Radiolysis of Cosmic Ice Analogs of Ammonia, an Interstellar Hydride

Leslie Gates and Chris Arumainayagam
Wellesley College, Massachusetts, USA

electron stimulated desorption

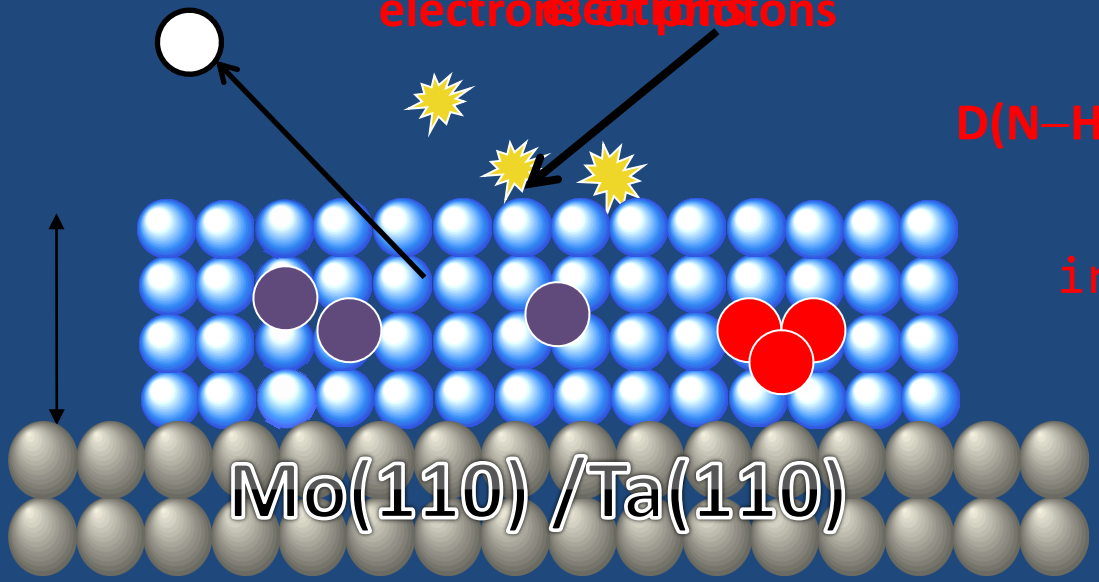
Low-Energy (2–20 eV) electrons

High-Energy (1000 eV) protons

D(N–H) ≈ 4.1 eV

post-irradiation analysis

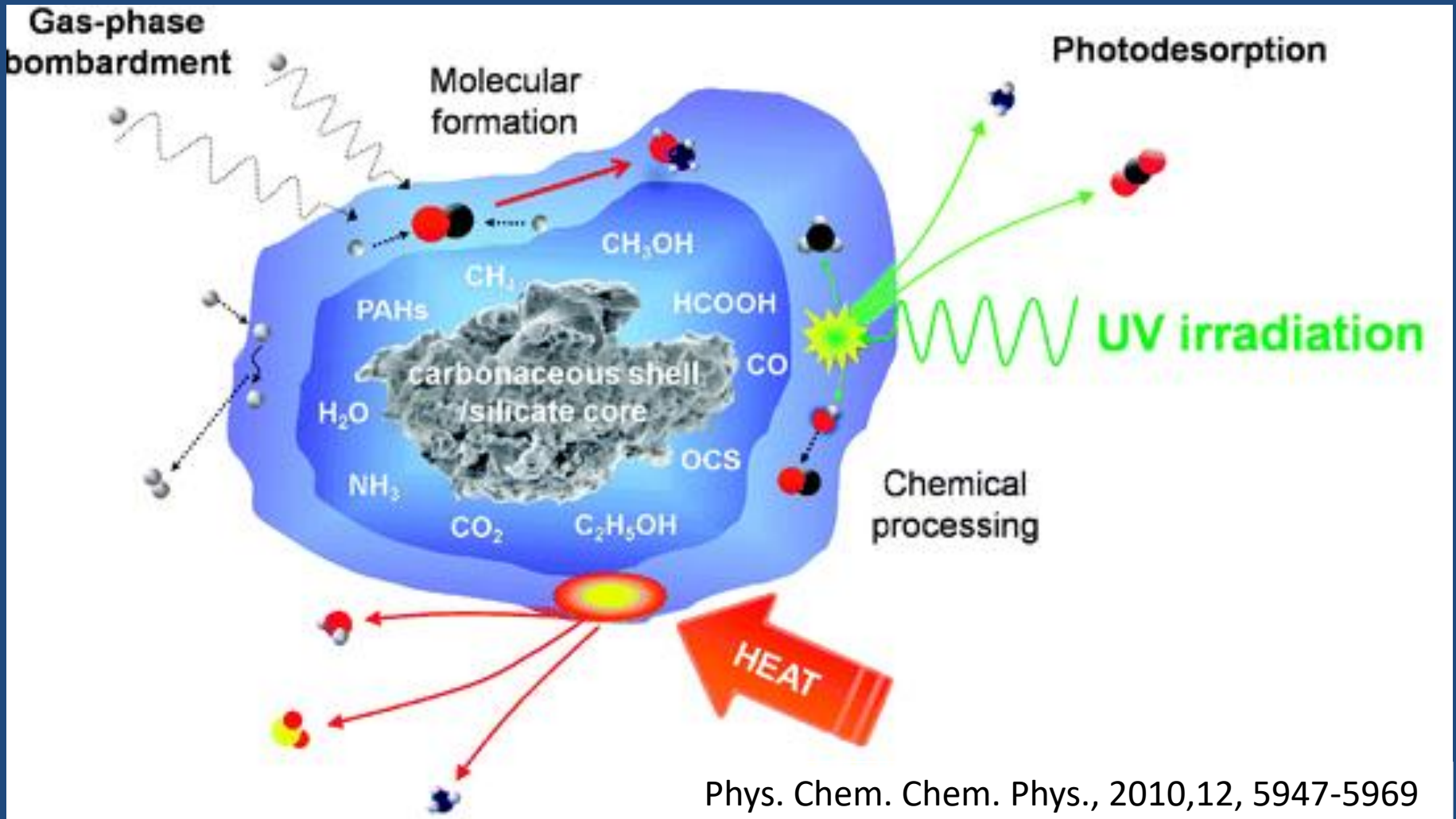
20 – 200 Å
NH_3



$P = 1 \times 10^{-9}$ Torr

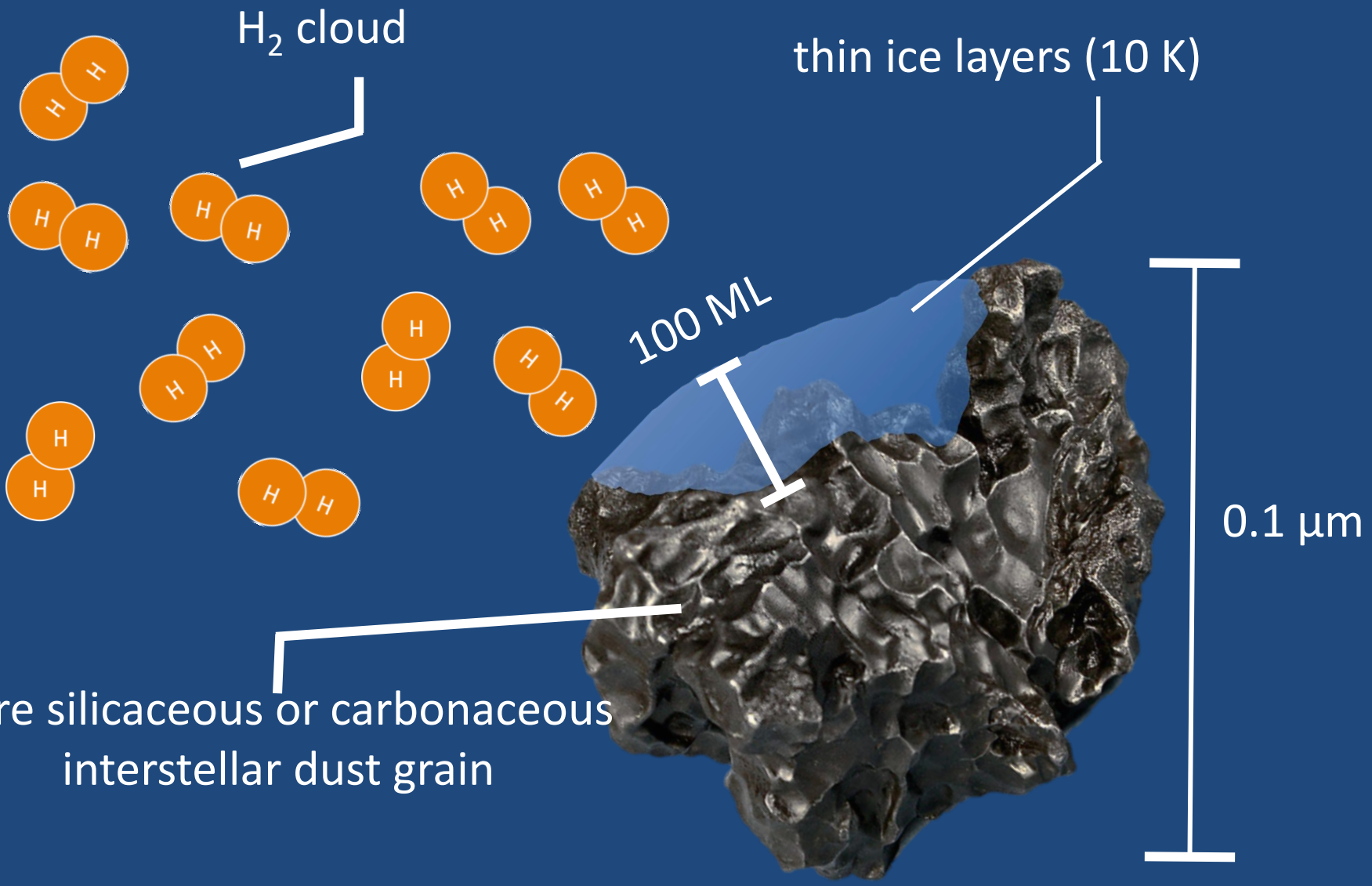
$T = 90$ K

Interstellar synthesis of prebiotics: Widely Accepted Hypothesis

