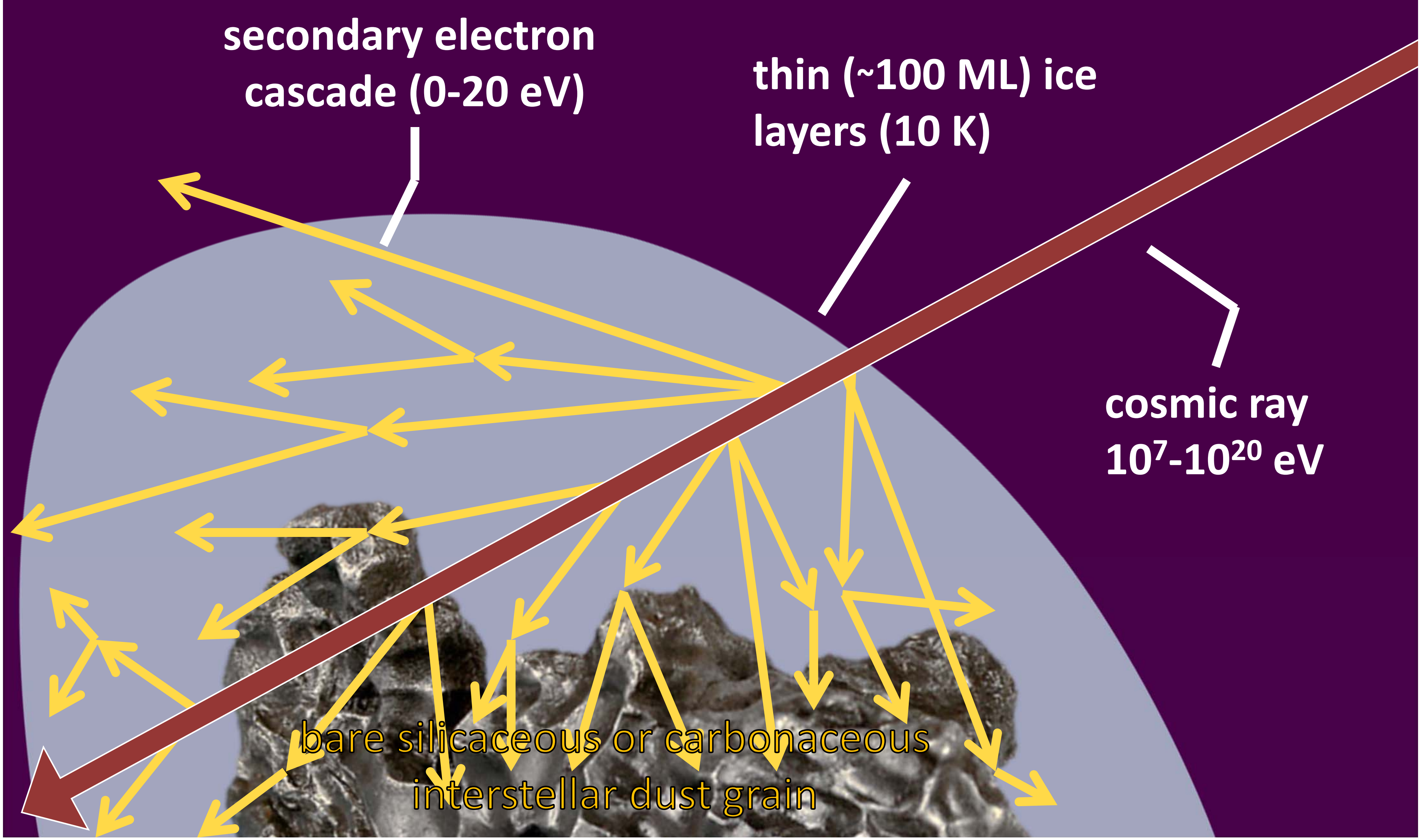
RADIATION CHEMISTRY INVOLVES IONIZATION.

R.J. Woods, Basics of Radiation Chemistry, in: R.D.C. William J. Cooper, Kevin E. O'Shea

