Low-Energy Electrons in Astrochemistry

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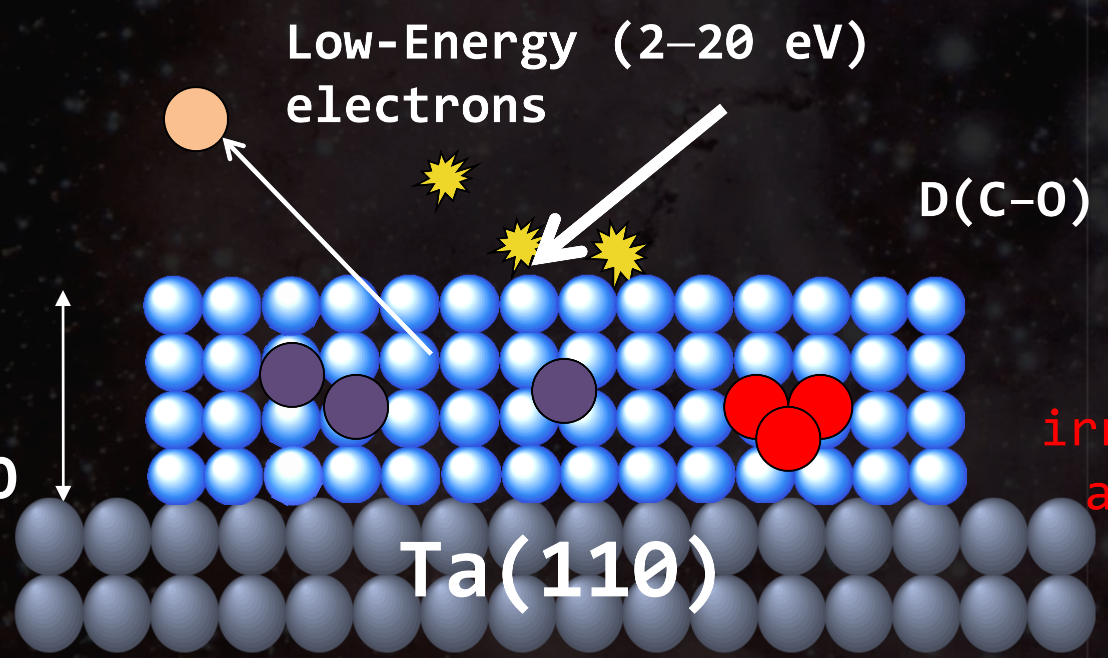
electron stimulated desorption