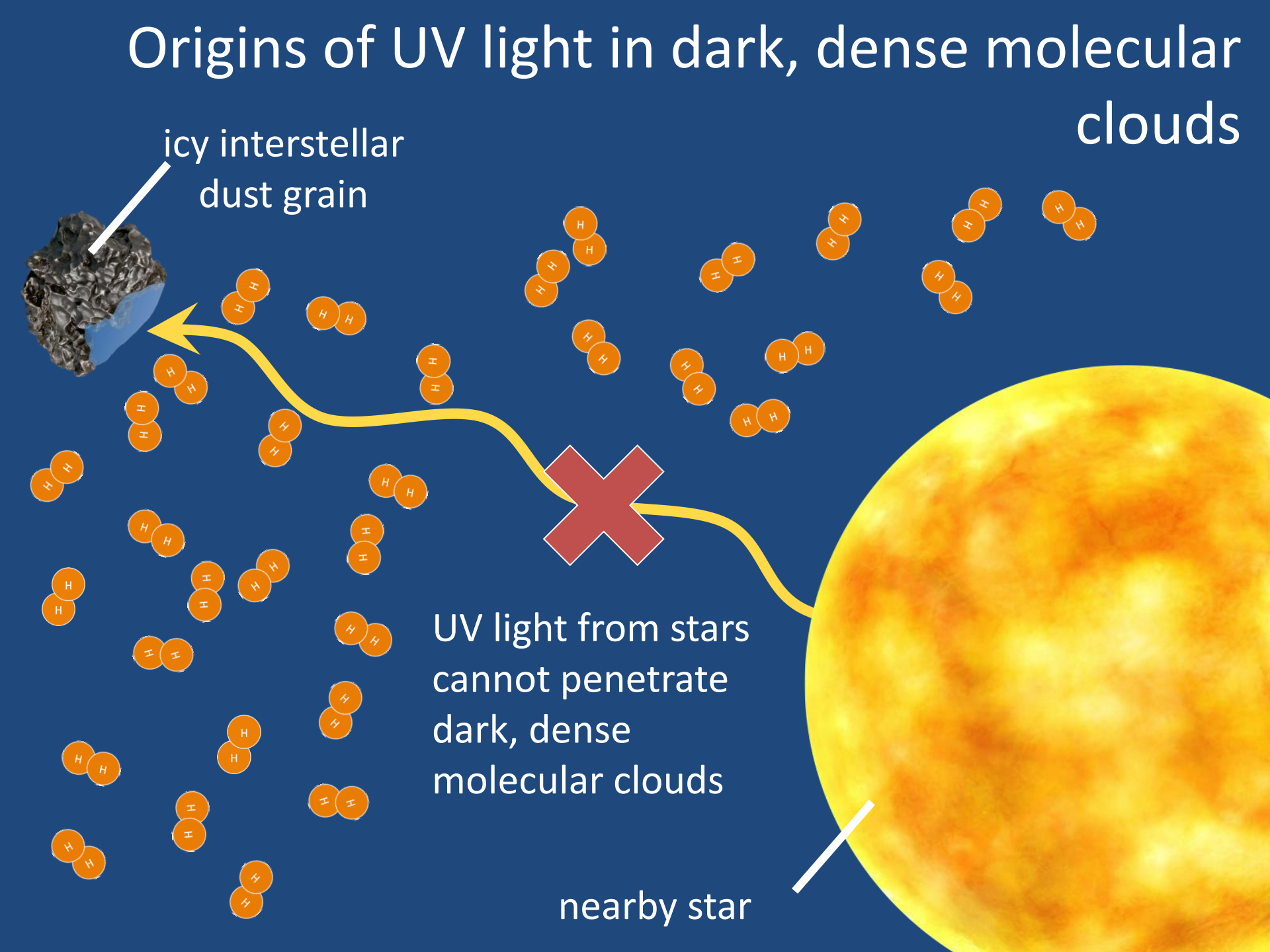


Phys. Chem. Chem. Phys., 2010,12, 5947-5969
DOI: 10.1039/B917005G

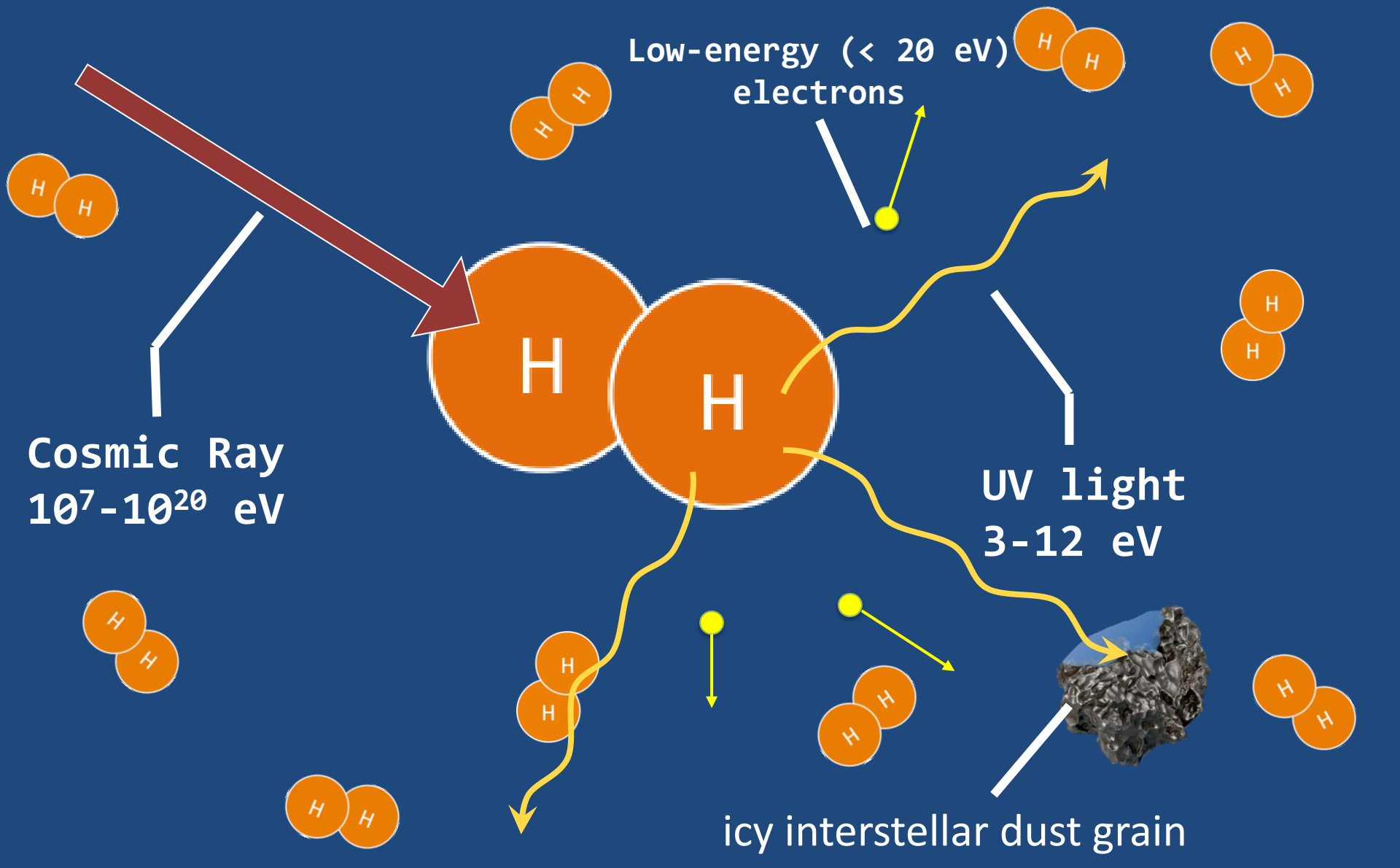
Dark dense molecular clouds

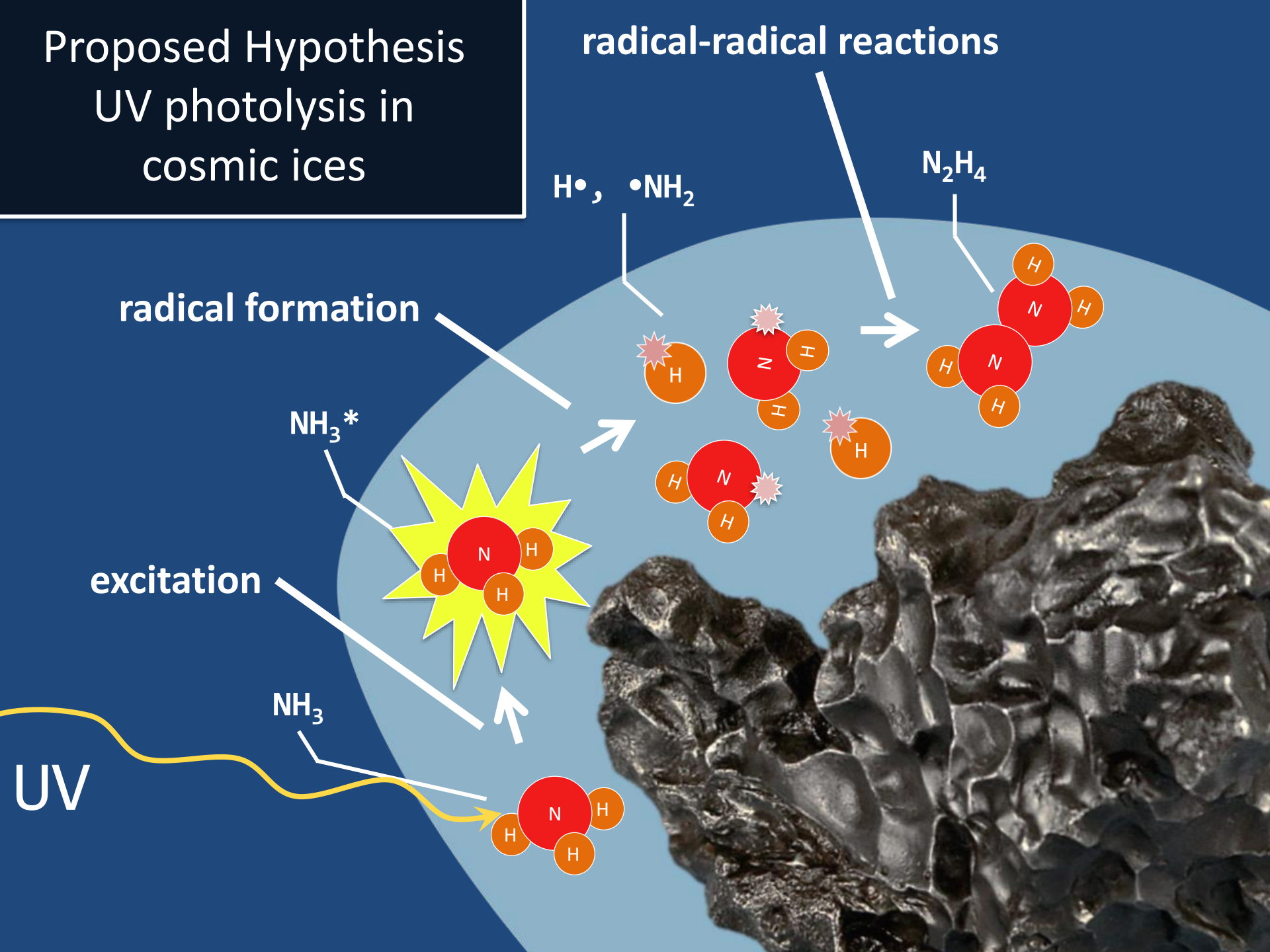


Origins of UV light in dark, dense molecular clouds



UV light formation within dark, dense molecular clouds

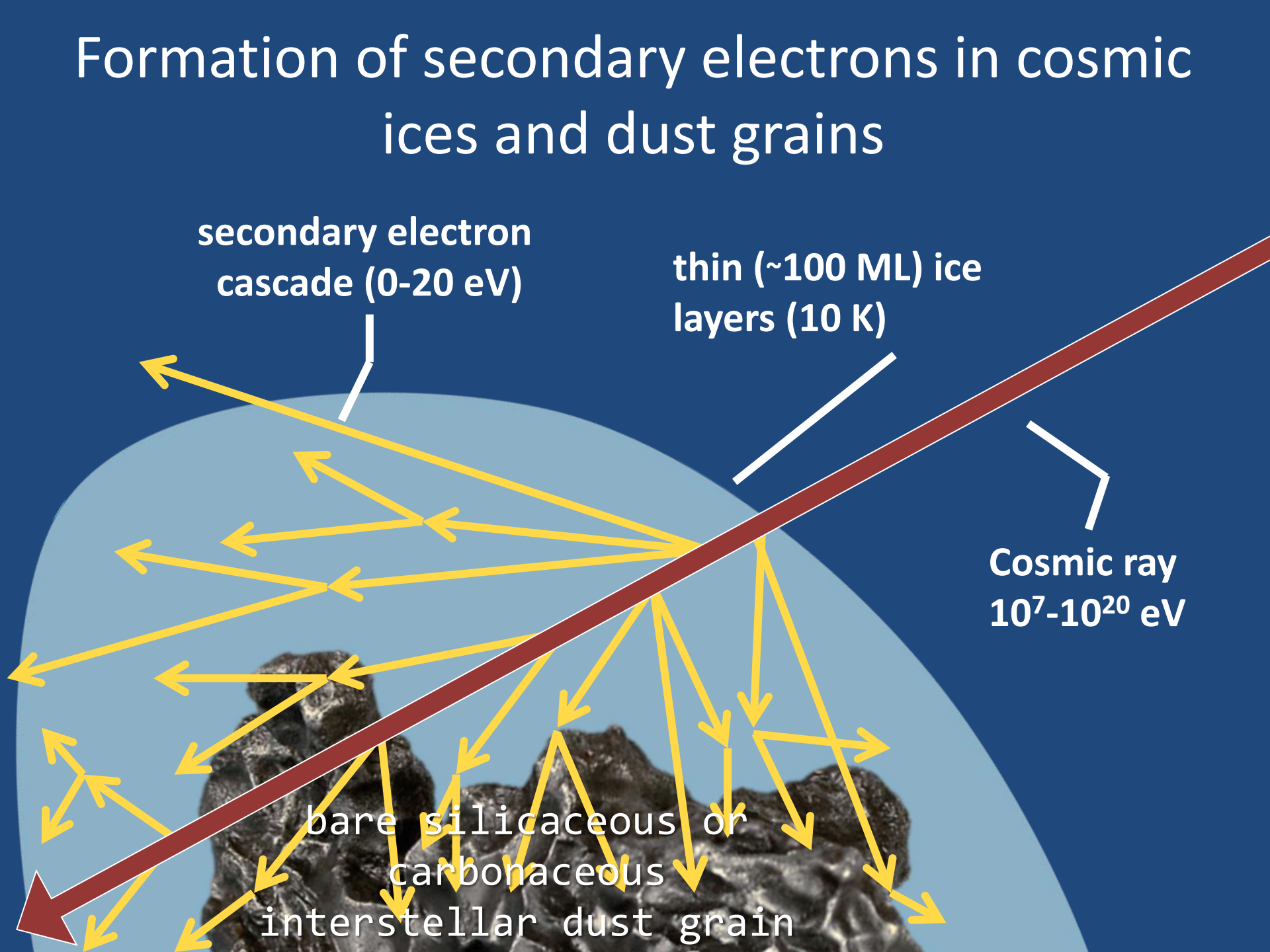



Proposed Hypothesis
UV photolysis in cosmic ices
radical-radical reactions
H•, •NH2
N2H4
radical formation
NH3*
excitation
NH3
UV

