Radiation Chemistry vs. Photochemistry in the Cosmic Synthesis of Prebiotic Molecules

Chris Arumainayagam
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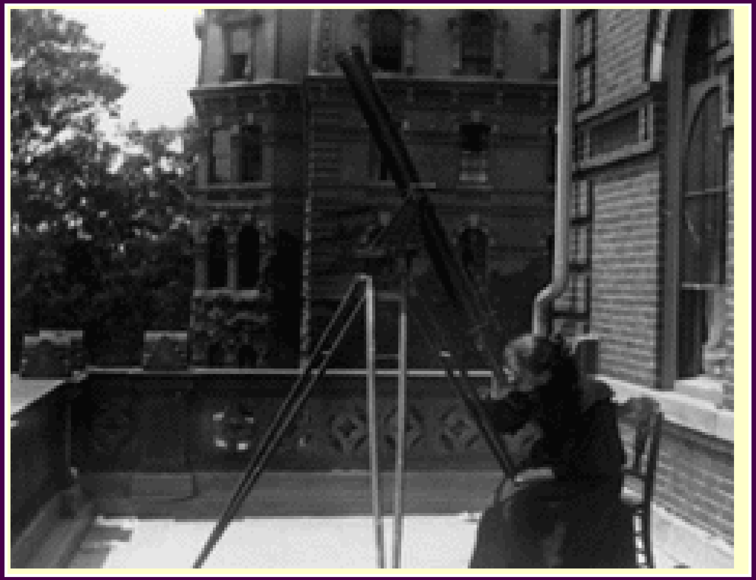
Annie Jump Cannon (1863-1941)

- Graduated from Wellesley College 1884



- Likely discoverer of the still enigmatic spectral diffuse interstellar bands (DIB) (~ 1918)
- Stellar classification: “OBAFGKM”
- Classified 350,000 stars
- Became a “special student” of astronomy at Radcliffe College (1894)
- First woman to receive an honorary degree from Oxford (1925)

Three Questions:

1. What is the difference between an electron and a photon?

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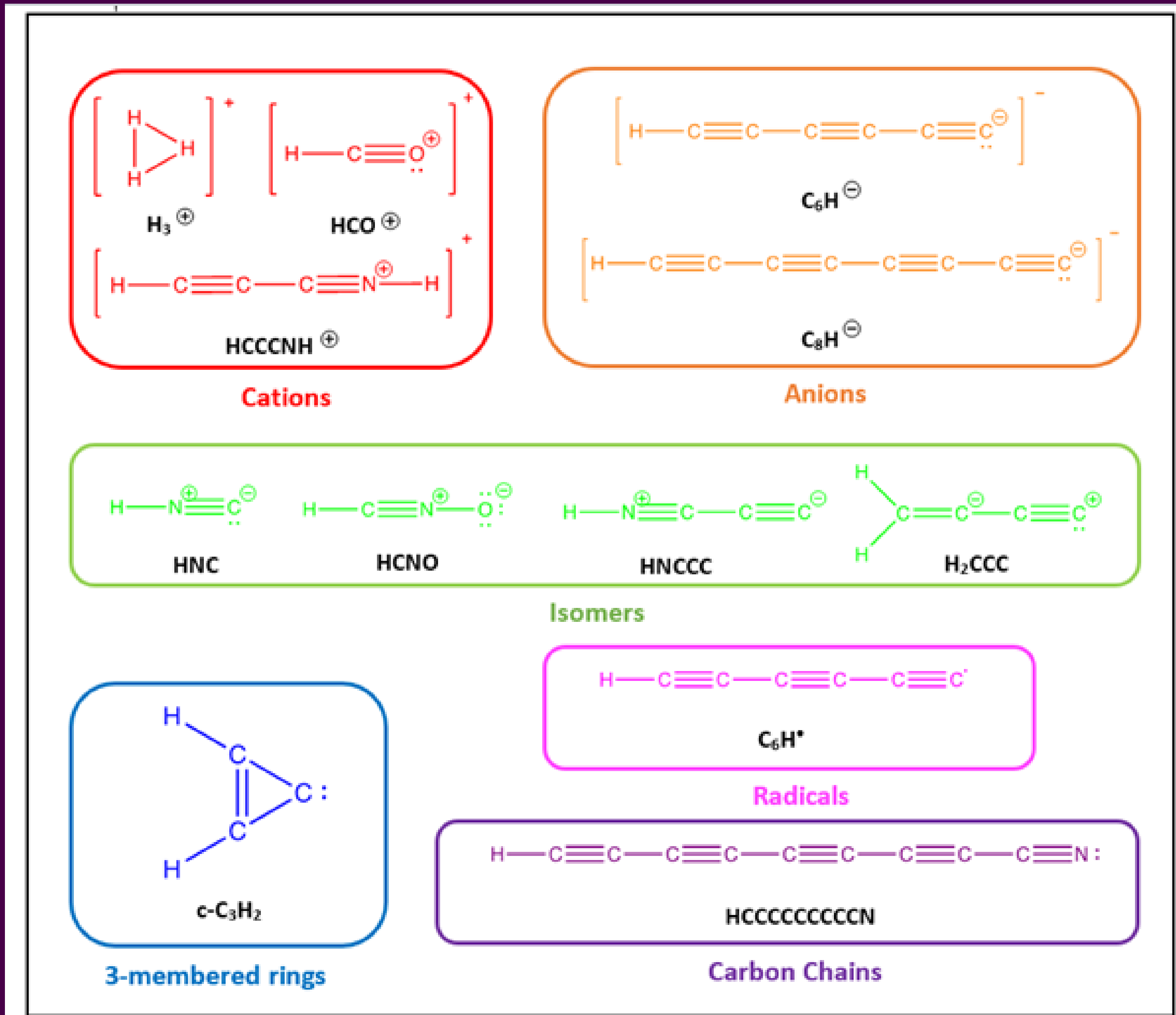
3. How do you create a little bit of heaven on earth?