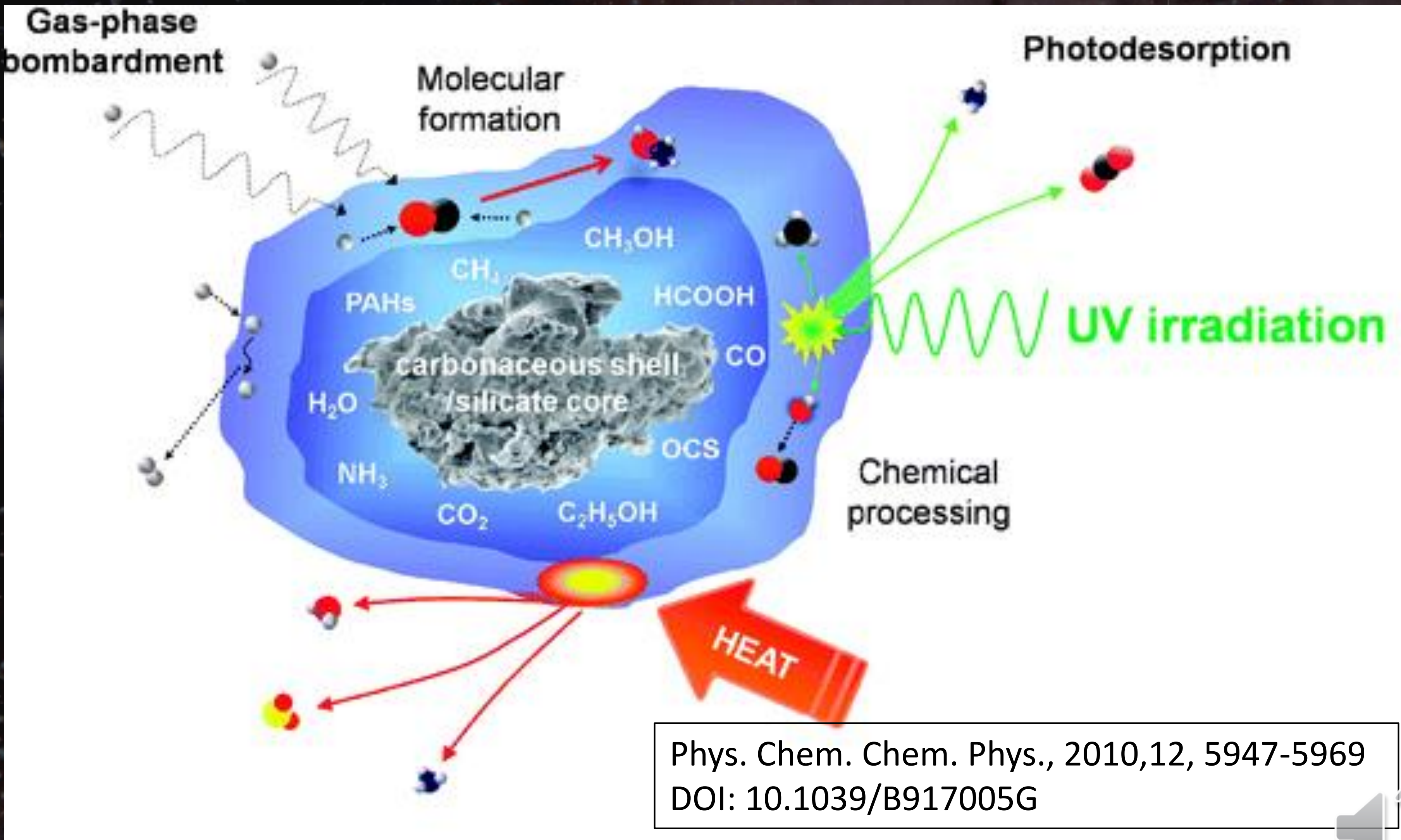
~20-200 Å
CH_3OH, NH_3, H_2O

post-irradiation analysis

P = 1×10^{-9} Torr

T = 90 K

Interstellar synthesis of prebiotics: Widely Accepted Hypothesis

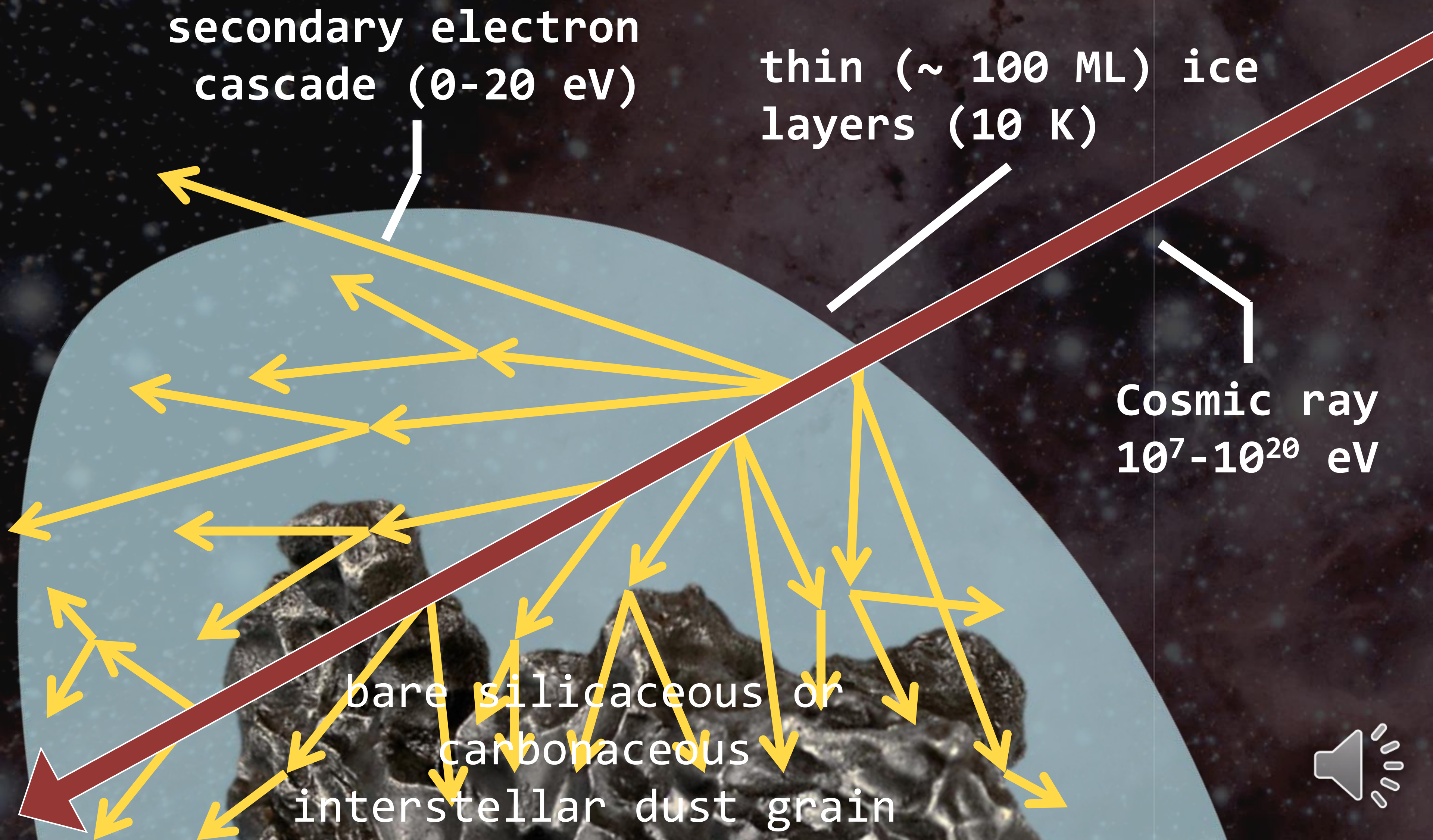


Phys. Chem. Chem. Phys., 2010,12, 5947-5969
DOI: 10.1039/B917005G

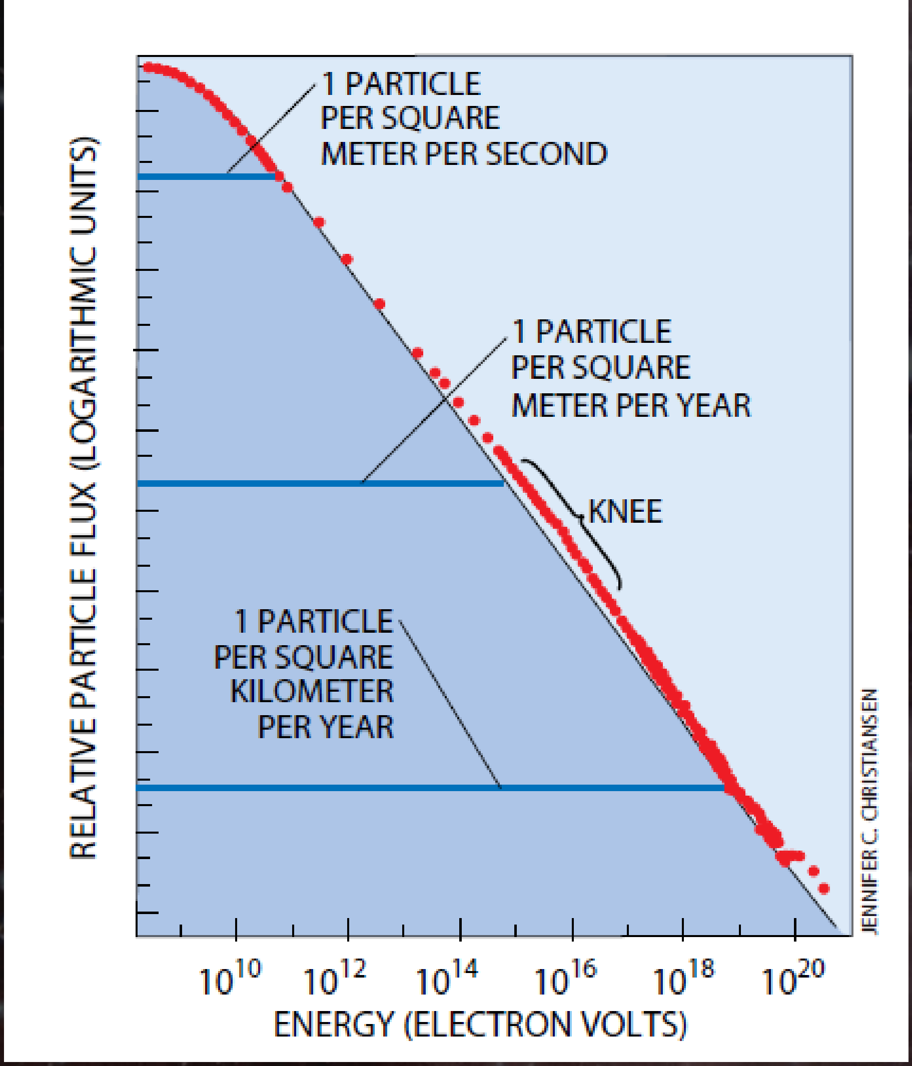
Our Hypothesis

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

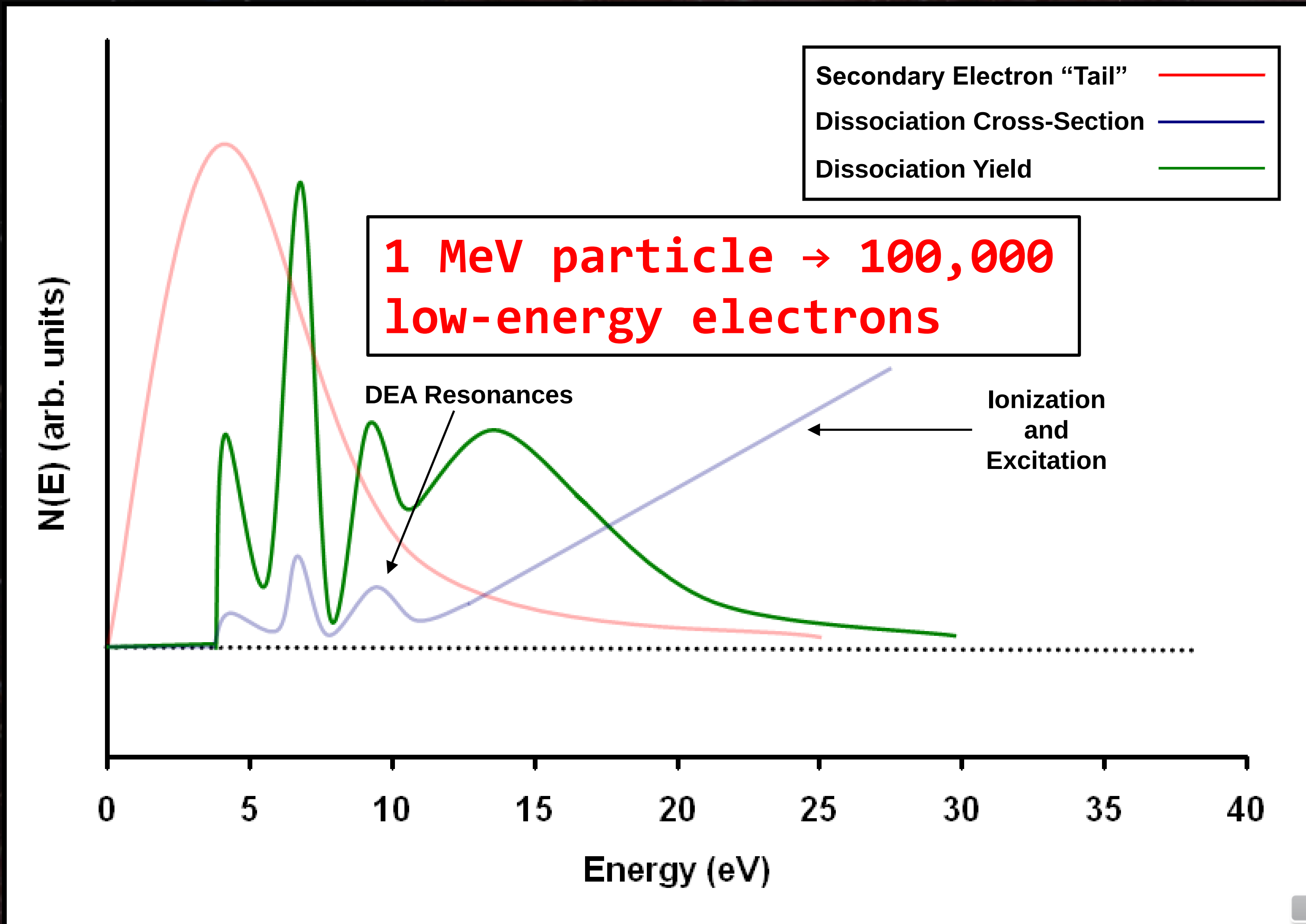
Formation of secondary electrons in cosmic ices and dust grains