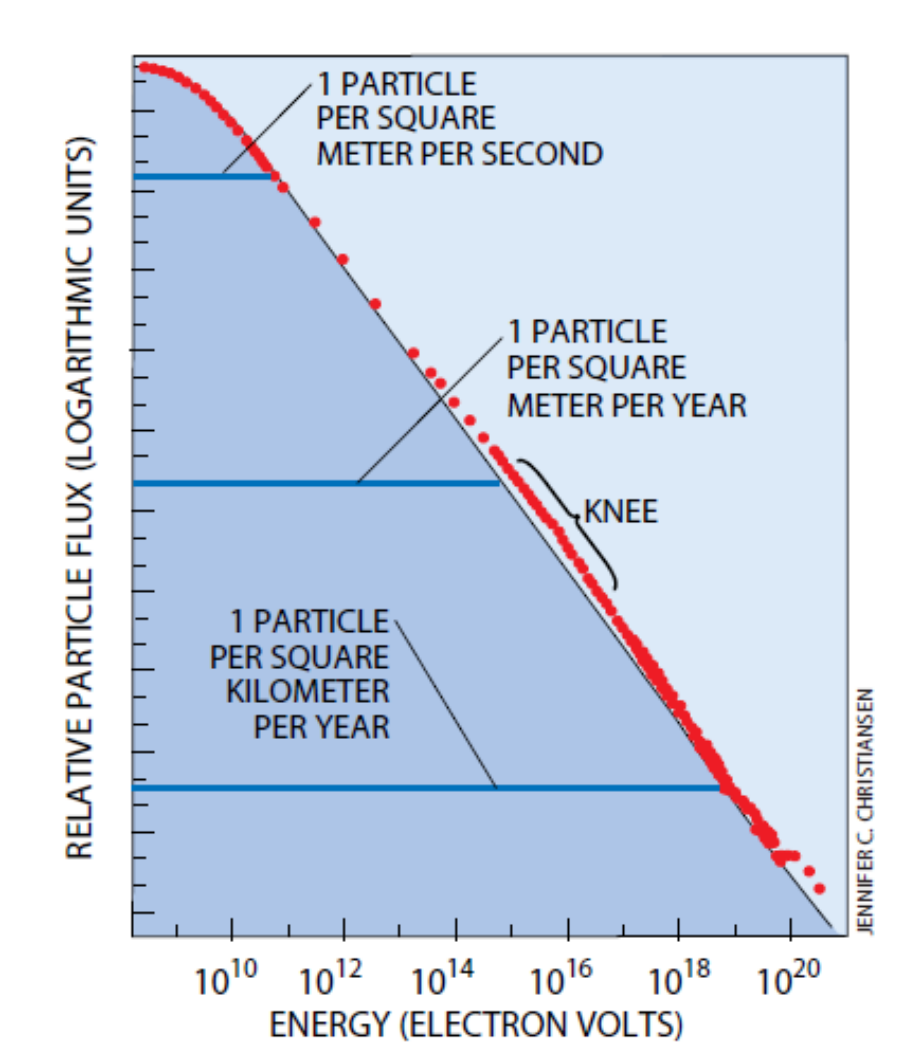
Our Hypothesis

Low-energy electrons (< 20 eV) could play a significant role in the synthesis of “complex” organic molecules previously thought to form exclusively via photons

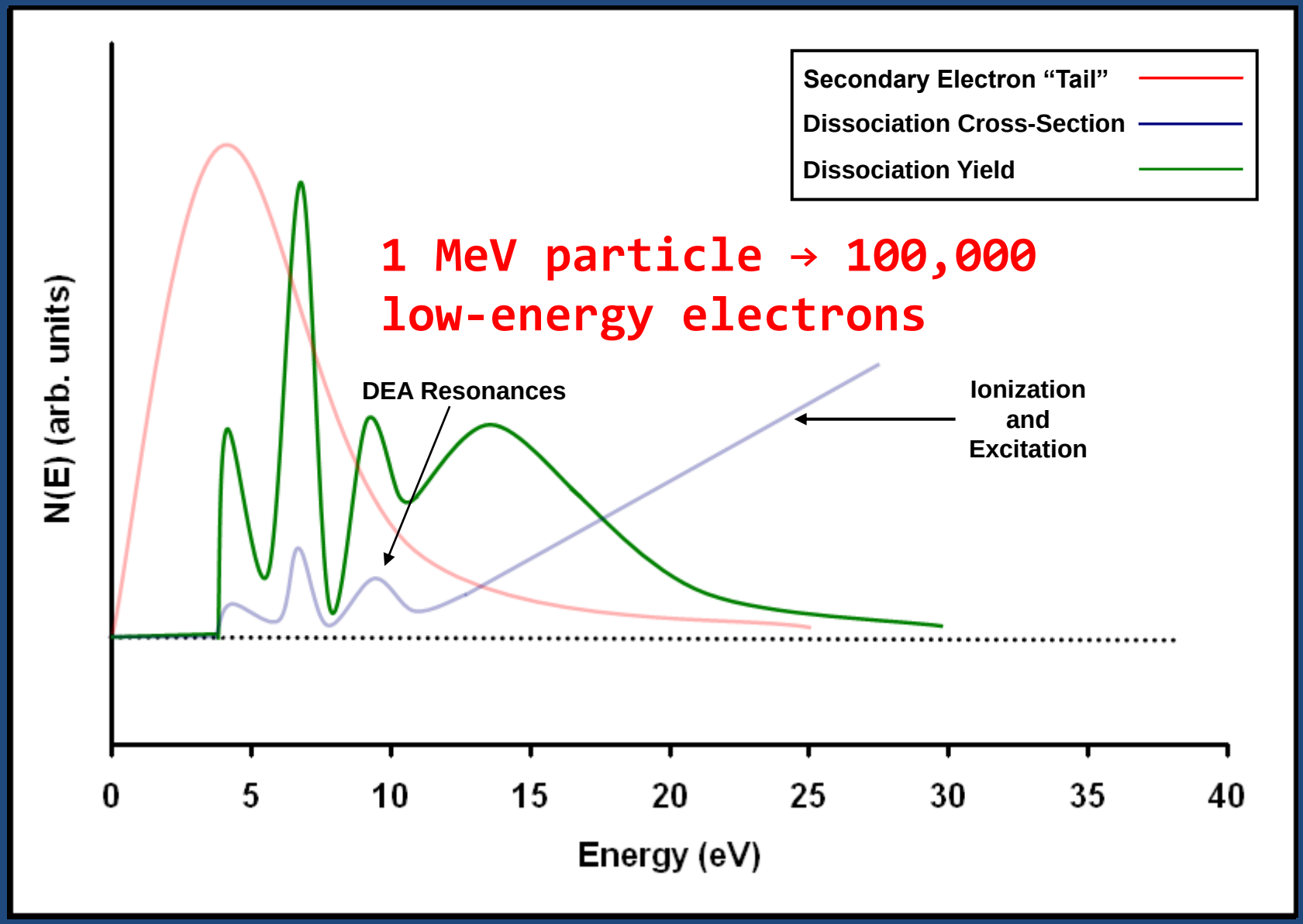
Formation of secondary electrons in cosmic ices and dust grains