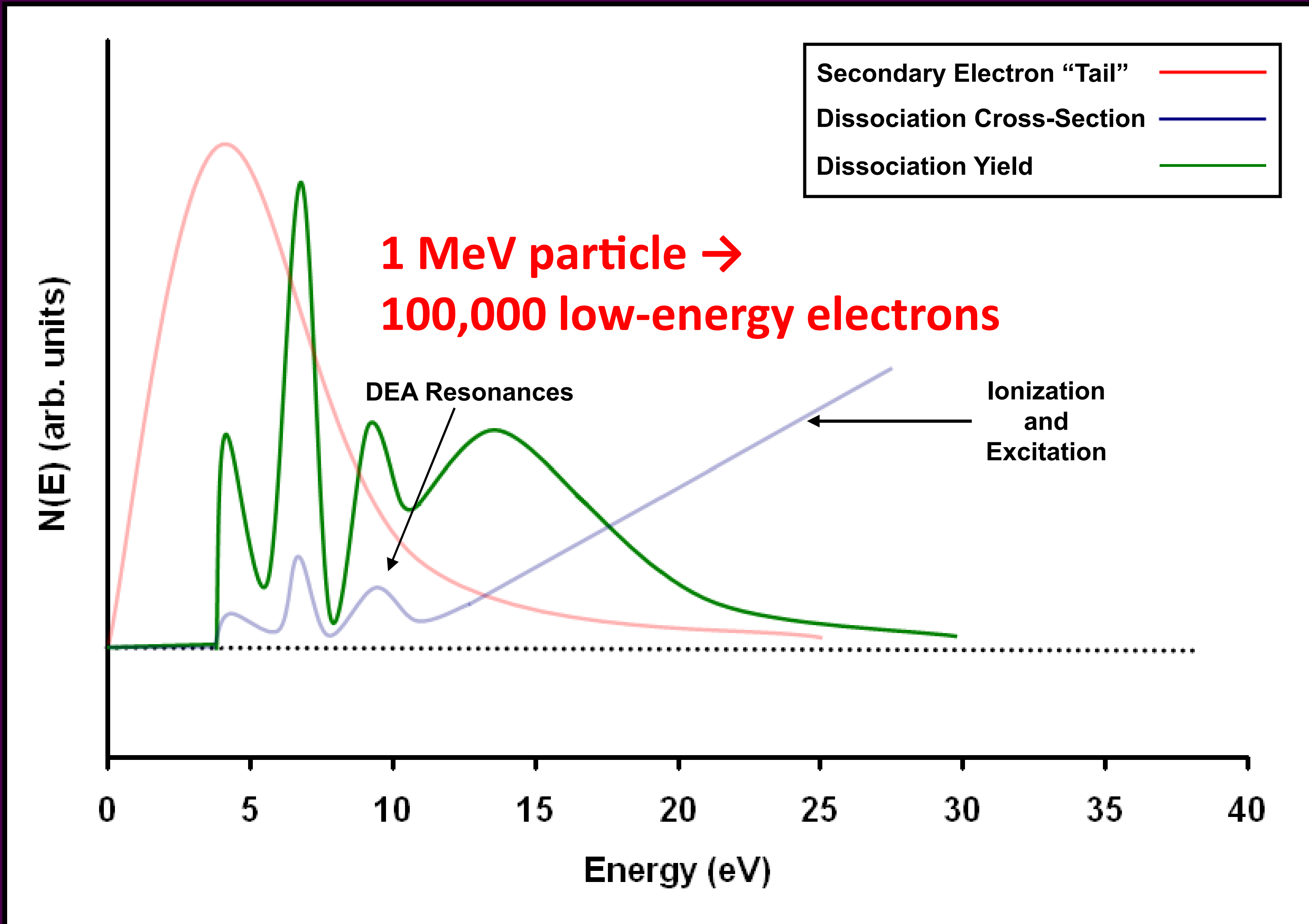
Flux of Cosmic Rays Reaching Earth



Formation of Secondary Electrons in Cosmic Ices and Dust Grains

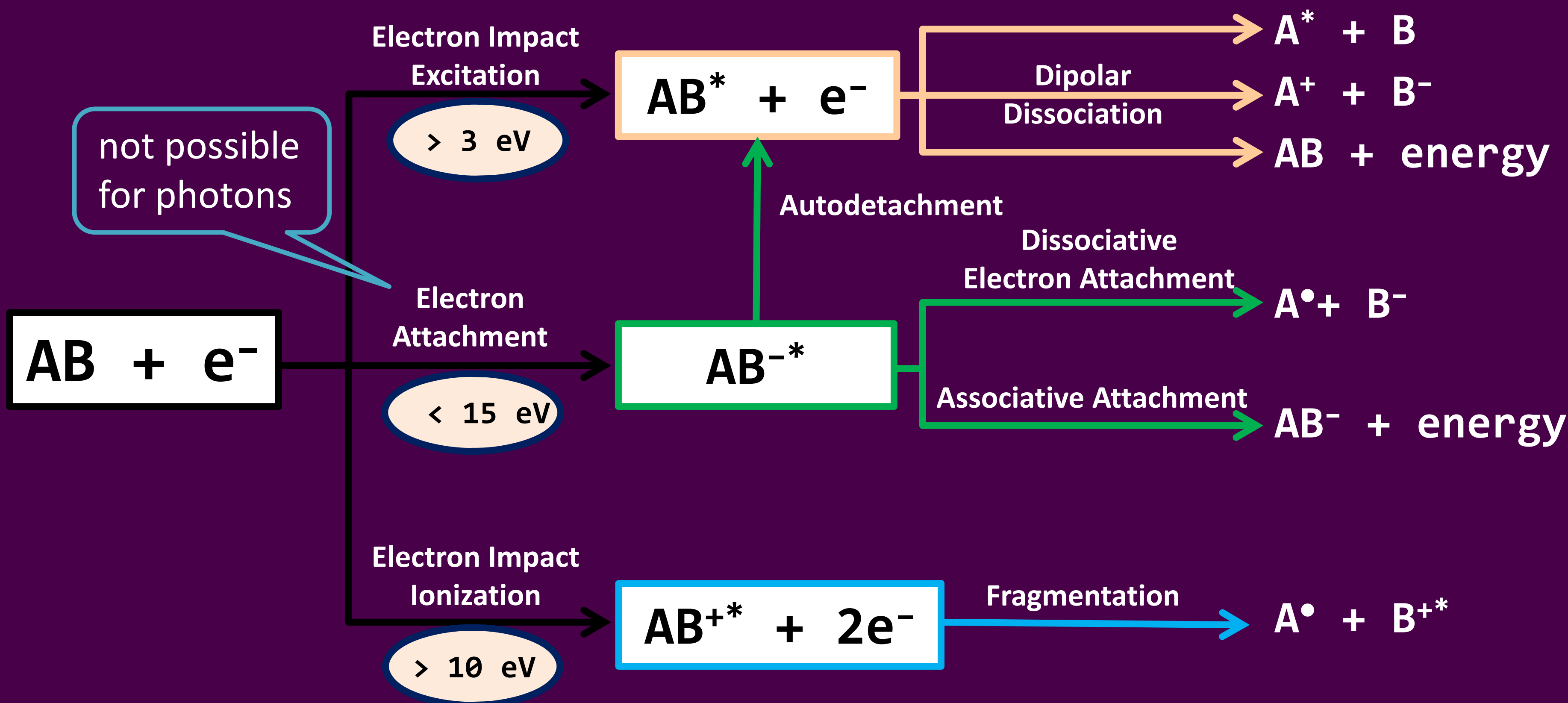


Importance of Low-Energy Electrons



C. Arumainayagam et al., *Surface Science Reports* 65 (**2010**) 1–44.

Electron-induced Dissociation Mechanisms



Photochemistry

Photochemistry involves "chemical processes which occur from the electronically excited state formed by photon absorption."

– visible (1.8 eV – 3.1 eV)
– near-UV (3.1 – 4.1 eV)
– far (deep)-UV (4.1 – 6.2 eV)

} no ionization; only excitation

– vacuum-UV (6.2 –12.4 eV)