Flux of Cosmic Rays Reaching Earth

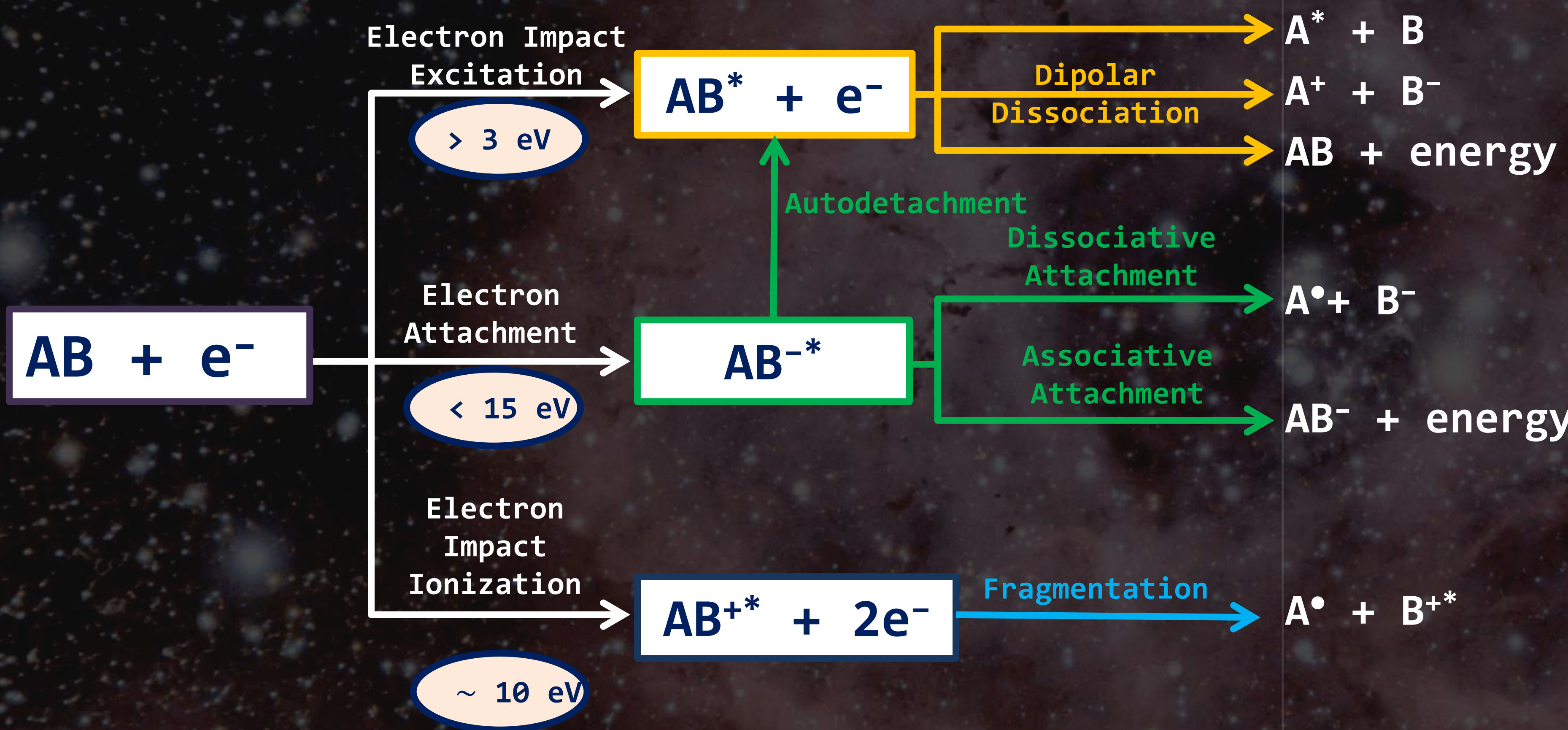


Importance of Low-Energy Electrons



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

Electron-induced dissociation mechanisms



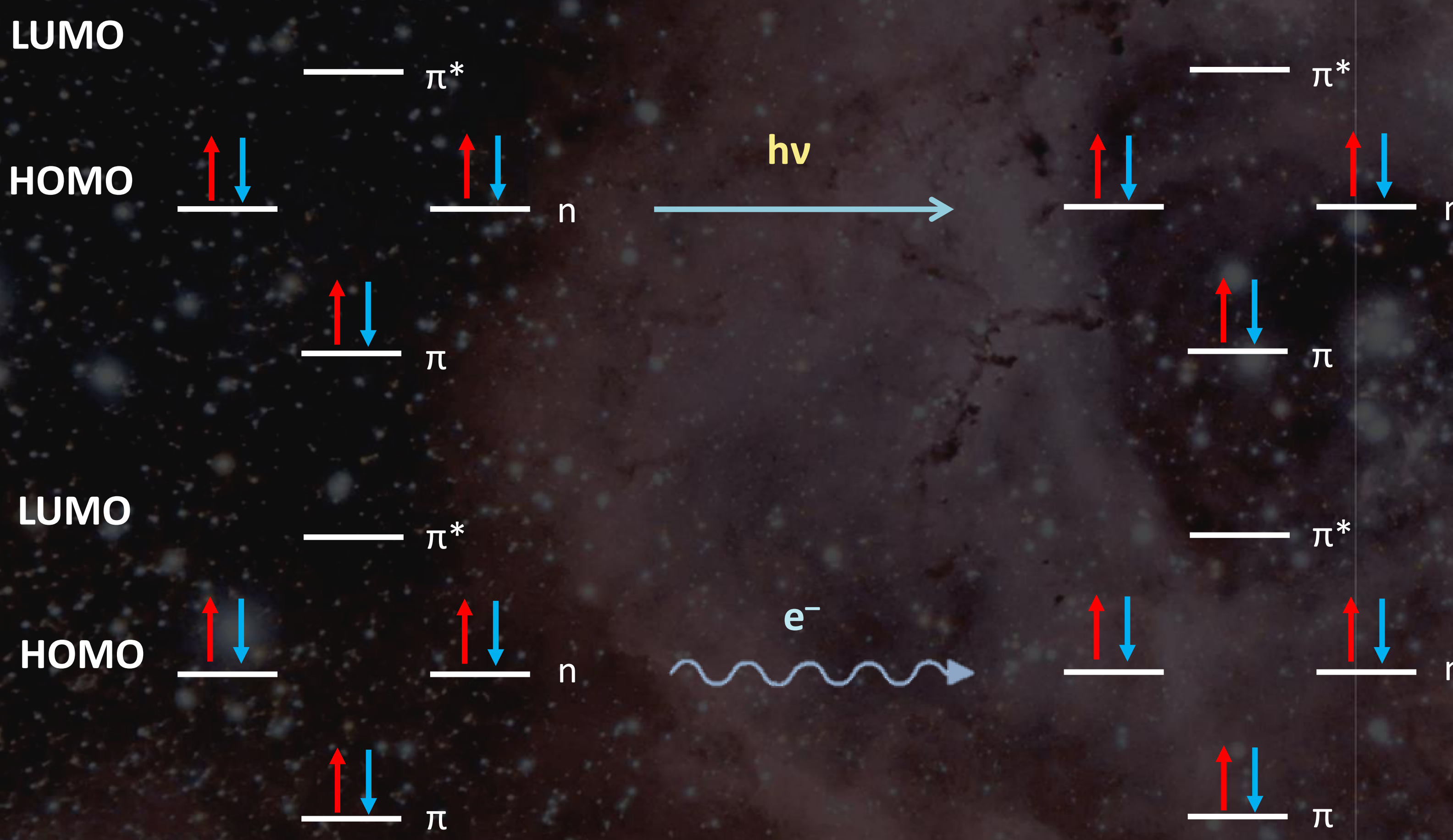
How to break a 5 eV bond with a 3 eV electron?

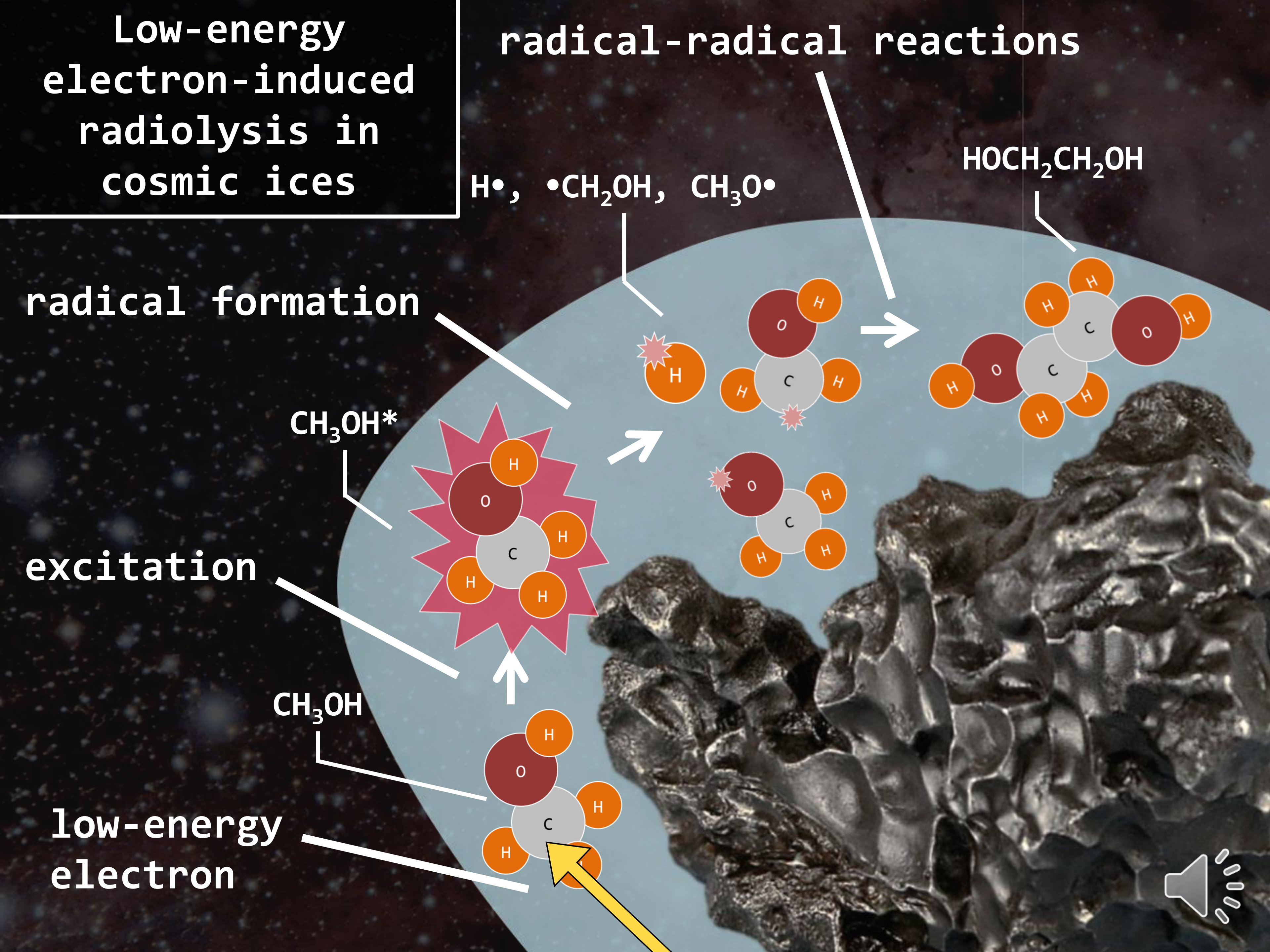
"Thermodynamic Threshold"