Flux of Cosmic Rays Reaching Earth

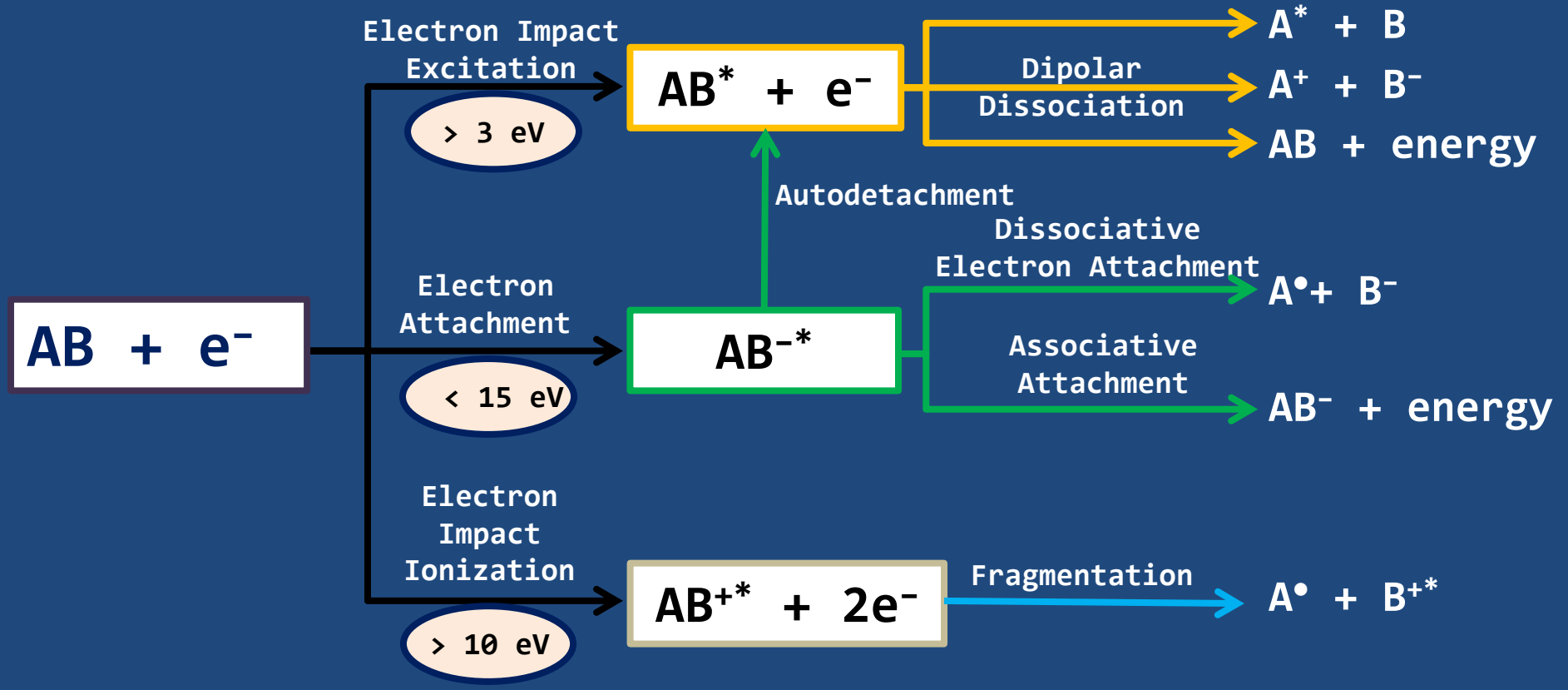


Importance of Low-Energy Electrons

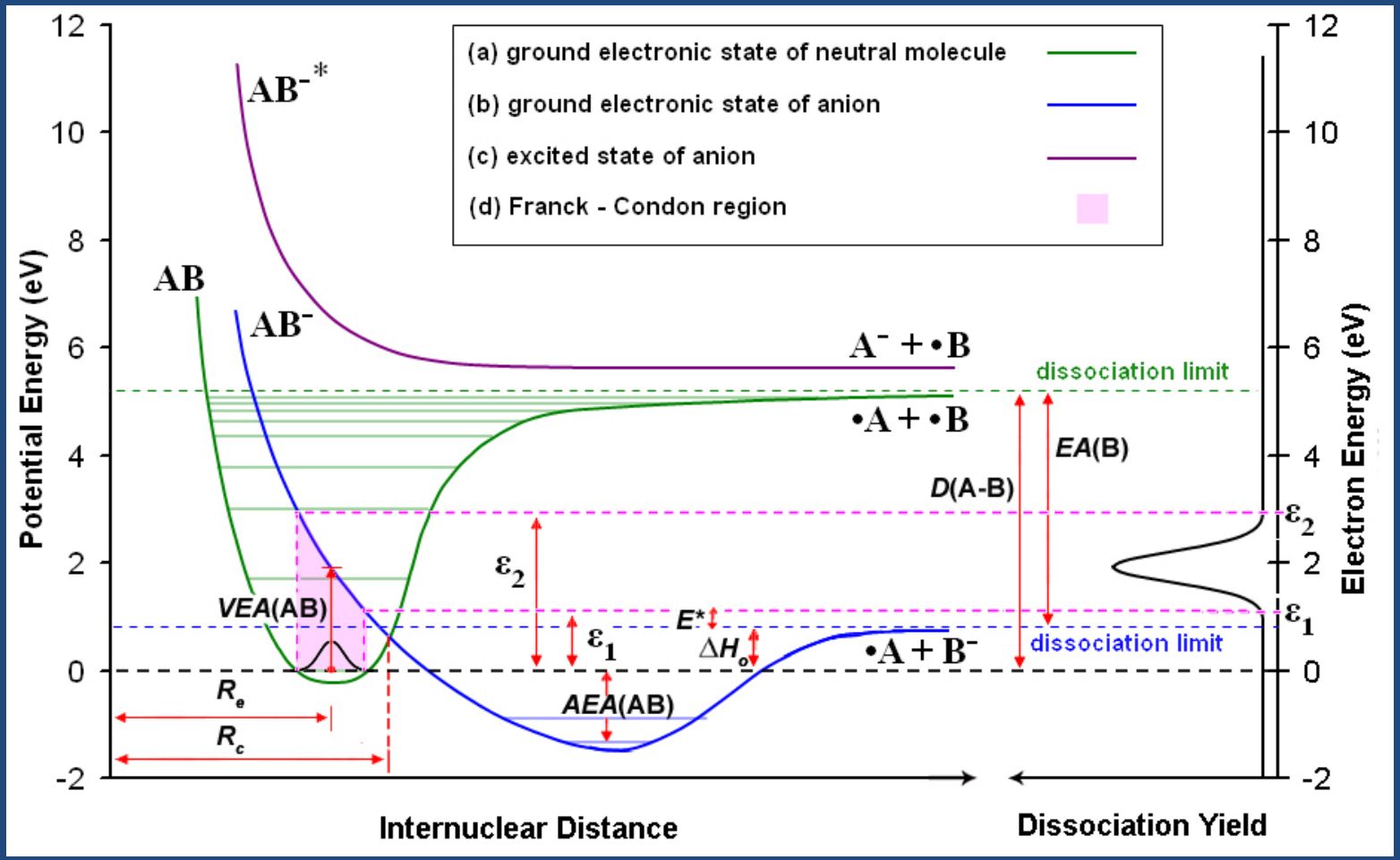


C. Arumainayagam et al., *Surface Science Reports* 65 (**2010**) 1–44.

Electron-induced dissociation mechanisms



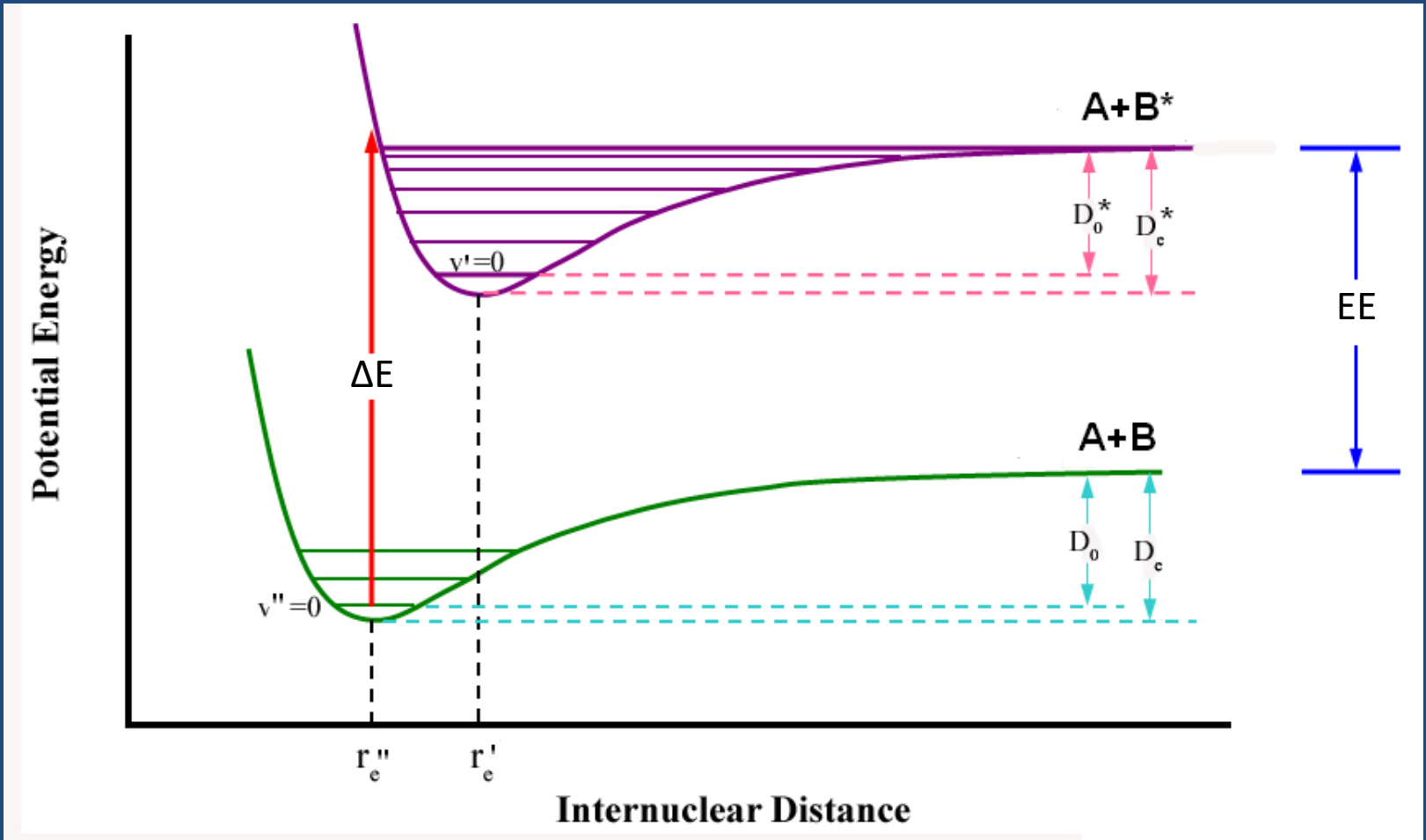
How to break a 5 eV bond with a 3 eV electron?



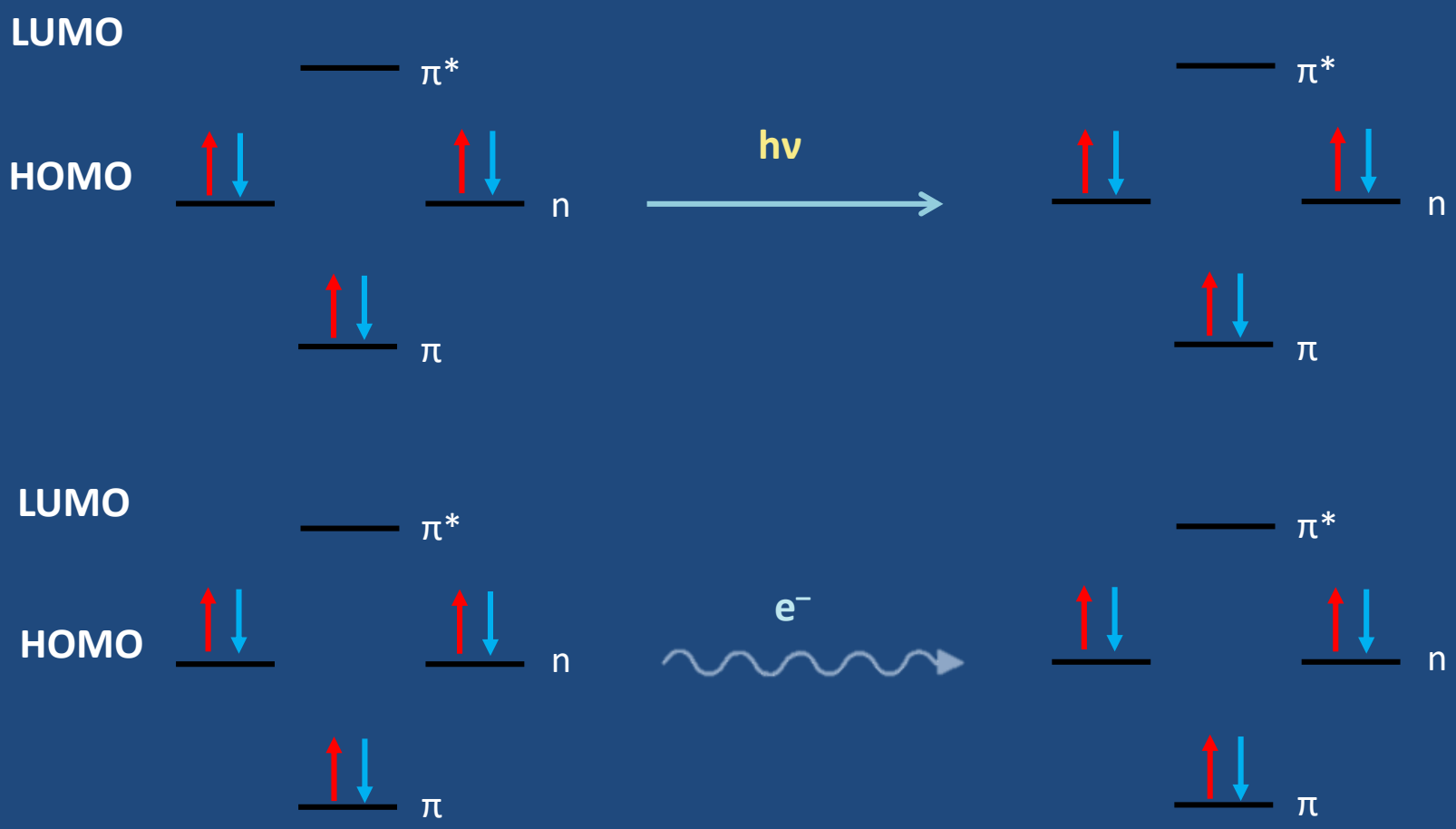
"Thermodynamic Threshold" $\Delta H_{o}(\mathrm{B}^{-}) = D(\mathrm{A}-\mathrm{B}) - EA(\mathrm{B})$

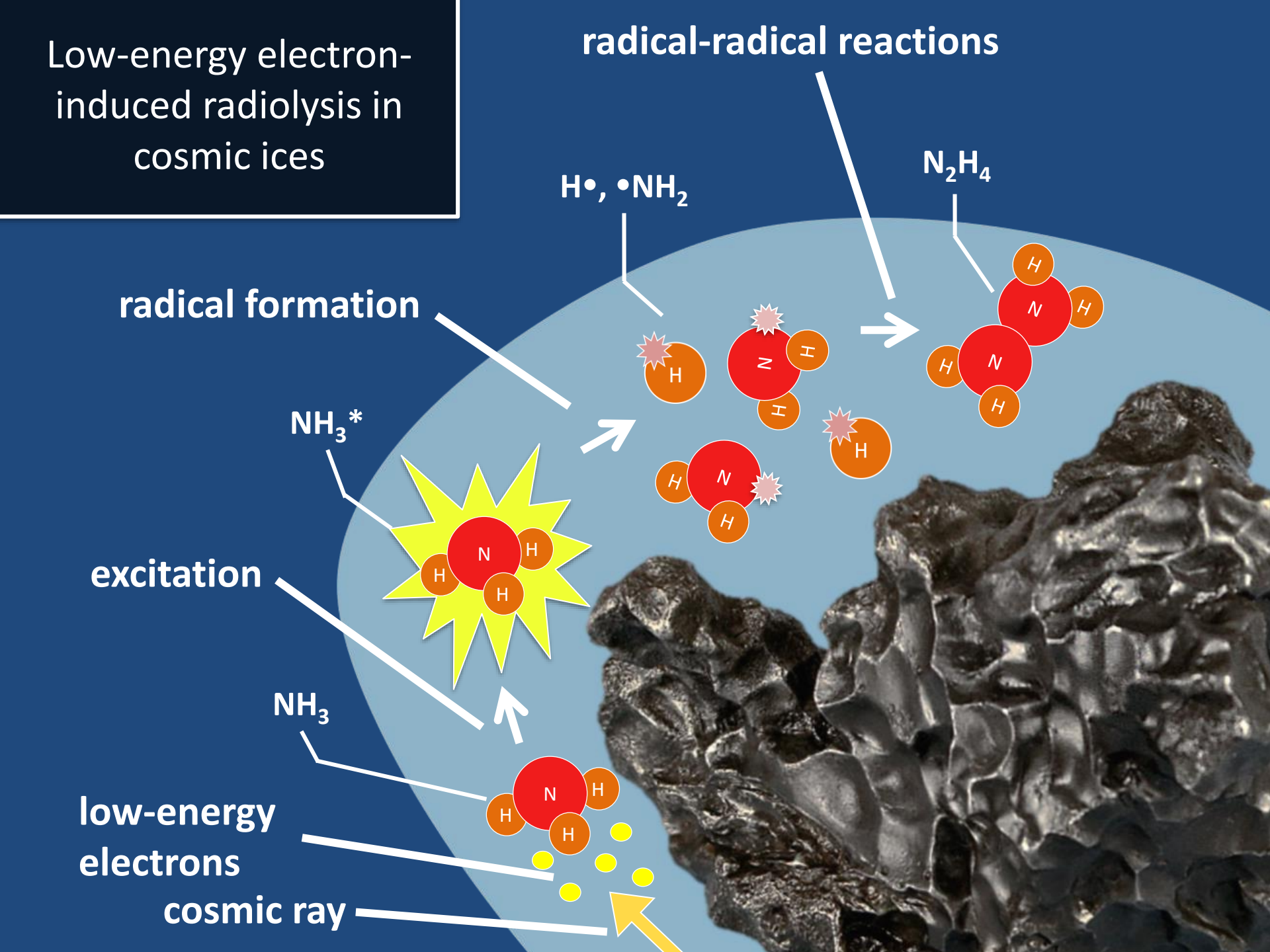
C. Arumainayagam *et al.*, *Surface Science Reports* 65 (**2010**) 1–44.