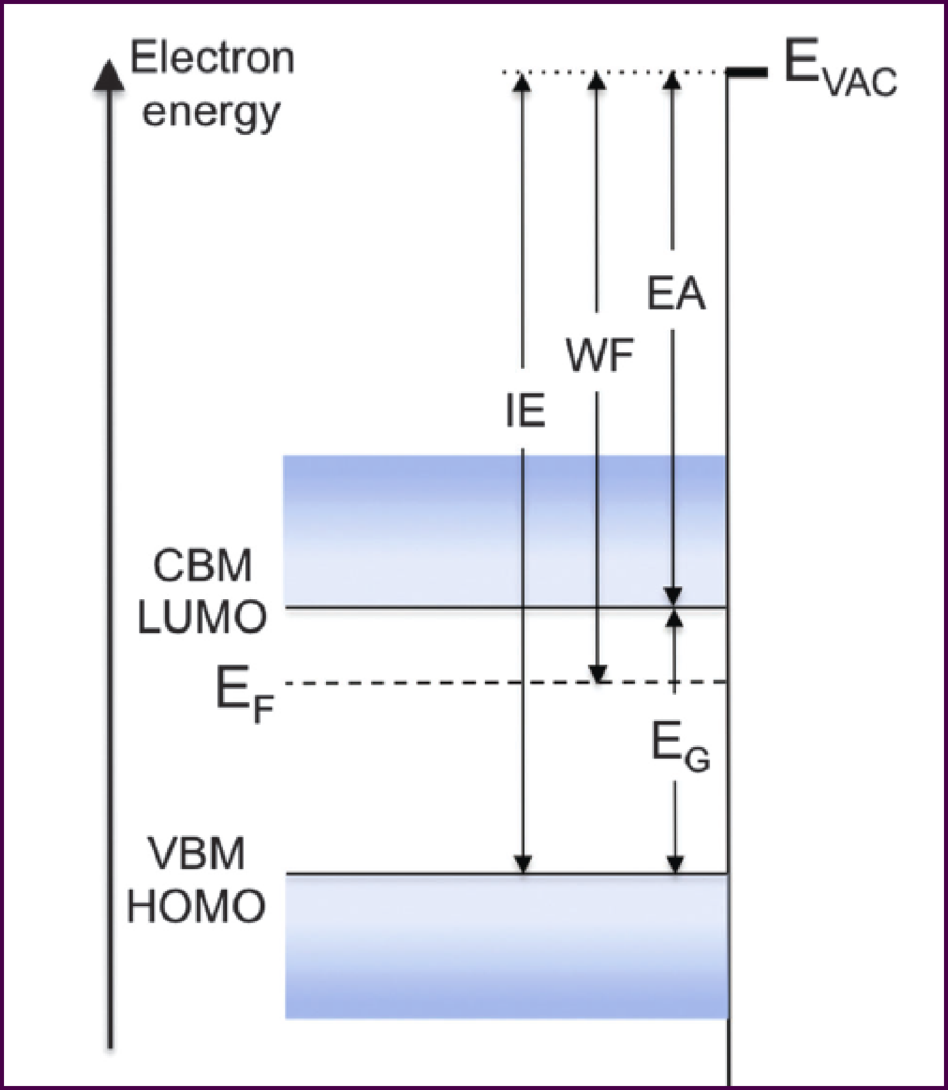
} ionization AND excitation

B. Wardle, Principles and Applications of Photochemistry, Wiley, Chichester, UK, 2009.

Condensed Phase Ionization Energy

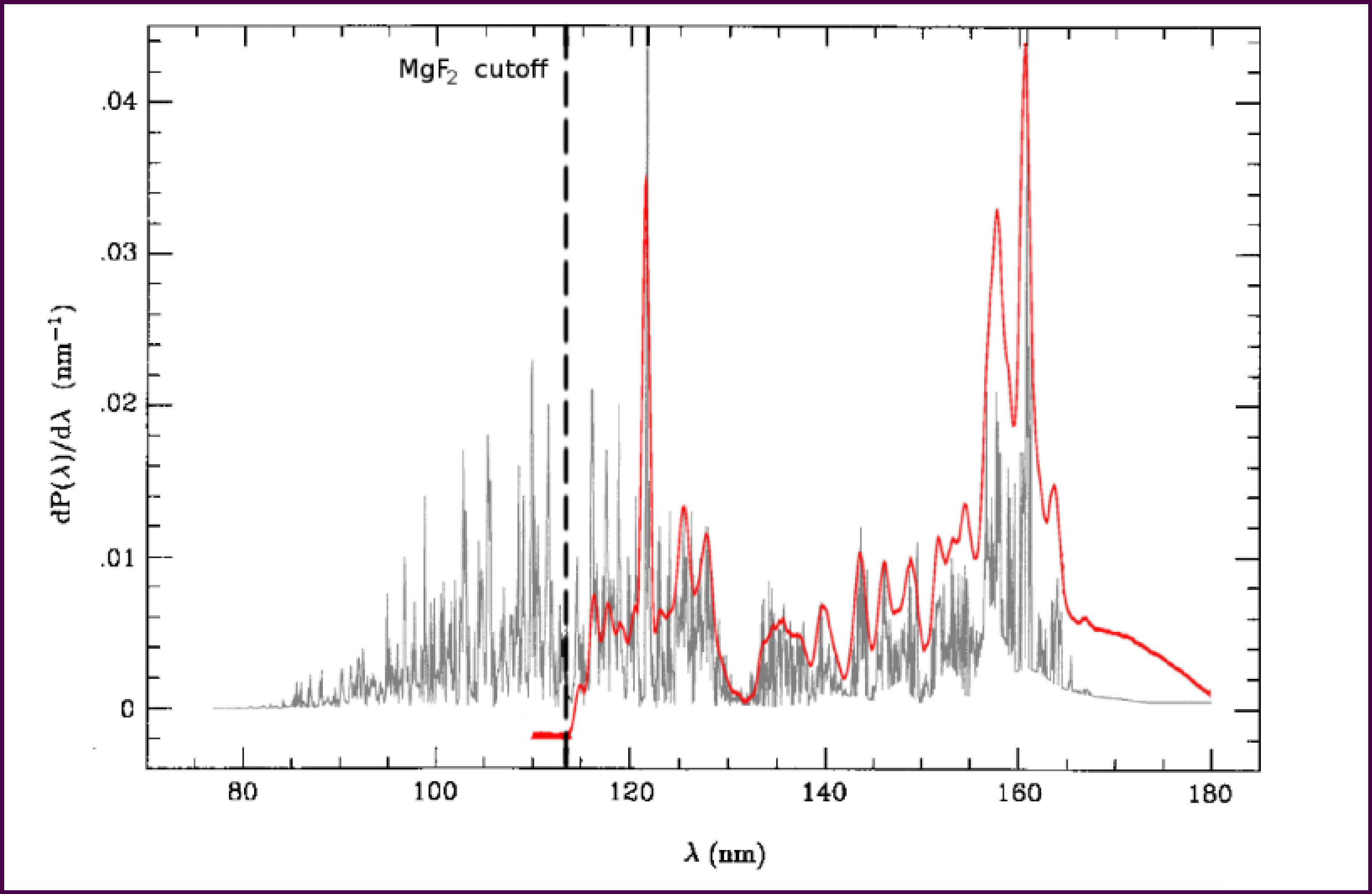
$$IE_{\substack{condensed \\ phase}} < IE_{\substack{gas \\ phase}}$$

Most previous "photochemistry" studies relevant to astrochemistry involve radiation chemistry in addition to photochemistry.