$$AB + e^- \rightarrow A + B^{-*}$$

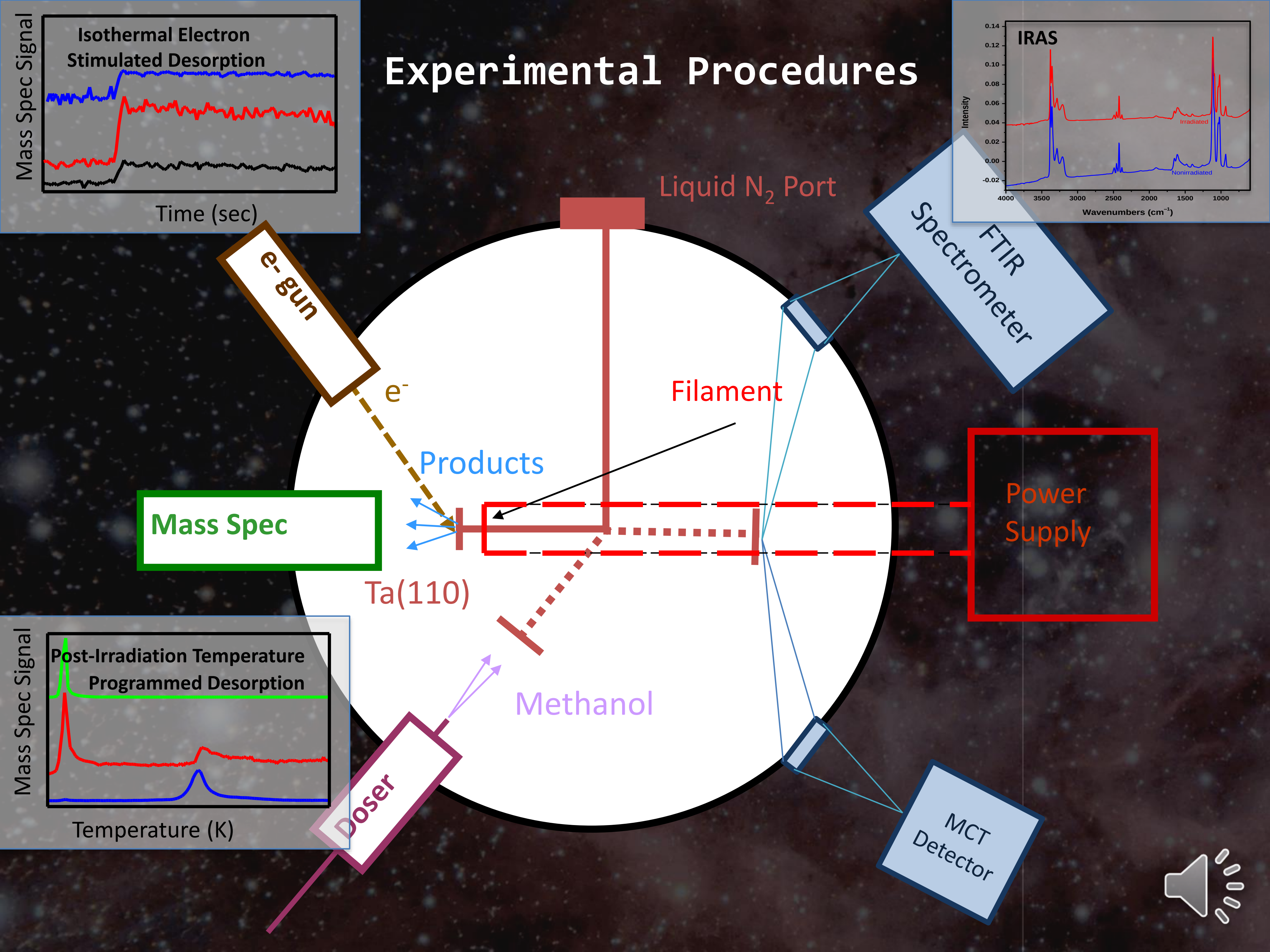
$$\Delta H_o(B^-) = D(A-B) - EA(B)$$

Another Key Difference between Photons and Electrons



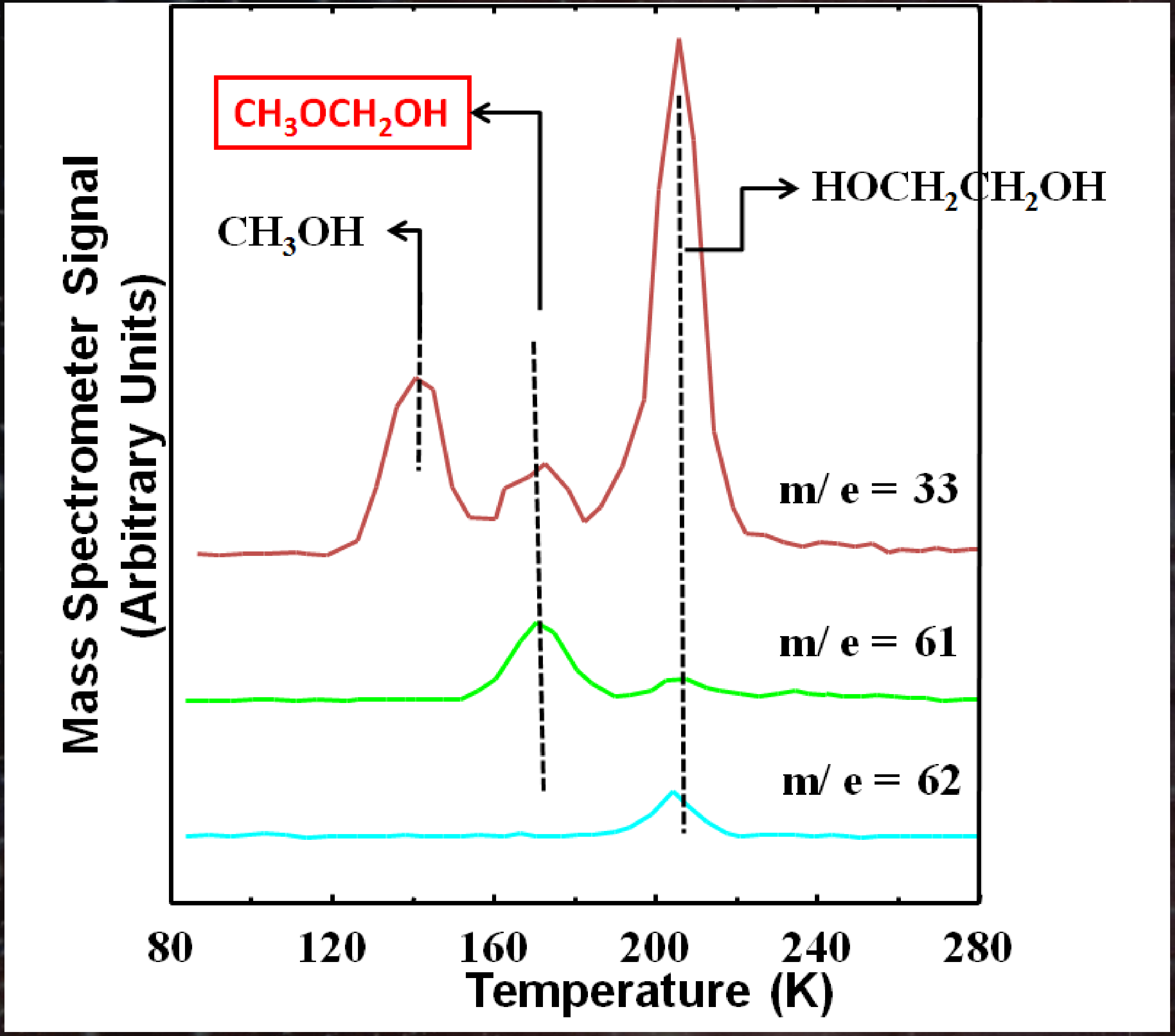

Low-energy electron-induced radiolysis in cosmic ices
radical-radical reactions
HOCH$_2$CH$_2$OH
H•, •CH$_2$OH, CH$_3$O•
radical formation
CH$_3$OH*
excitation
CH$_3$OH
low-energy electron
H
O
C