Energetics of Photochemistry

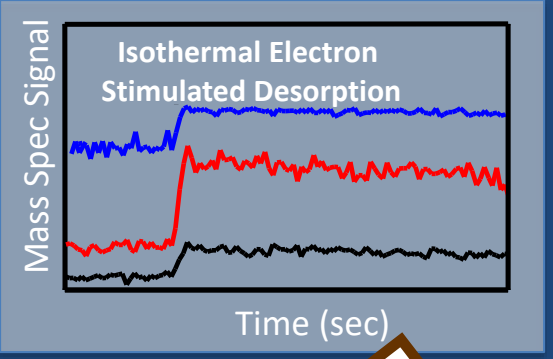


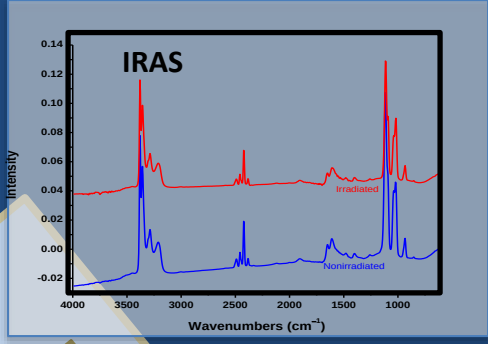
Another Key Difference between Photons and Electrons




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

Experimental Procedures





Liquid N_2 Port

e- gun

e^-

Filament

Products

Mass Spec

Power Supply

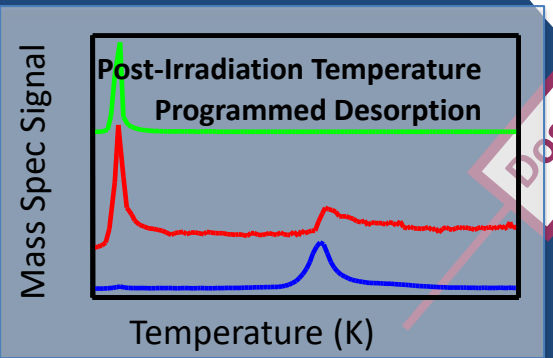
Ta(110)

Ammonia

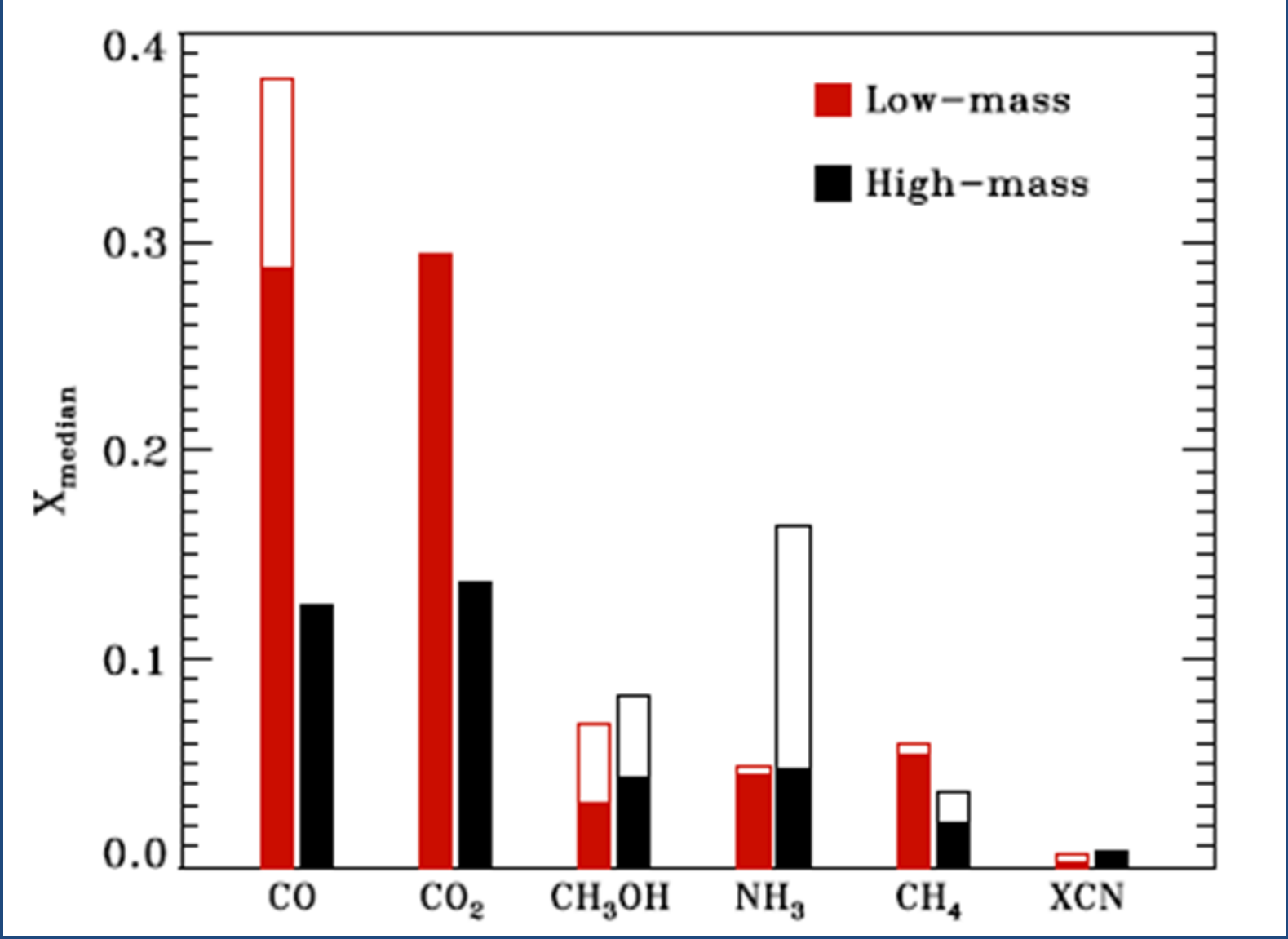
Doser

FTIR Spectrometer

MCT Detector

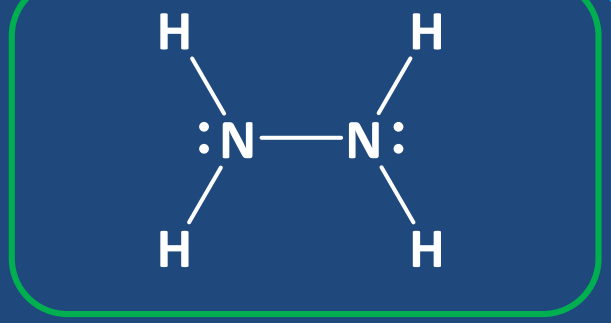


Why study Ammonia?

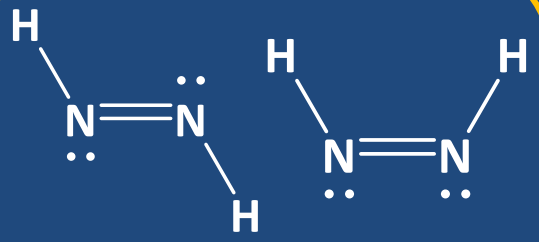


Öberg, K., et al. "The Spitzer Ice Legacy: Ice Evolution from cores to protostars." *The Astrophysical Journal* 740(2011): 16 pp.