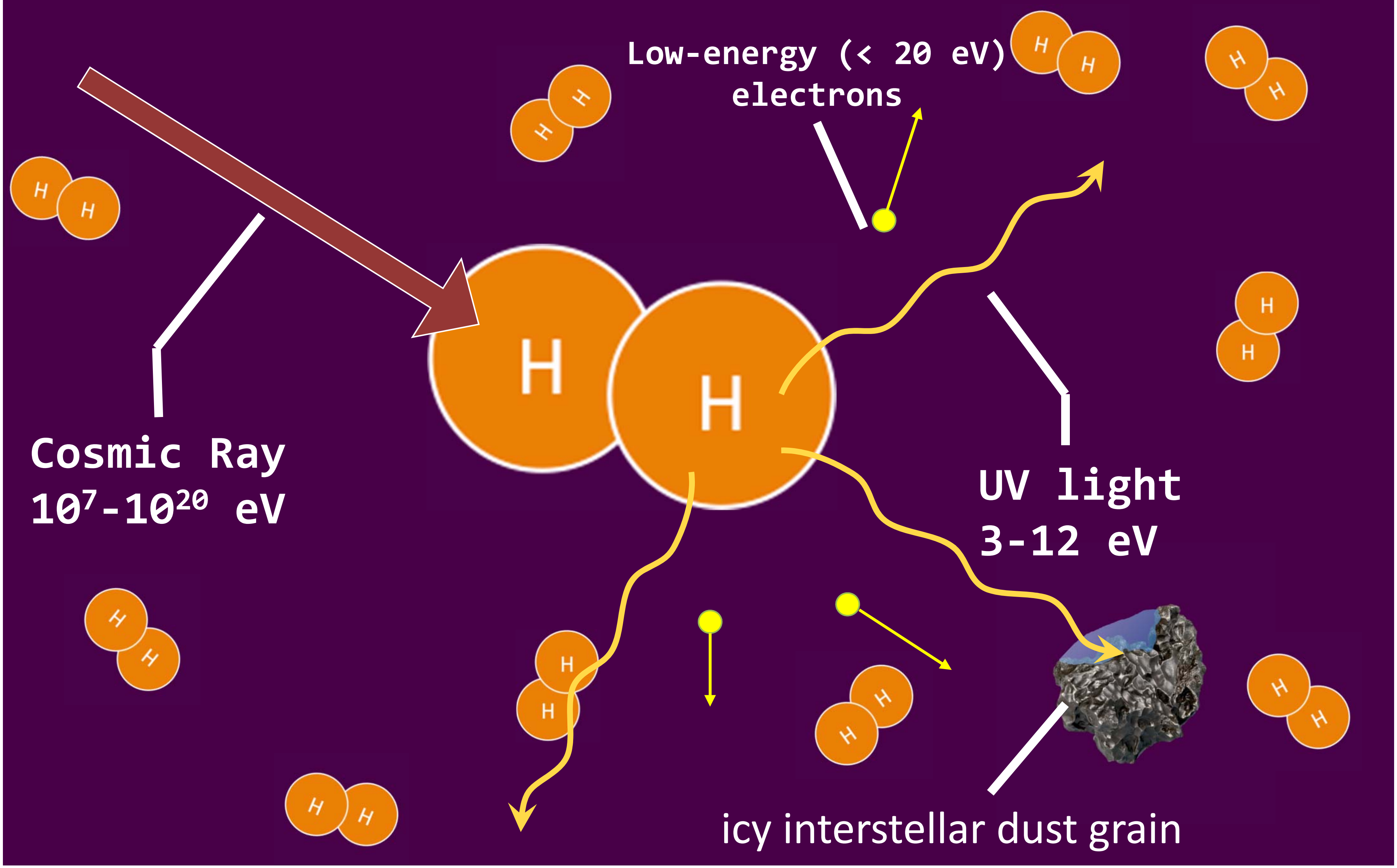
Mater. Horiz., 2016, 3, 7--10

VUV-emission spectrum of Microwave-Discharge Hydrogen-Flow Lamps (MDHL)