Experimental Procedures



PART I
RADIOLYSIS OF METHANOL

Post-Irradiation Temperature-Programmed Desorption
$^{12}CH_3OH$ on Mo(110)

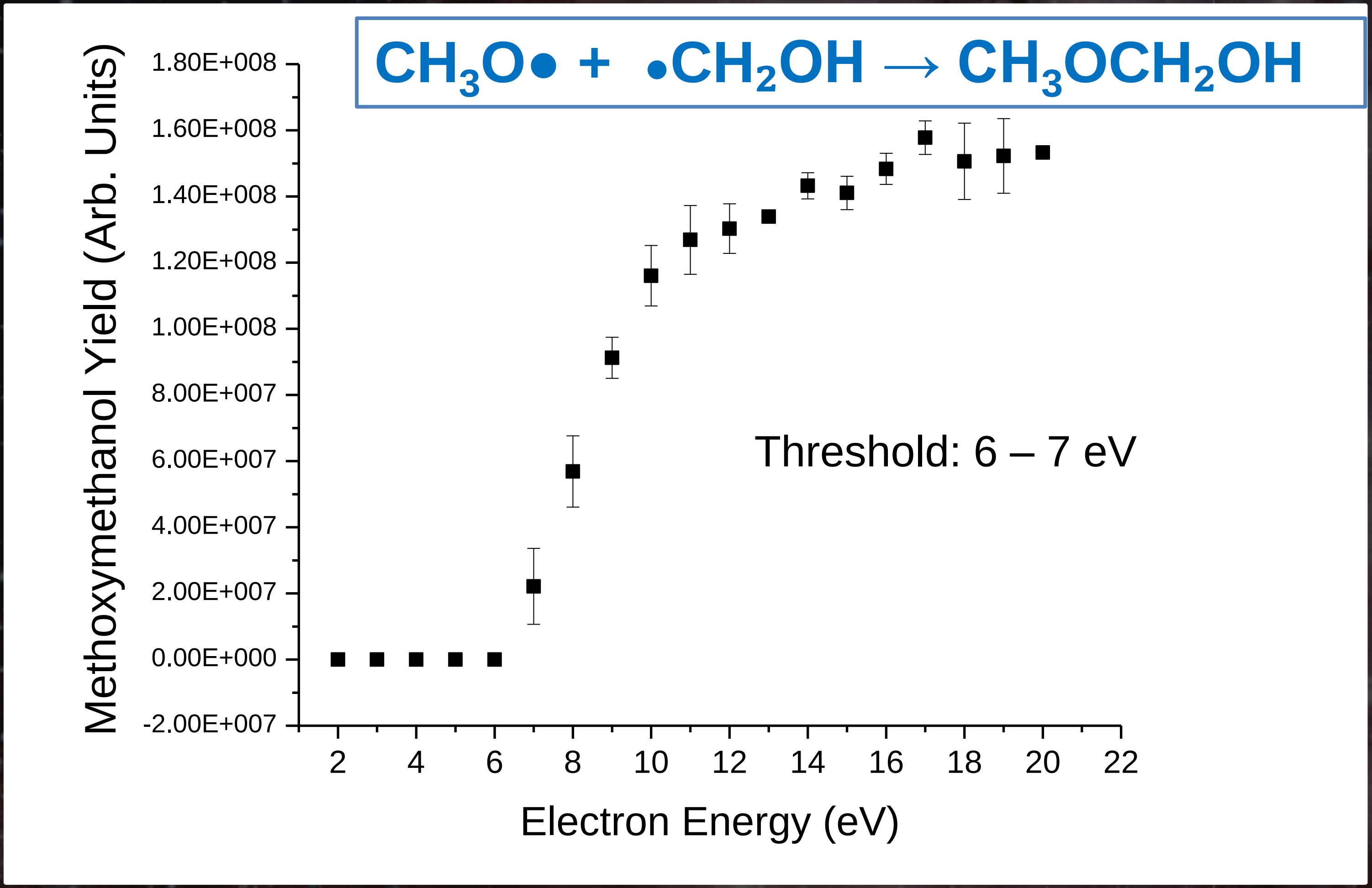


C.R. Arumainayagam, et. al. *J. Phys. Chem.*, **99** (1995) 9530

Conclusion 1

Post-irradiation temperature programmed desorption is useful for identifying labile radiolysis products (e.g., CH_3OCH_2OH)

Radiolysis Yield vs. Incident Electron Energy
Methoxymethanol: CH_3OCH_2OH (m/e = 61)



Boyer, Boamah, Sullivan, Arumainayagam, Bass, Sanche, (*J. Phys. Chem. C*, 2014, 118, 22592-22600)

Conclusion 2

- Dissociative electron attachment may not play an importance role in radiation-induced chemical synthesis reactions of methanol
- Radical-radical reactions are the likely mechanism for the formation of ethylene glycol and methoxymethanol
- Barrier-less radical-radical reactions may be rapid in interstellar ices because of the low temperatures (10 to 100 K).

Methanol Radicals

Radical 1 / Radical 2	•CH_2OH	•HCO	CH_3O•	•CH_3	•OH	•H
•CH_2OH						
•HCO						
CH_3O•						
•CH_3						
•OH						
•H						

What is the difference between a photon and an electron?

	Electrons (≤20 eV)	UV Study[1]
•CH_2OH	√	√
H_2CO	√	√
HCO		√
CO	√	√
CO_2	√	√
CH_4	√	√
HCOOH		√
CH_3OCHO	√	√
CH_3OCH_3	√	√
$HOCH_2CH_2OH$	√	√
CH_3OCH_2OH	√	
$HCOCH_2OH$	√	√
CH_3CH_2OH	√	√
C_2H_6		√
CH_3CHO	√	√
CH_3COOH	√	√

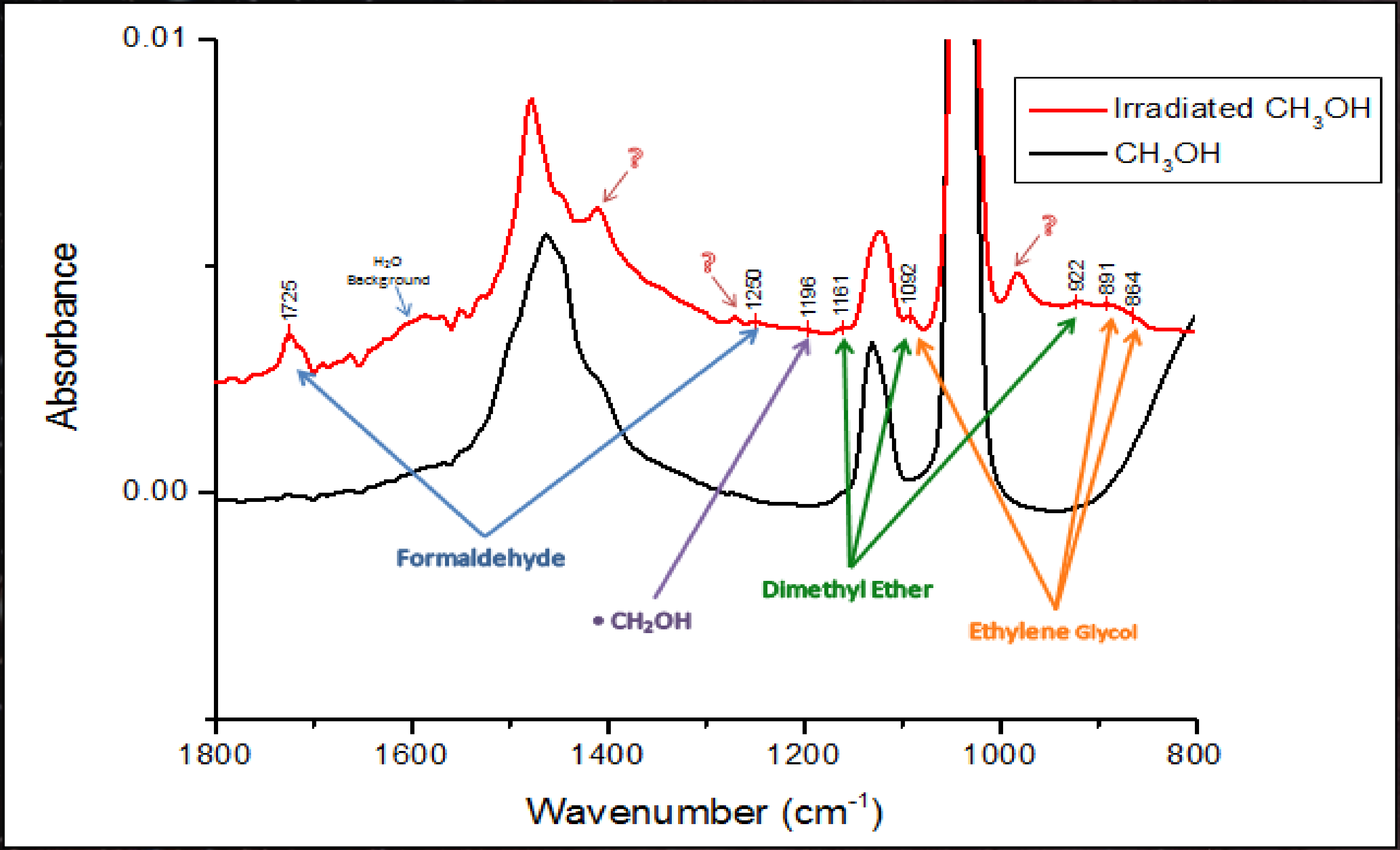
[1]Oberg et. al. (A&A 504, 891–913 (2009))