Possible Radiolysis Products of Ammonia

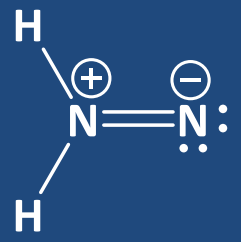


Hydrazine



Trans

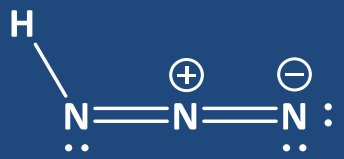
Cis



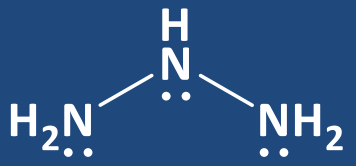
Iso

Diazene

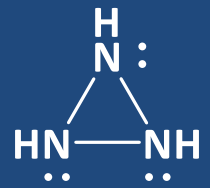
N-2 Species



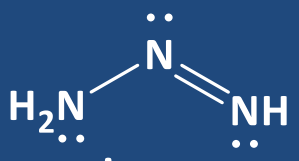
Hydrazoic Acid



triazane



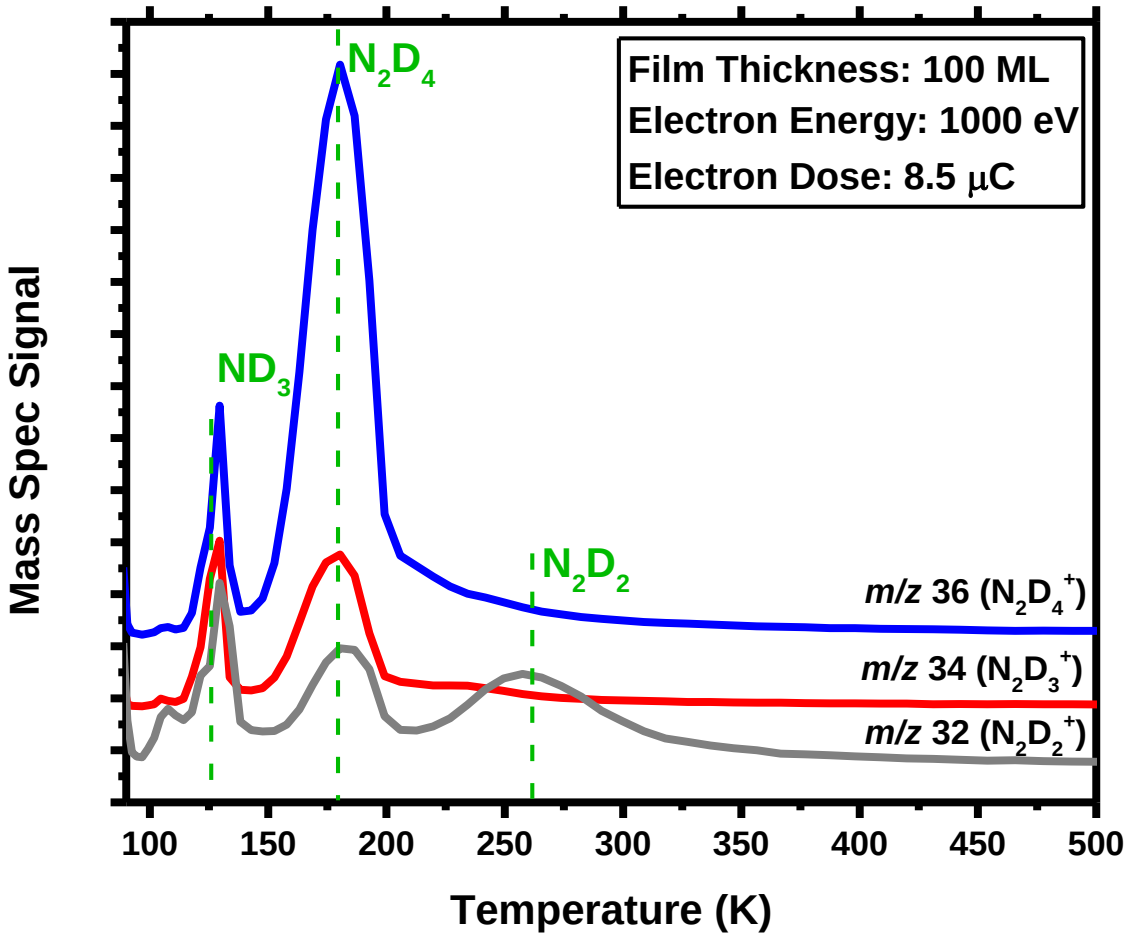
cyclotriazane



triazene

N-3 Species

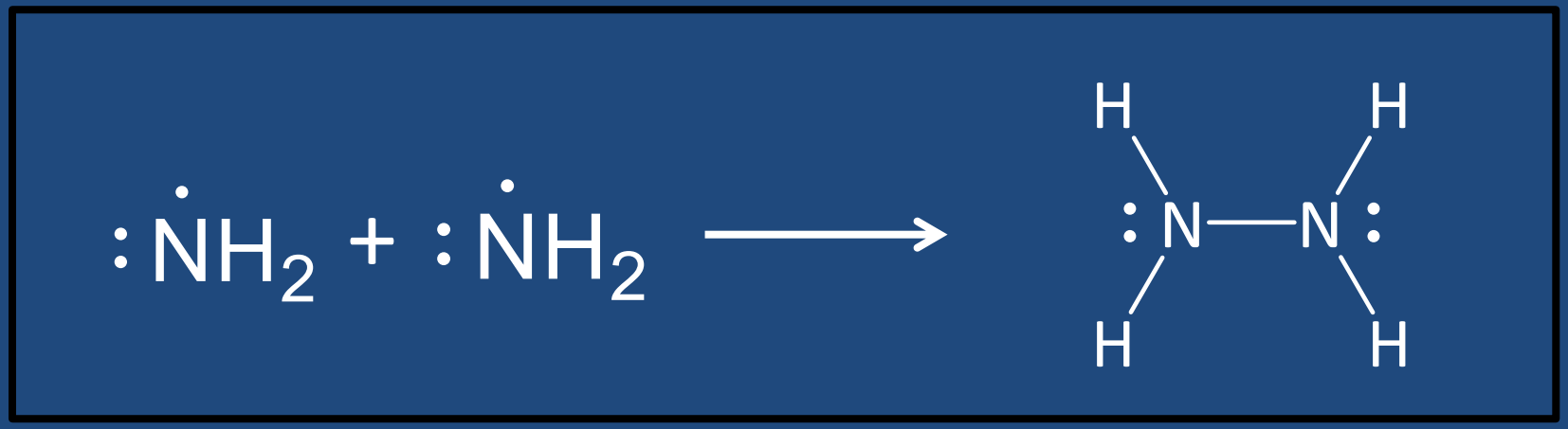
Detection of Hydrazine and Diazene at High Incident Electron Energies



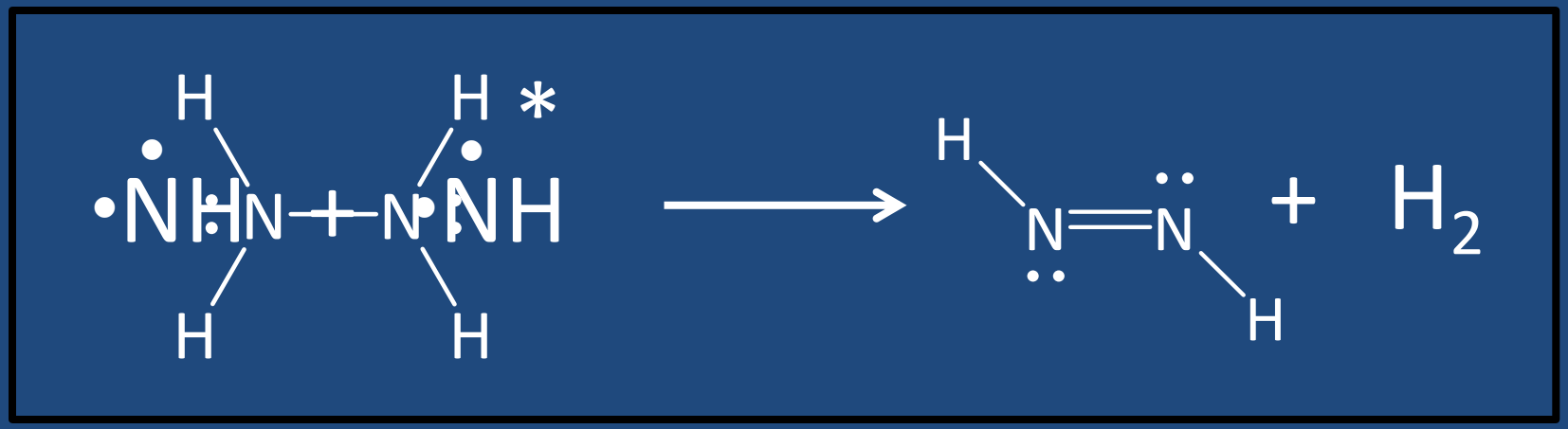
Katie Shulenberger `14 (Wellesely College)

Proposed Mechanisms of Hydrazine and Diazene from Ammonia

Hydrazine (N_2H_4)

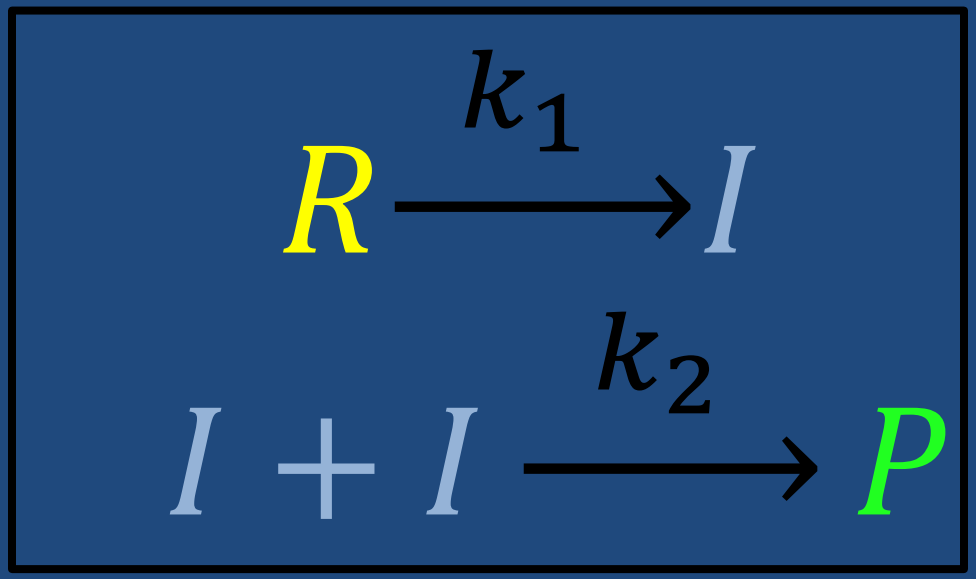


Diazene (N_2H_2)



Zheng, W. et al. *The Astrophysical Journal*. 674:1242-1250, 2008 February 20

Model: Bimolecular Intermediate Step



$$\frac{dR}{dt} = -k_1 R$$

$$R(t) = R_0 e^{-k_1 t}$$

$$\frac{dI}{dt} = k_1 R - k_2 I^2$$

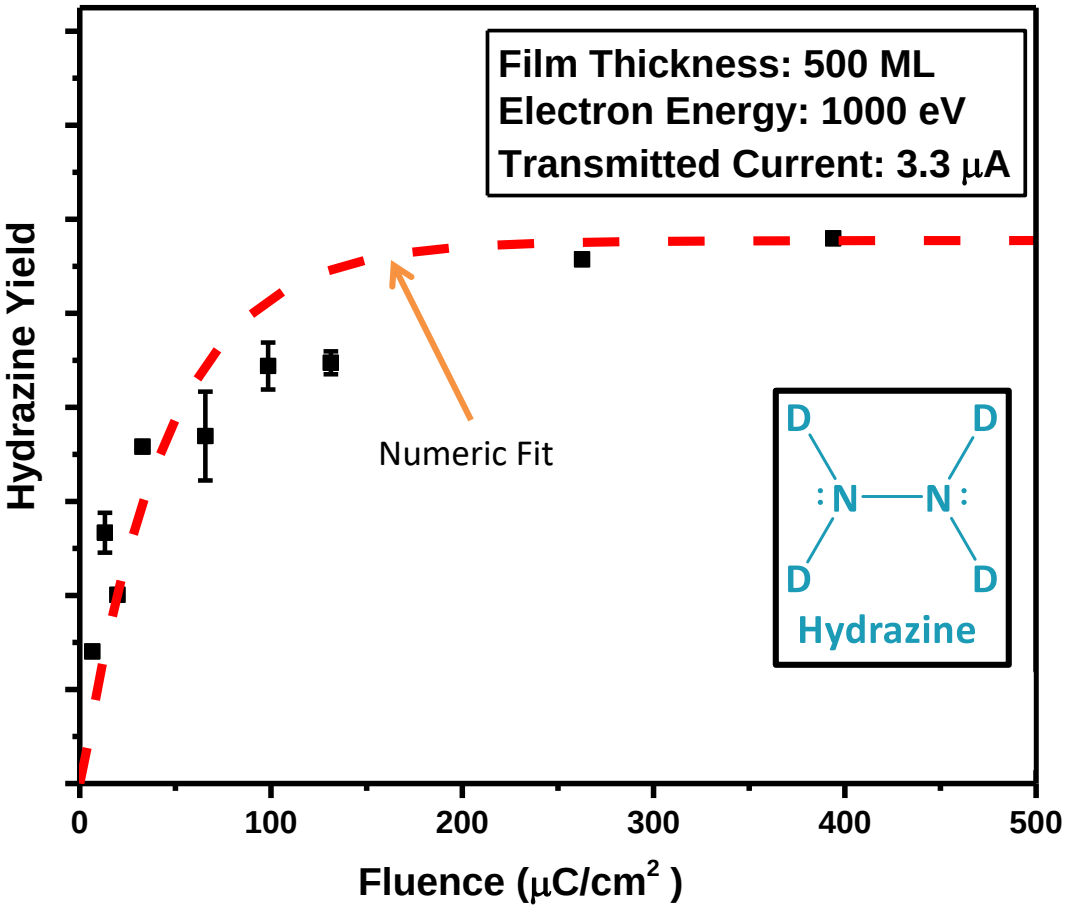
$$I(t) = ?$$

$$\frac{dP}{dt} = \frac{k_2}{2} I^2$$

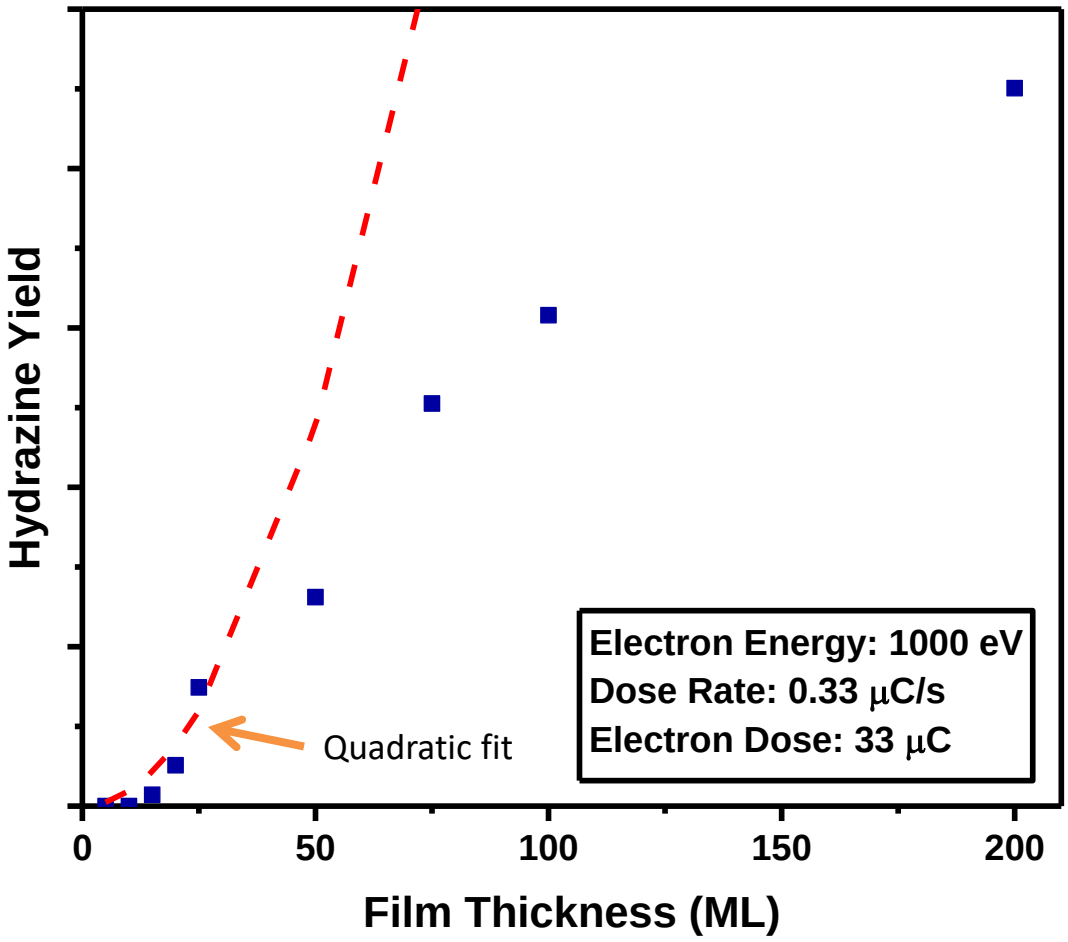
$$P(t) = ?$$

Katherine Tran ’15
(Wellesley College)