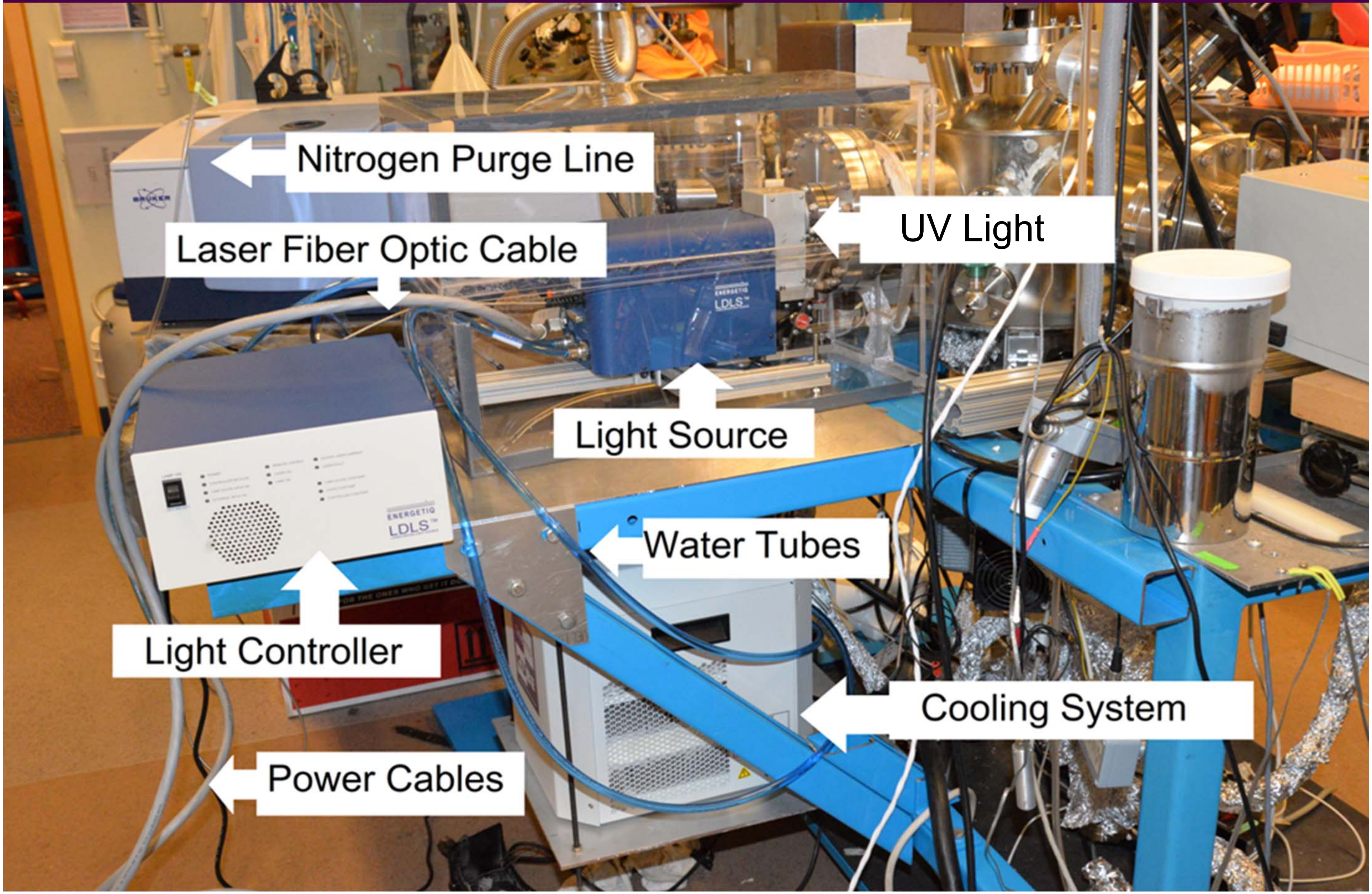


CREDIT: Gustavo Adolfo Cruz Diaz

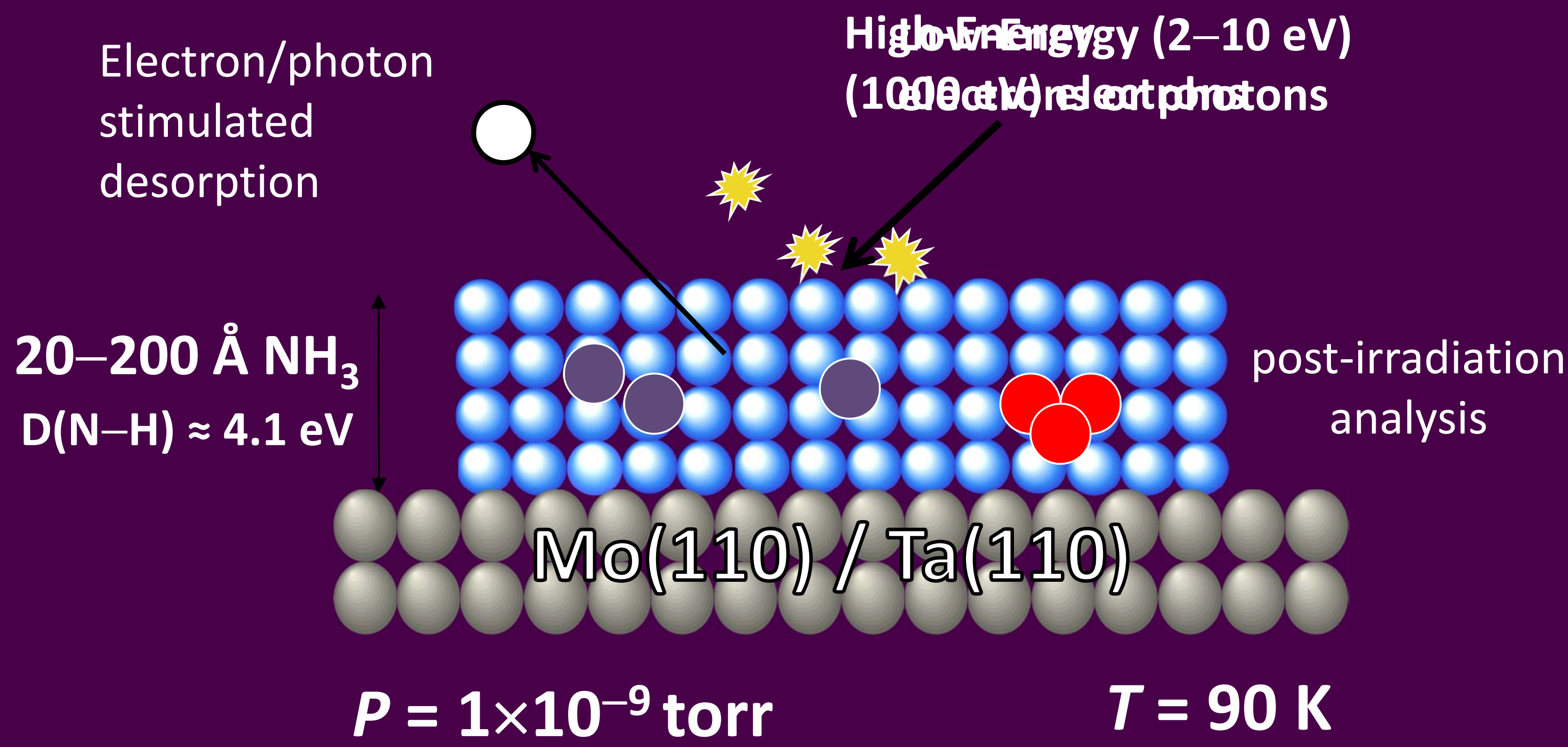
UV light formation within dark, dense molecular clouds