Conclusion 3

- Post-irradiation temperature programmed desorption can be used to identify components in a complex mixture of radiolysis products
- The identified electron-induced methanol radiolysis products include many that have been previously identified as being formed by methanol UV photolysis in the interstellar medium
- Post-irradiation temperature programmed desorption results cannot be used to conclude if identified products are nascent radiolysis products

Irradiated Methanol: IRAS Product Analysis

100 monolayers CH_3OH at 90 K irradiated with 14 eV electrons 2400 μC



Sullivan, Boamah, Shulenberger, Chapman, Atkinson, Boyer, Arumainayagam, *Monthly Notices of the Royal Astronomical Society* (doi: 10.1093/mnras/stw593)

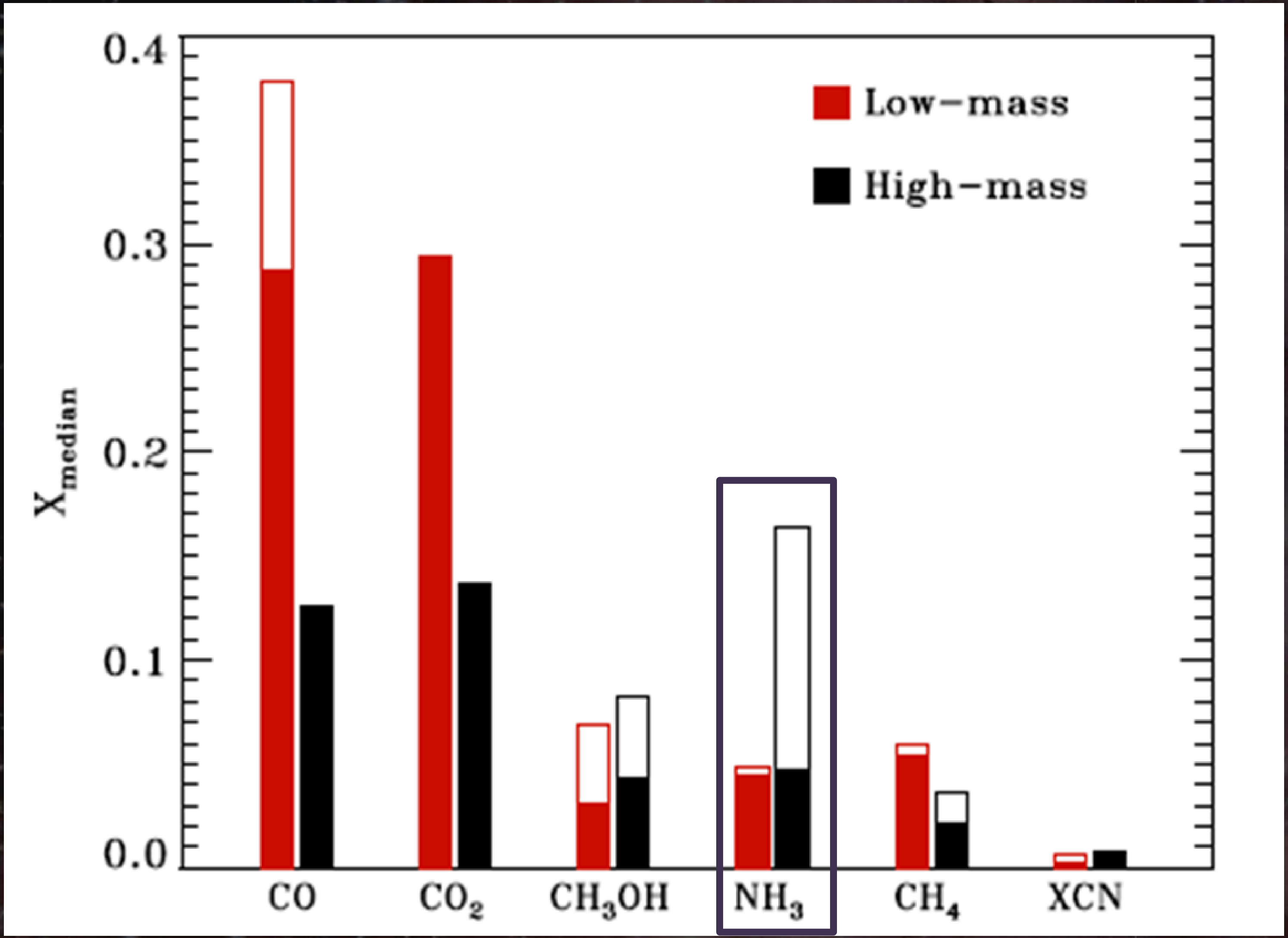
Conclusion 4

- Thermal processing above 90 K not necessary for product formation

- IRAS not as effective as TPD for identifying species in complex product mixture

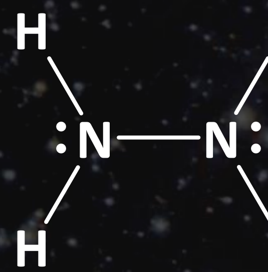
PART II
RADIOLYSIS OF AMMONIA

Why study ammonia?

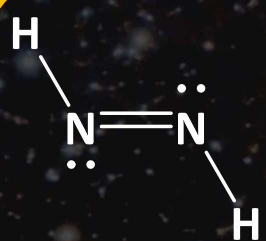


Öberg, K., et al. "The Spitzer Ice Legacy: Ice Evolution from cores to protostars." *The Astrophysical Journal* 740(2011): 16 pp.