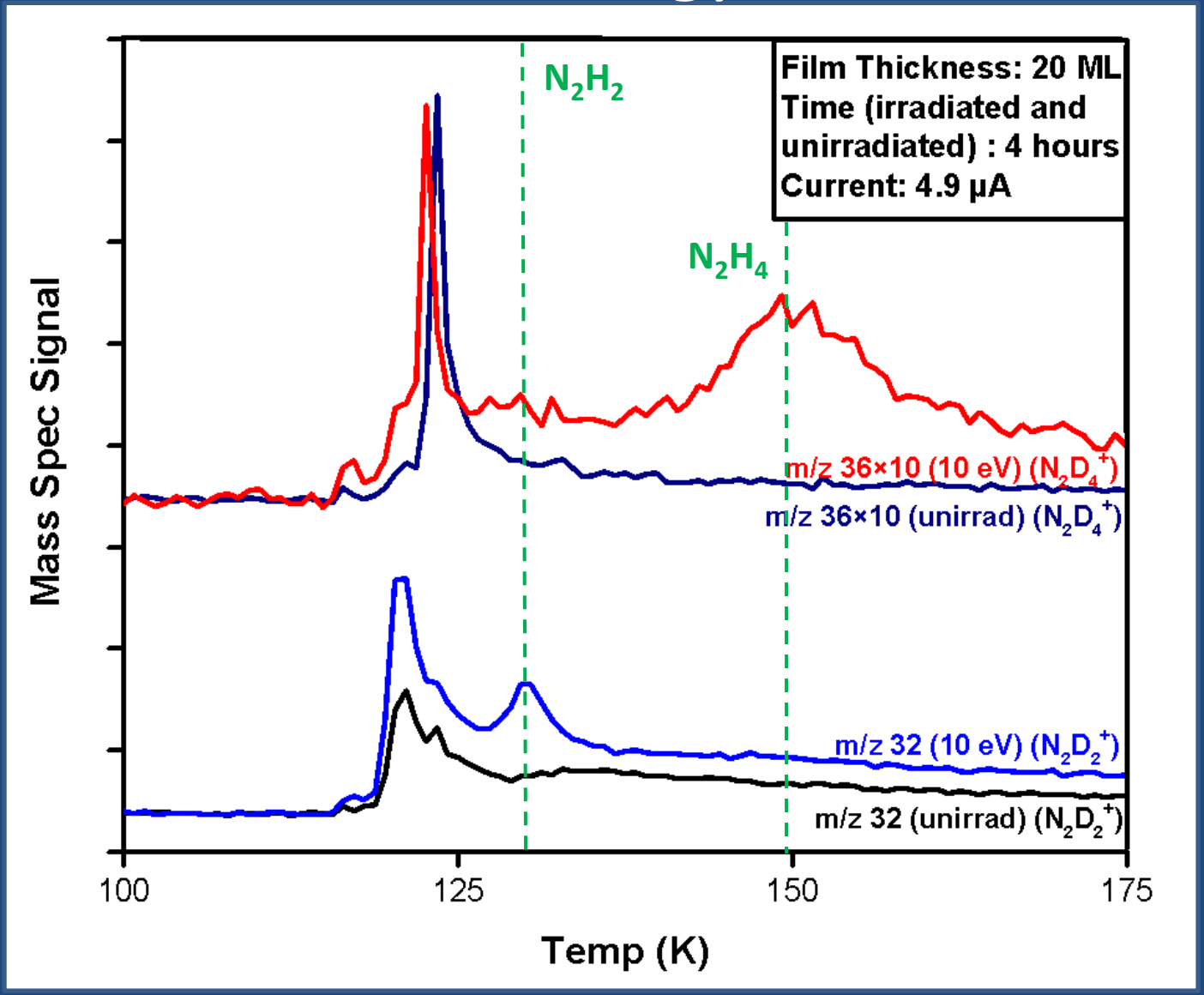
Results: Hydrazine Yield vs Electron Fluence



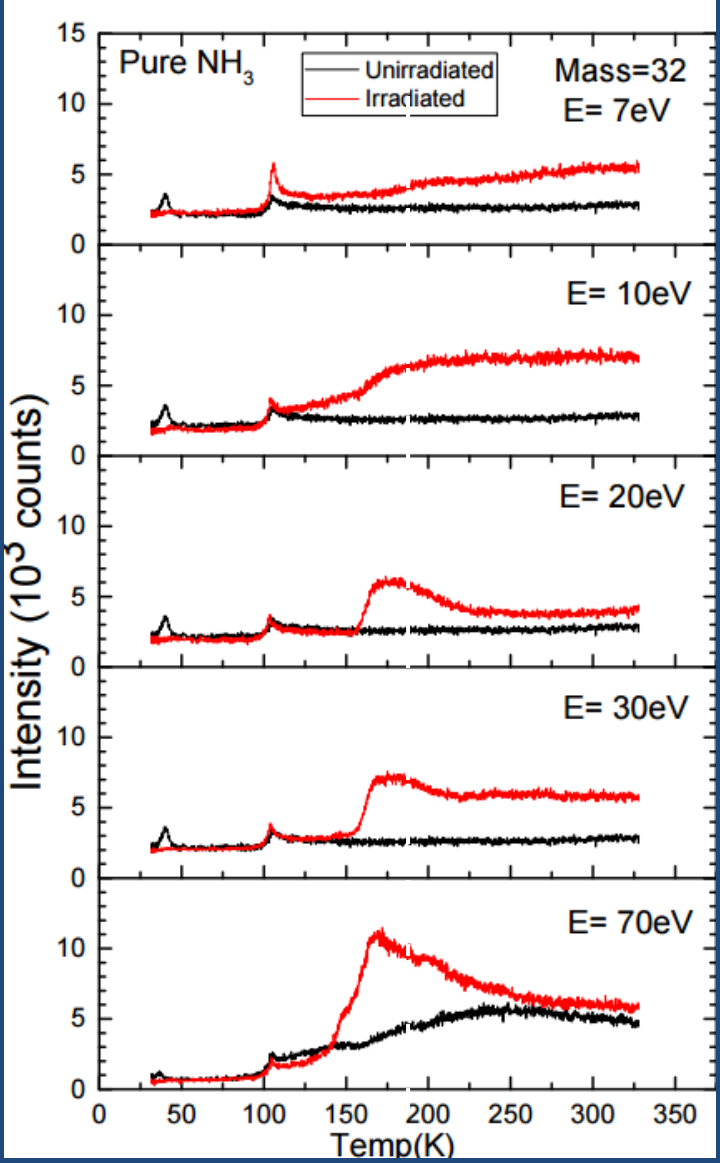
Results: Yield vs Film Thickness



Production of Hydrazine and Diazene at Incident Electron Energy of 10 eV at 90 K

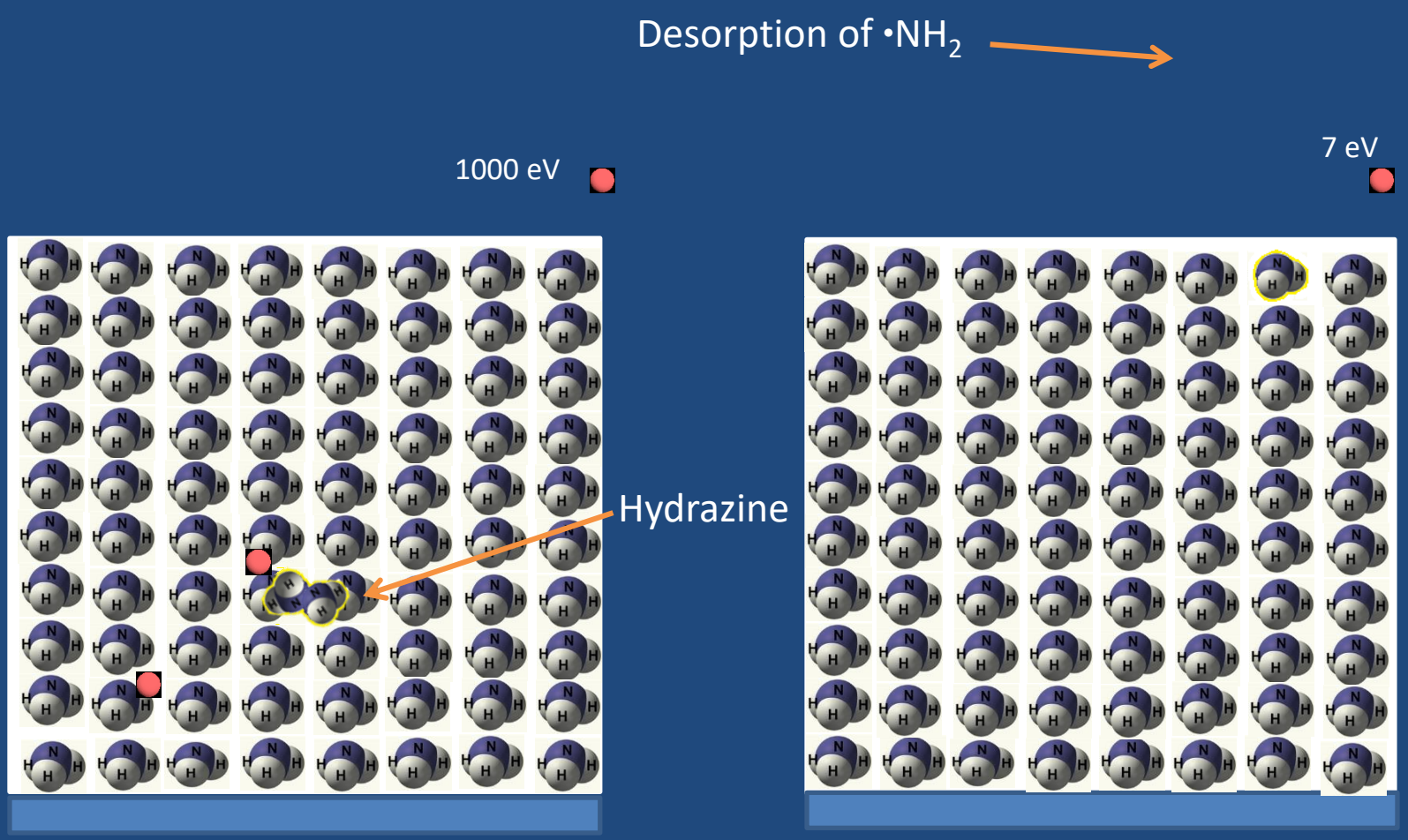


Production of Hydrazine at Incident Electron Energy of 7 eV at 25 K



Leon Sanche, Andrew Bass & Sasan Esmaili

Importance of Surface Temperature



Final Conclusions

- Electron–induced reaction of ammonia yields hydrazine (N_2H_4) and diazene (N_2H_2) with high-(1000 eV) or low-energy (7-20 eV) electrons.
- The results are consistent with our hypothesis that high energy radiolysis is mediated by low-energy electrons

Acknowledgements

Collaborators

Dr. Andrew Bass, Université de Sherbrooke

Sasan Esmaili, Université de Sherbrooke

Leon Sanche, Université de Sherbrooke

Dr. Petra Swiderek, University of Bremen

Esther Bohler, , University of Bremen

Former lab members

Katie Shulenberger ‘14
Katherine D Tran ’15
Sebiha Abdullahi ‘15
Jane L. Zhu ’16
Carina Belvin ‘16
Kathleen Regovish ‘16
Lauren Heller ‘17
Milica Markovic ‘17

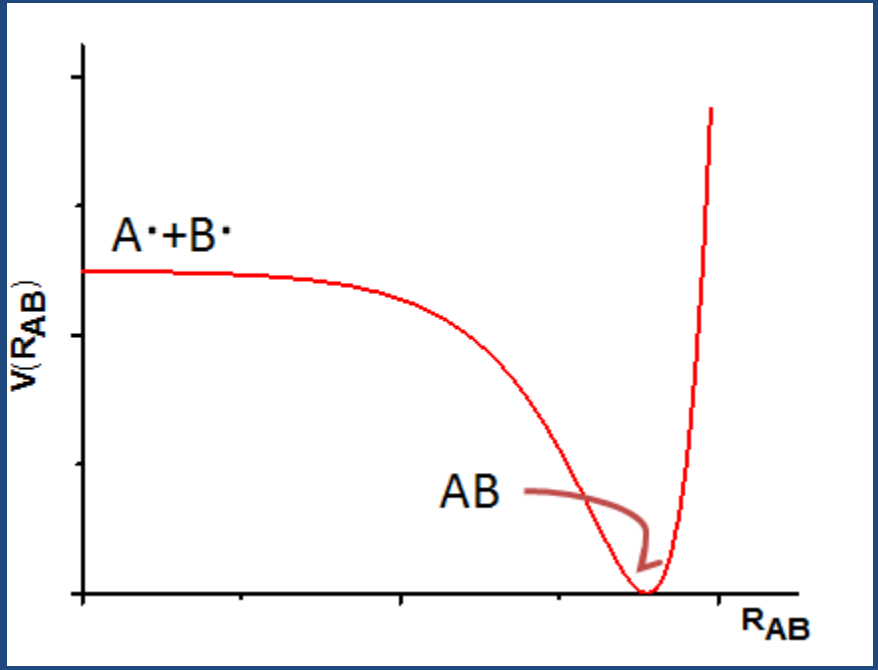
Funding Source

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

Current Lab Members

Helen Cumberbatch
Julia Lukens
Zoe Peeler
Alice Zhou
Jyoti Campbell
Kendra Cui
Jean Huang
Hope Schneider
Anna Caldwell-Overdier
Jeniffer Perea
Ally Bao
Christina Buffo
Eliana Marosica
Mayla Thompson
Rhoda Tano-Menka
Stephanie Villafane
Subha Baniya
Ella Mullikin
Ally Bao
Justine Huang
Aury Hay