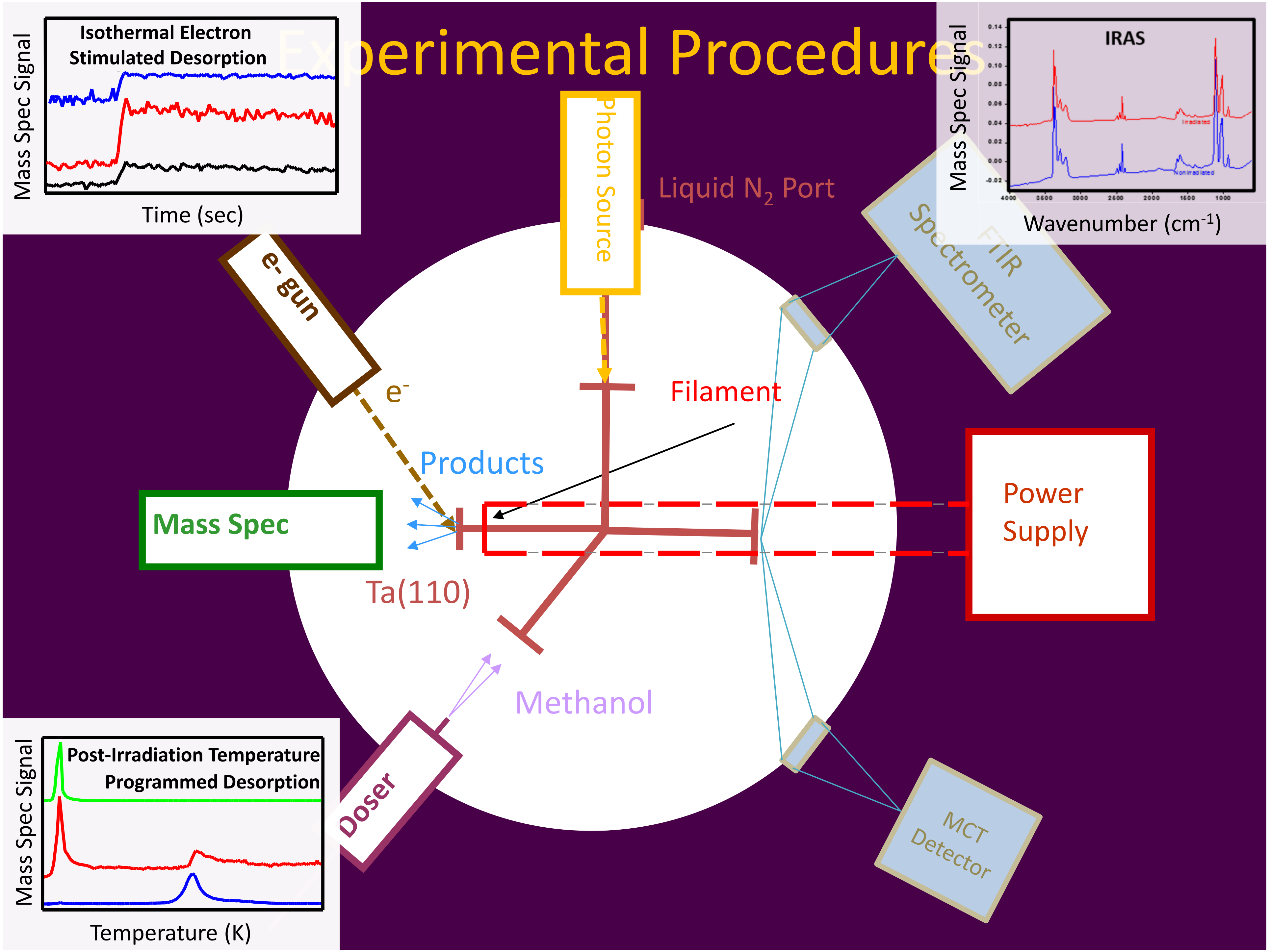
How do you create a little bit of heaven on earth?