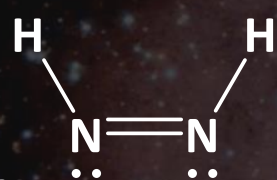
Possible Radiolysis Products of Ammonia



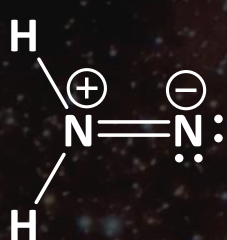
Hydrazine



Trans



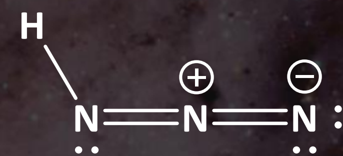
Cis



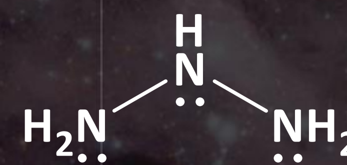
Iso

Diazene

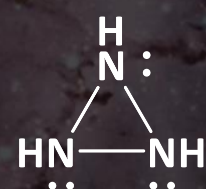
N-2 Species



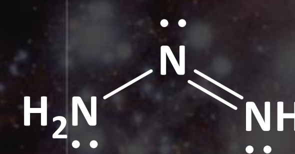
Hydrazoic Acid



triazane



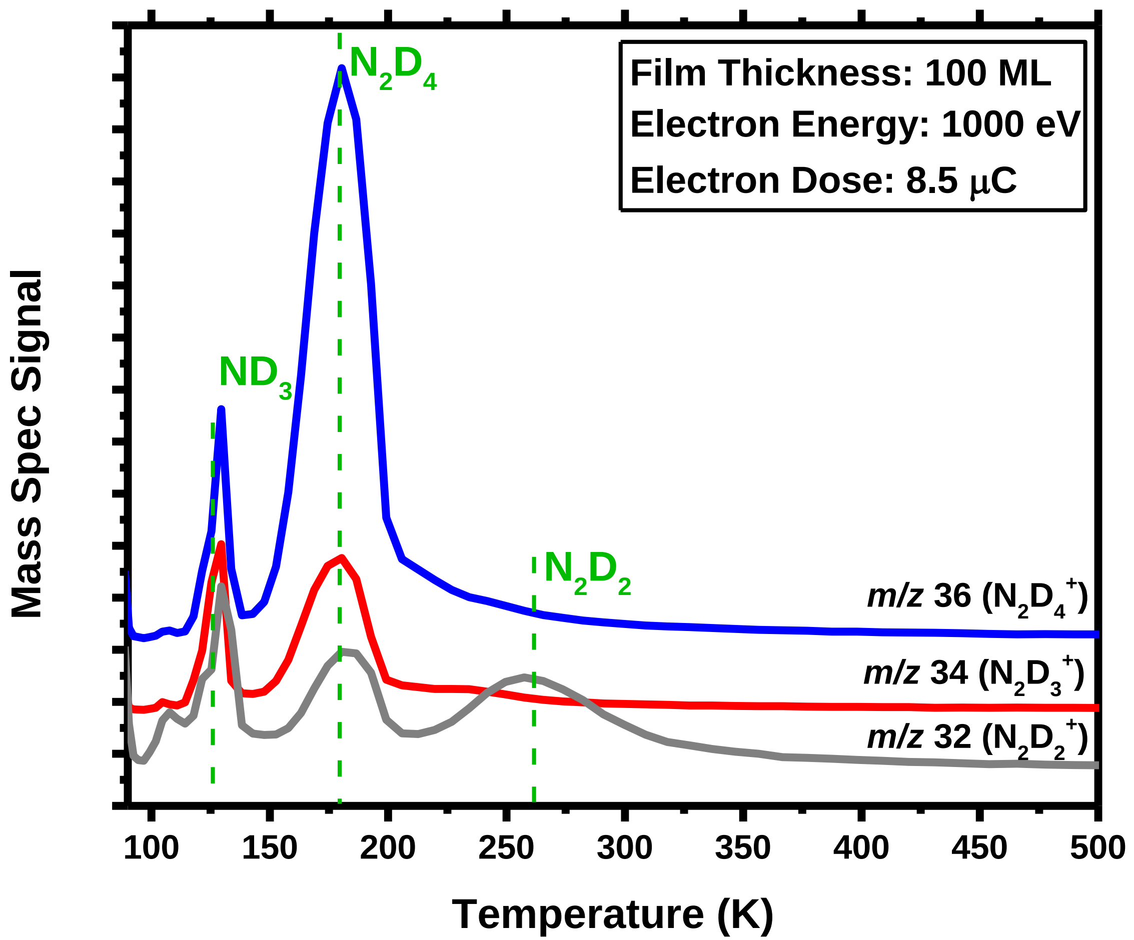
cyclotriazane



triazene

N-3 Species

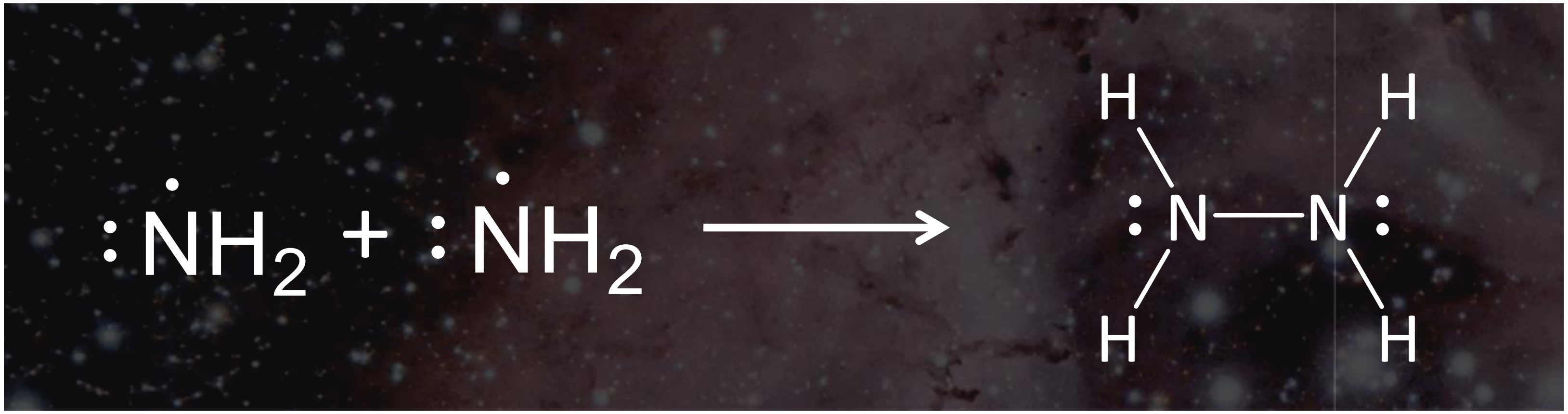
Detection of Hydrazine and Diazene at High Incident Electron Energies



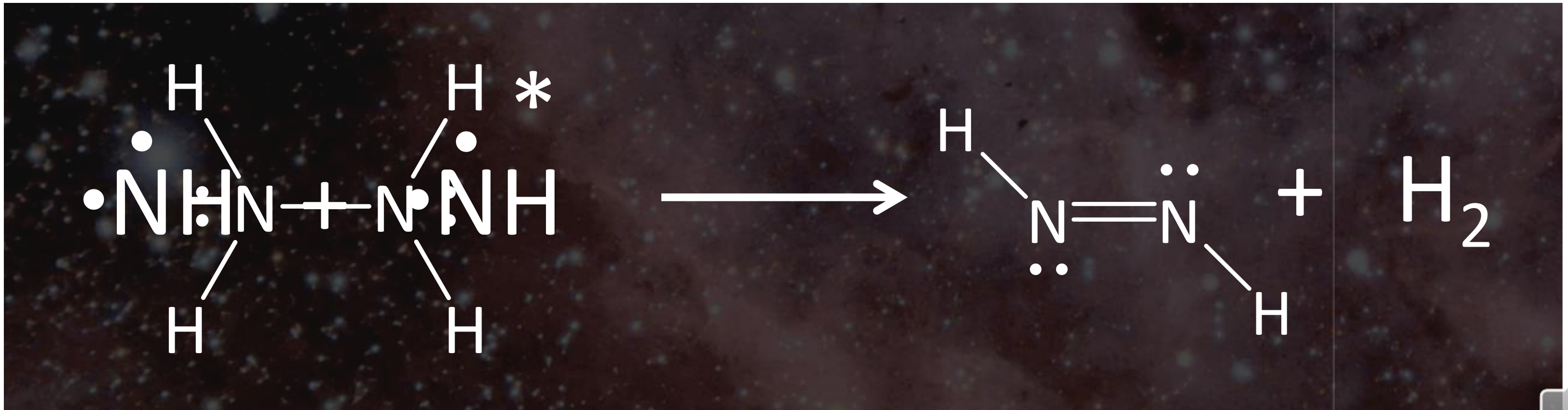
Katie Shulenberger `14 (Wellesely College)