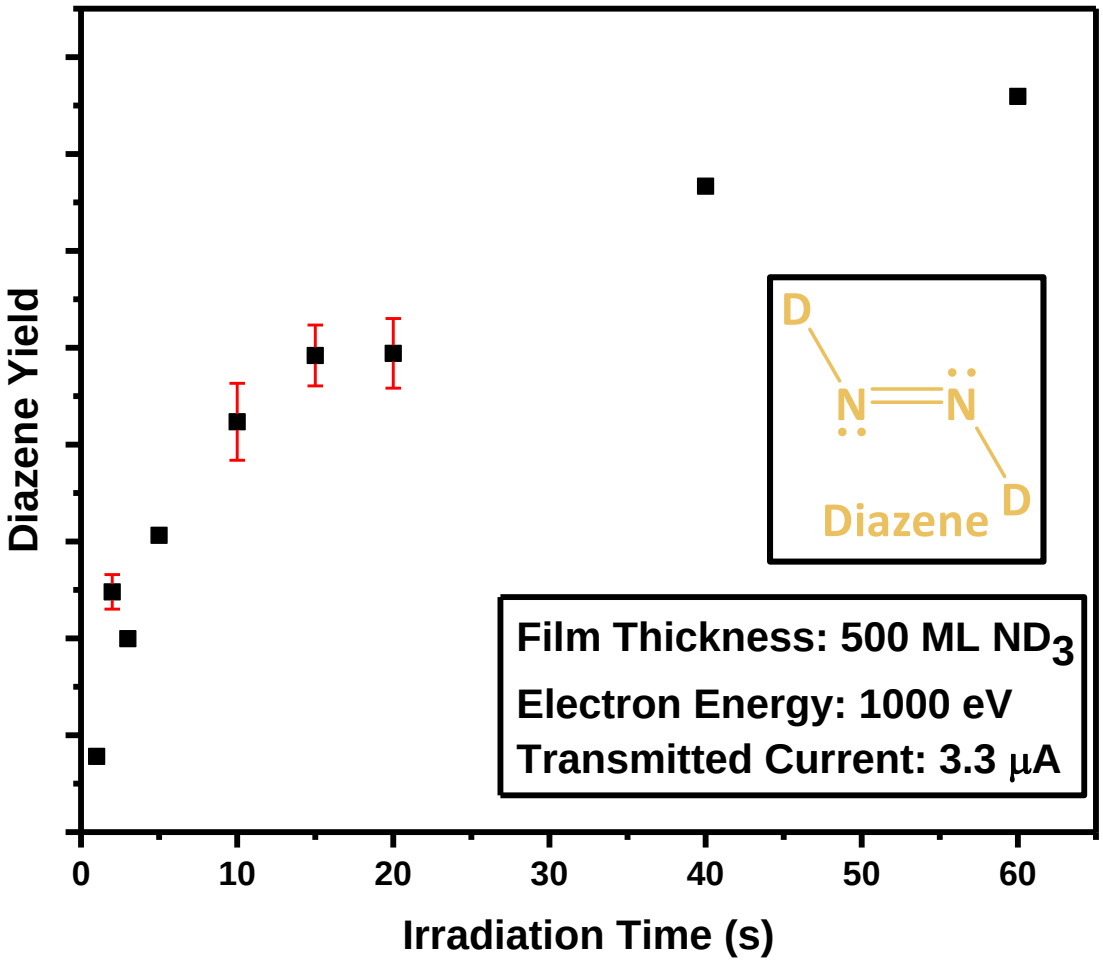
Kinetics of Radical-Radical Association Reactions



- Radical-radical reactions: no energy barrier
- PE falls monotonically as distance ↓
- Radical energy ↑ ⇒ Reaction probability ↓
- Temperature ↑ ⇒ Rate constant ↓

Assume reaction is not diffusion limited

Results: Yield vs Irradiation Time

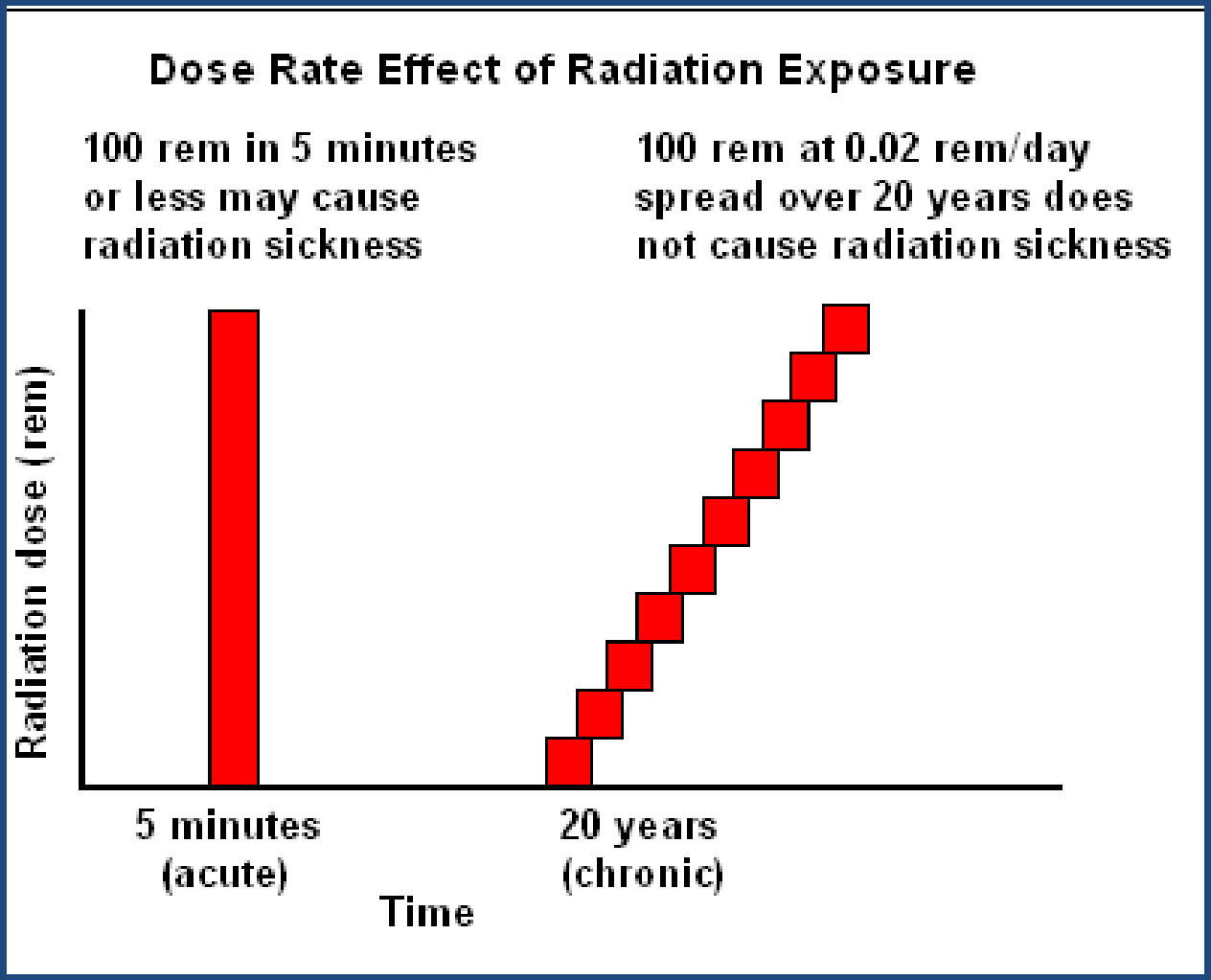


Bunsen-Roscoe Law of Photochemistry

A photochemical effect is directly proportional to the total energy dose, irrespective of the time required to deliver that dose

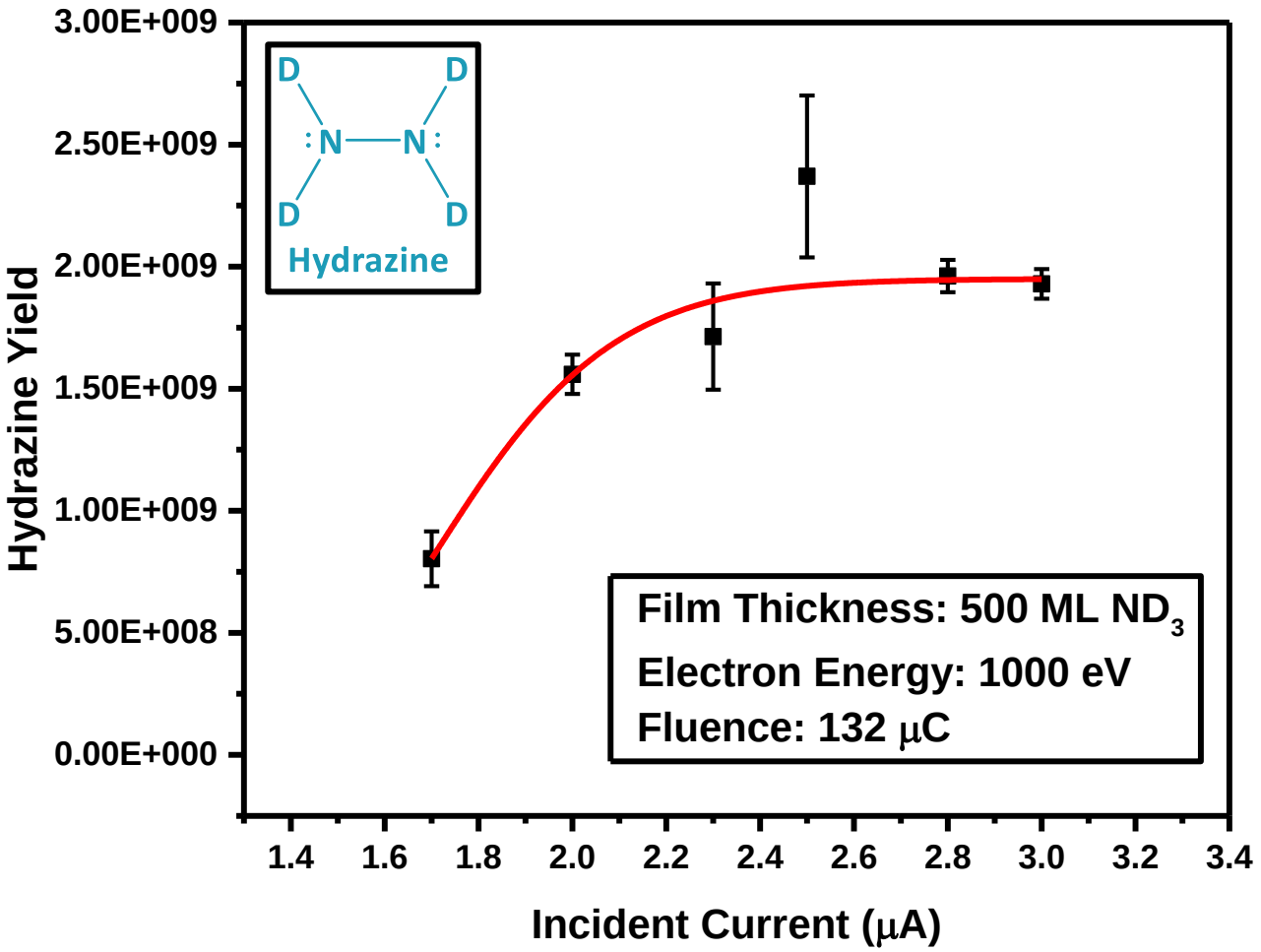
Despite constant electron dose across experiments, we observe varying ammonia radiolysis product yields

Dose Rate Effect in Radiation Chemistry



U.S. Department of Health & Human Services

Hydrazine Data



Diazene Data