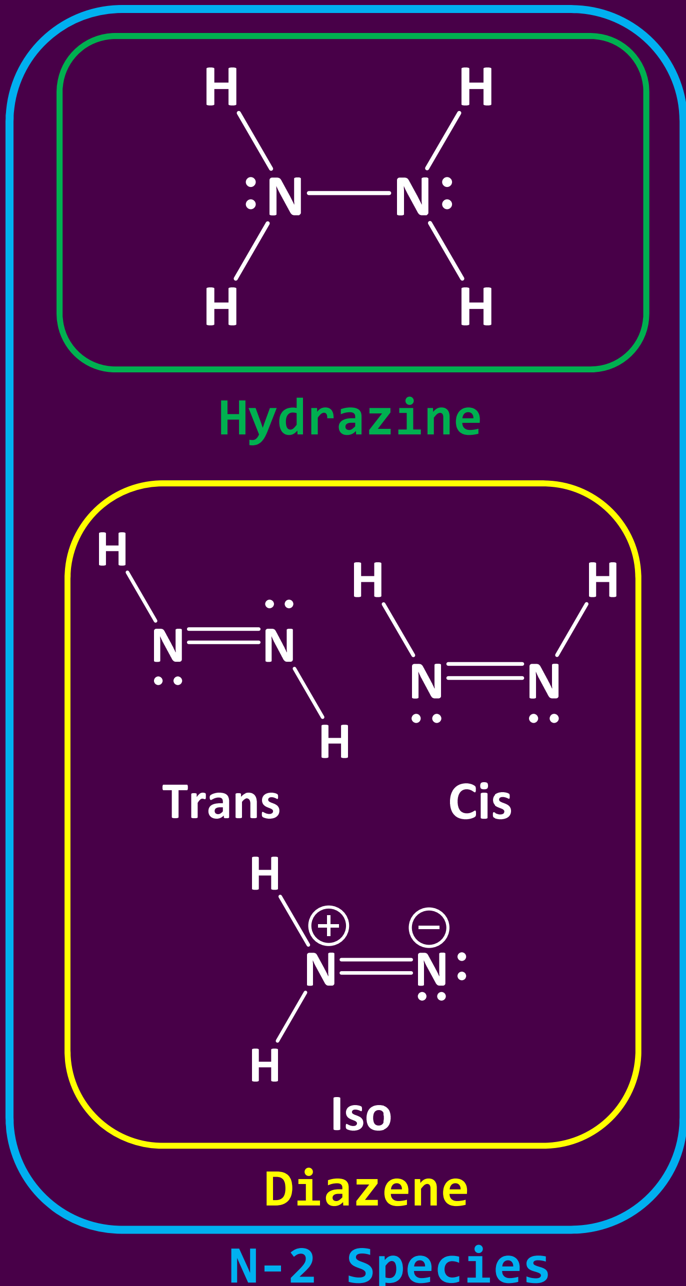


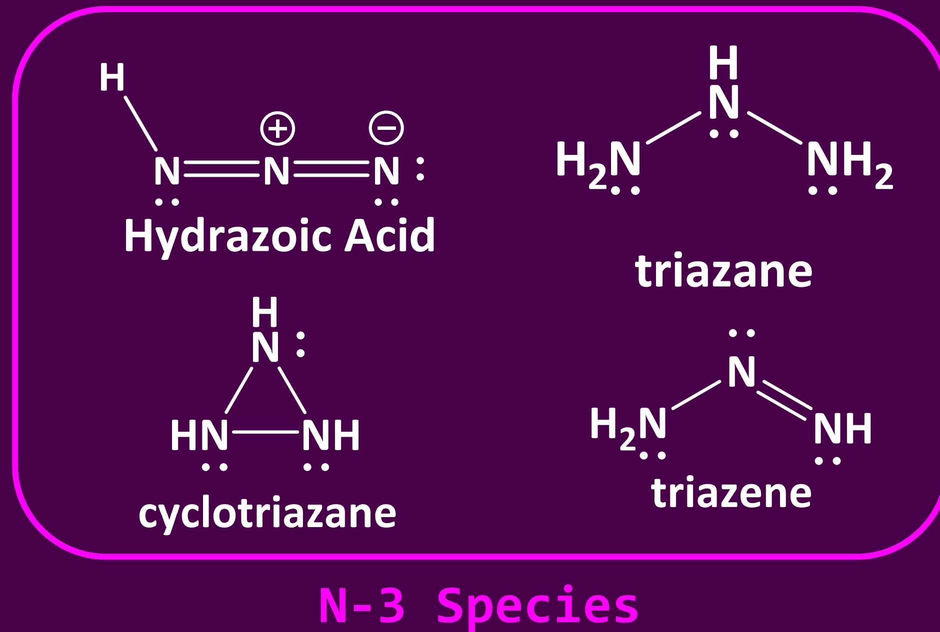
Experimental Procedures



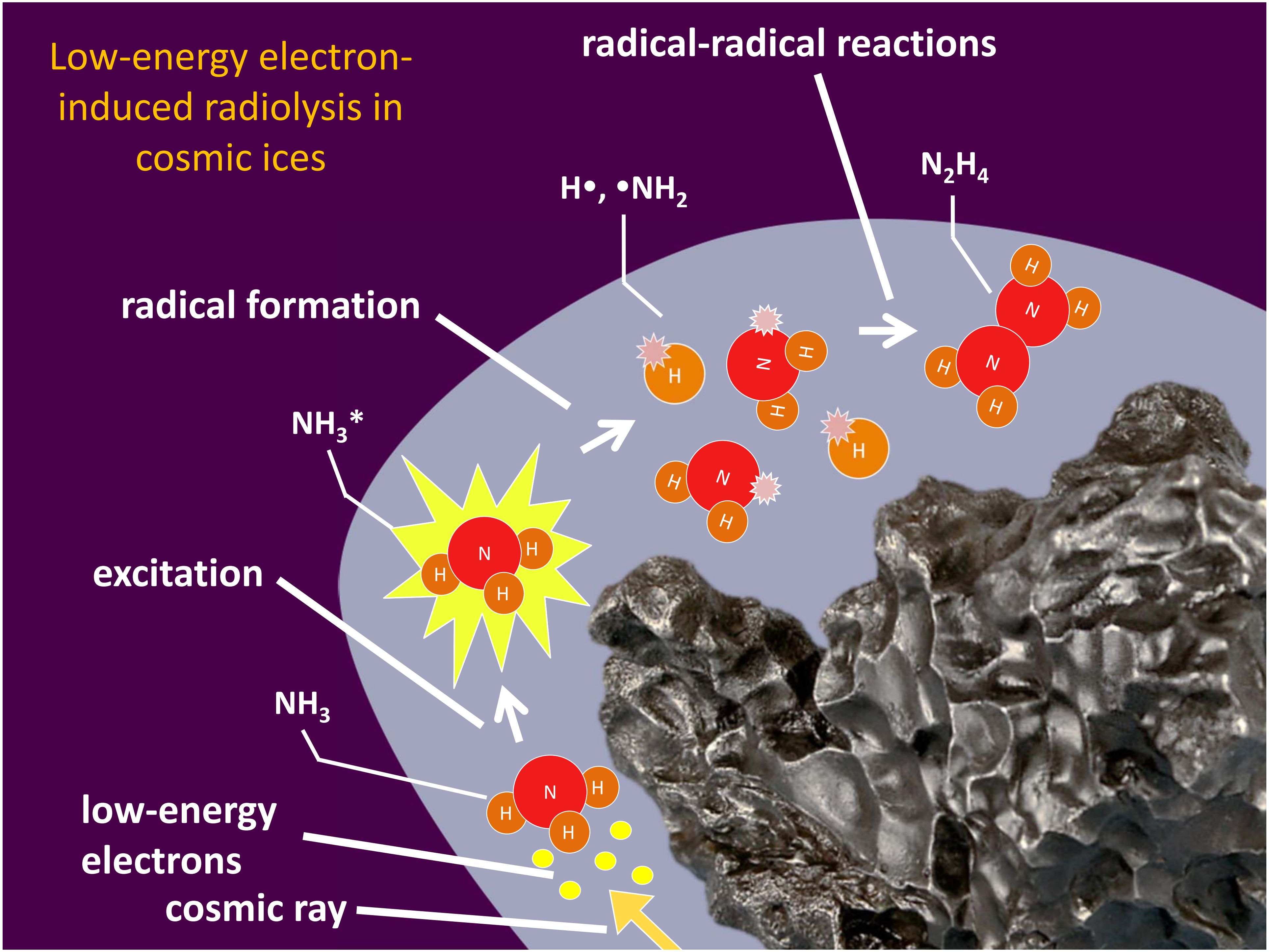
Experimental Procedures



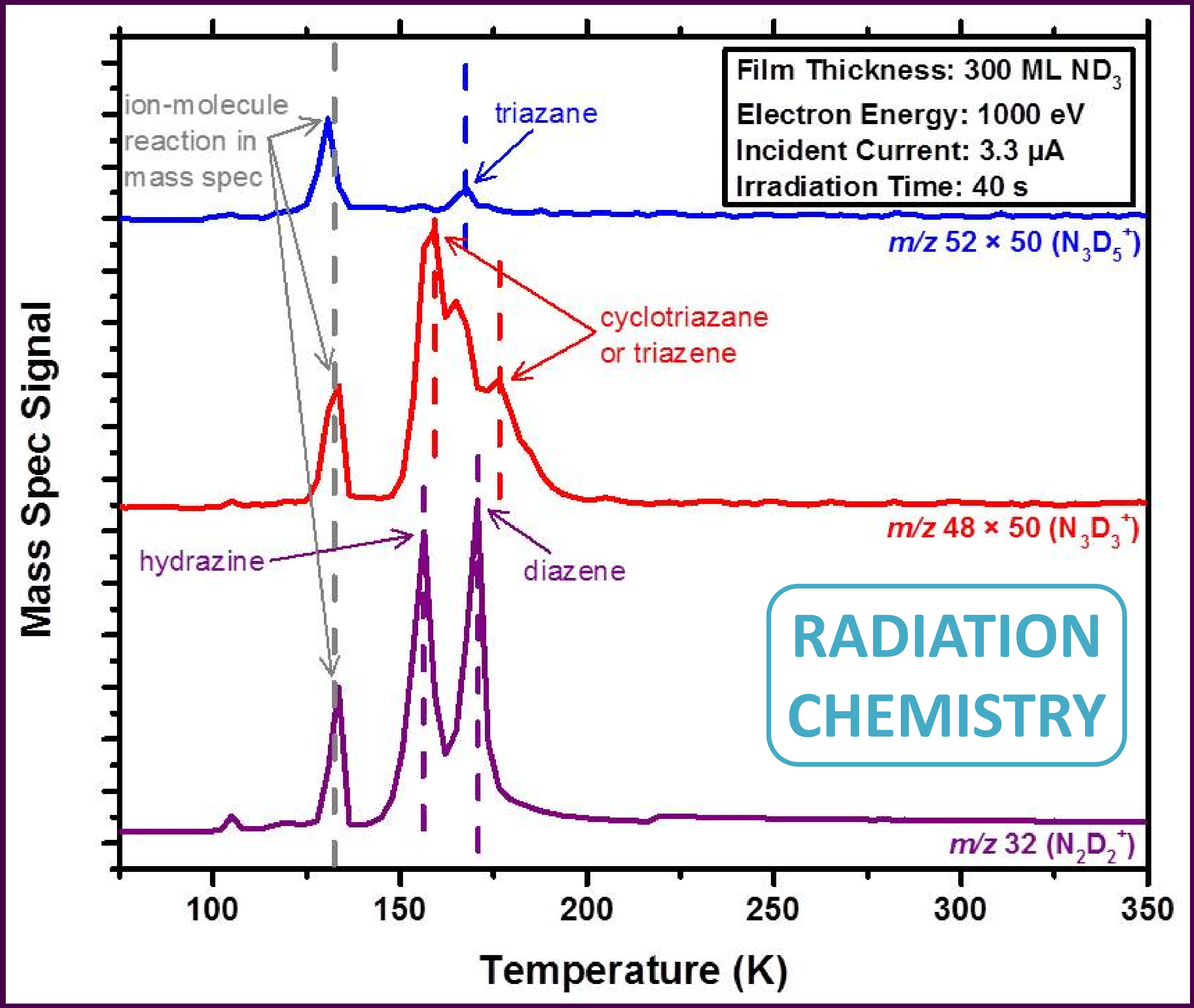




Possible Radiolysis/Photolysis Products of Ammonia

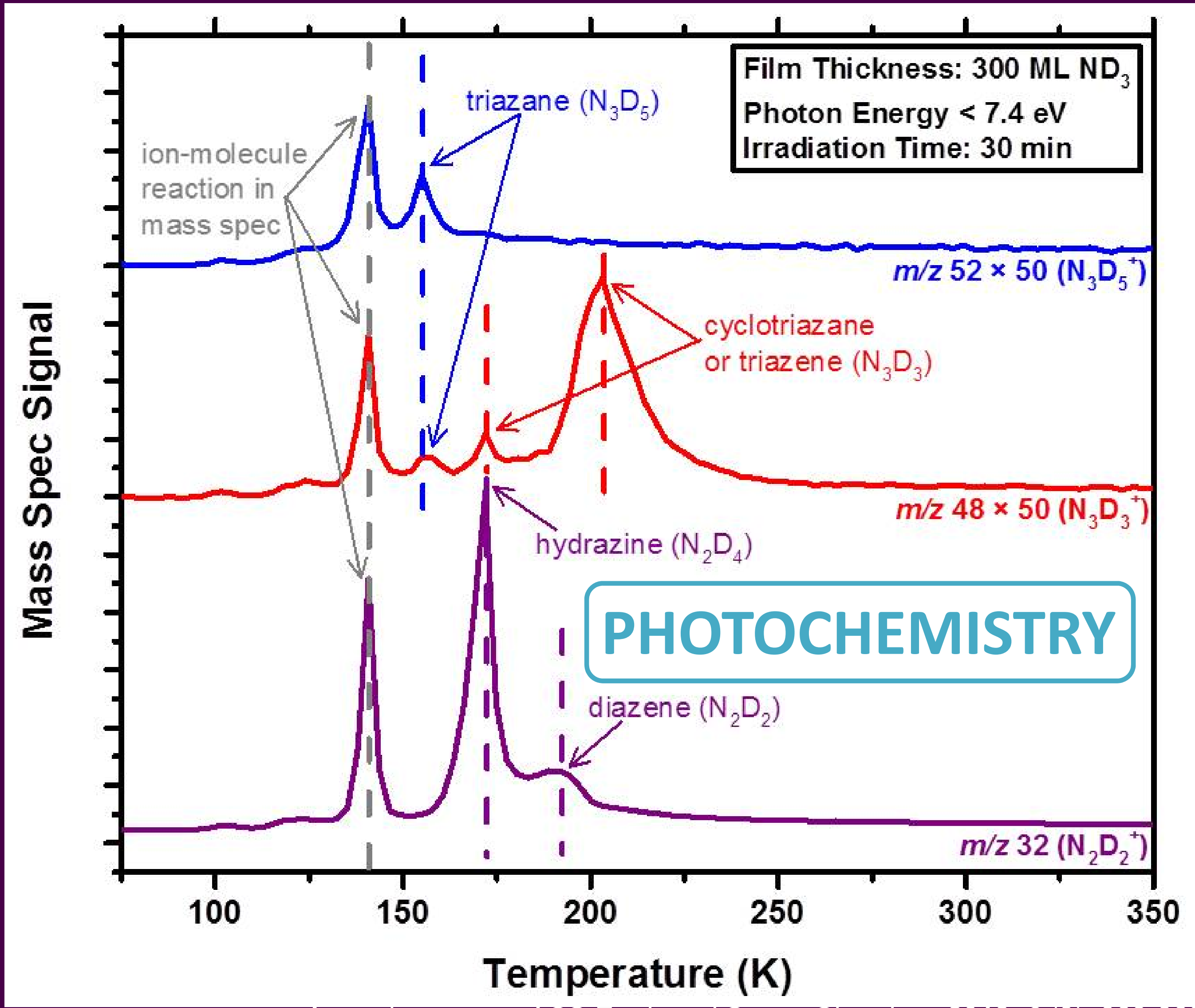

Low-energy electron-induced radiolysis in cosmic ices
radical-radical reactions
N2H4
H•, •NH2
radical formation
NH3*
excitation
NH3
low-energy electrons
cosmic ray
N
H

Products of High Energy Electrons From Condensed Ammonia



Arumainayagam, *ACS Earth and Space Chemistry* **2019**, 3, 800−810

Products of Low-Energy Photons From Condensed Ammonia



Arumainayagam, *ACS Earth and Space Chemistry* **2018,** *2* (9), 863-868.

Energetics of Ammonia Photolysis

- Ionization energy for gas phase ammonia: 10.1 eV
- Threshold for low-energy secondary electrons: 8.5 eV
- Absorption threshold photon energy: 6.2 eV

Our experiments were done at < 7.4 eV.

Most previous "photochemistry" studies relevant to astrochemistry involve radiation chemistry in addition to photochemistry.

Our experiments involve only photochemistry.

Conclusions

- Low-energy (< 20 eV) electrons may be the dominant species responsible for the synthesis of prebiotic molecules in the interstellar medium

Acknowledgements

Collaborators

Dr. Andrew Bass, Université de Sherbrooke
Dr. Leon Sanche, Université de Sherbrooke
Dr. Petra Swiderek, University of Bremen
Dr. Michael Boyer (Clark University)

Funding Source

National Science Foundation (CHE-1465161, CHE-1012674, CHE-1005032)

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