Radiolysis Products of 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

$$R \xrightarrow{k_1} I$$

$$I + I \xrightarrow{k_2} P$$

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

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

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

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

$$I(t) = ?$$

$$P(t) = ?$$

Katherine Tran ’15
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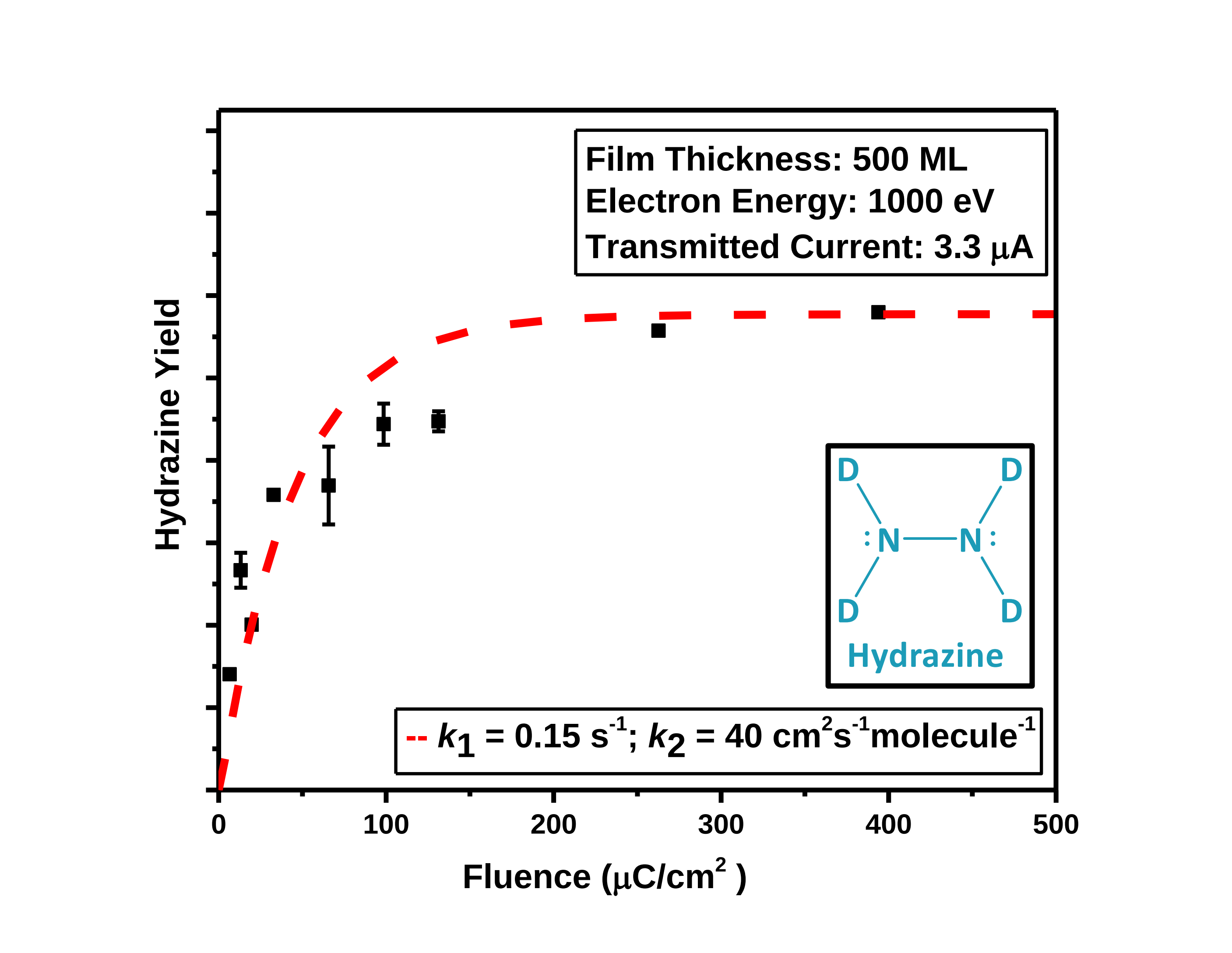
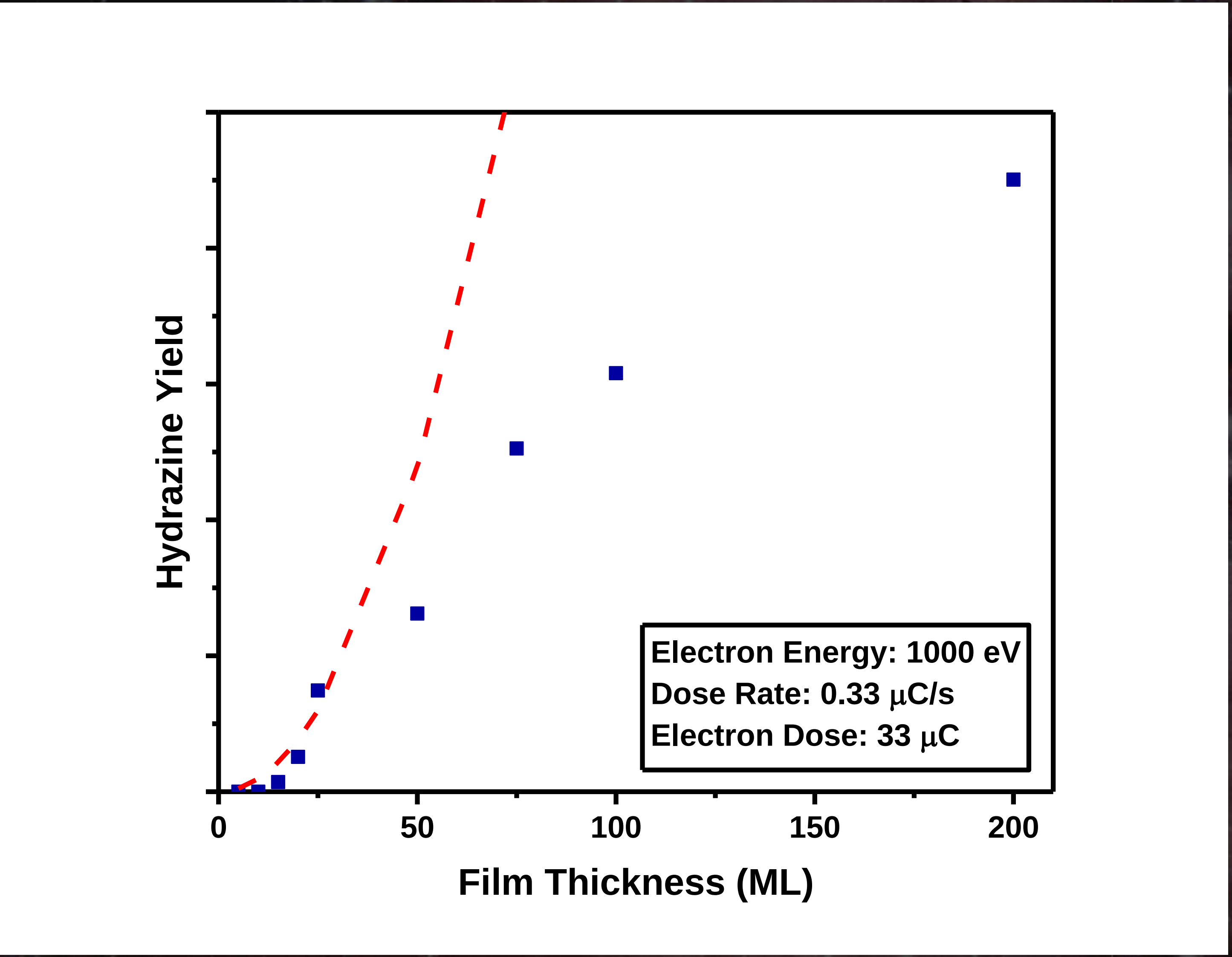
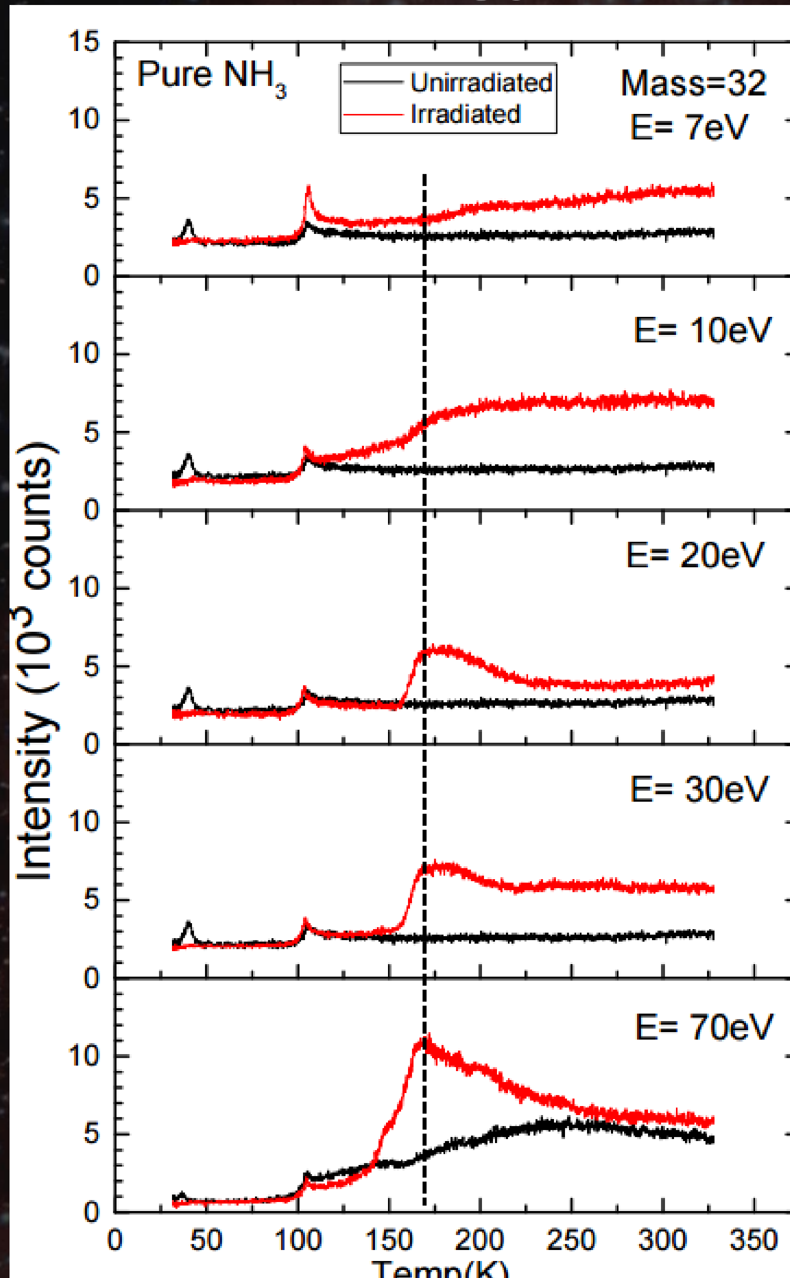
Results: Yield vs Fluence



Results: Yield vs Film Thickness



Results: Low Energy Experiments



Leon Sanche, Andrew Bass & Sasan Esmaili

Final Conclusions

- Low-energy (< 20 eV) electron-induced condensed phase reactions may contribute to the interstellar synthesis of "complex" molecules previously thought to form exclusively via UV photons
- Molecules such as methoxymethanol may serve as tracer molecules for the differences between photon- and electron-induced reactions.

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