Molecules Found in interstellar and circumstellar clouds

2 atoms	SiS	HCN	HCP	H_2CO	HC_3N	HC_3NH^+	$HC(O)OCH_3$	$(CH_3)_2CO$
H_2	CS	HCO	CCP	H_2CN	HC_2NC	HC_2CHO	CH_3COOH	$(CH_2OH)_2$
AlF	HF	HCO^+	AlOH	H_2CS	HCOOH	NH_2CHO	C_7H	CH_3CH_2CHO
AlCl	SH	HCS^+	H_2O^+	H_3O^+	H_2CNH	C_5N	H_2C_6	CH_3CHCH_2O
C_2	SH^+	HOC^+	H_2Cl^+	NH_3	H_2C_2O	*l*-HC_4H	CH_2OHCHO	11 atoms
CH	FeO ?	H_2O	KCN	c-SiC_3	H_2NCN	*l*-HC_4N	*l*-HC_6H	HC_9N
CH^+	O_2	H_2S	FeCN	CH_3	HNC_3	*c*-H_2C_3O	CH_2CHCHO ?	CH_3C_6H
CN	CF^+	HNC	HO_2	C_3N^-	SiH_4	H_2CCNH ?	CH_2CCHCN	C_2H_5OCHO
CO	SiH^+ ?	HNO	TiO_2	PH_3	H_2COH^+	C_5N^-	H_2NCH_2CN	$CH_3OC(O)CH_3$
CO^+	PO	MgCN	C_2N	HCNO	C_4H^-	HNCHCN	CH_3CHNH	12 atoms
CP	AlO	MgNC	Si_2C	HOCN	HC(O)CN	7 atoms	9 atoms	*c*-C_6H_6
CSi	CN^-	N_2H^+	4 atoms	HSCN	HNCNH	C_6H	CH_3C_4H	*n*-C_3H_6CN
HCl	HD	N_2O	*c*-C_3H	H_2O_2	CH_3O	CH_2CHCN	CH_3CH_2CN	*i*-C_3H_7CN
KCl	HCl^+	NaCN	*l*-C_3H	C_3H^+	NH_4^+	CH_3C_2H	$(CH_3)_2O$	$C_2H_5OCH_3$?
NH	TiO	OCS	C_3N	HMgNC	H_2NCO^+ ?	HC_5N	CH_3CH_2OH	>12 atoms
NO	ArH^+	SO_2	C_3O	HCCO	$NCCNH^+$	CH_3CHO	HC_7N	C_{60}
NS	N_2	*c*-SiC_2	C_3S	5 atoms	6 atoms	NH_2CH_3	C_8H	C_{60}^+
NaCl	NO^+ ?	CO_2	C_2H_2	C_5	C_5H	*c*-C_2H_4O	$CH_3C(O)NH_2$	C_{70}
OH	3 atoms	NH_2	CH_2D^+ ?	C_4H	*l*-H_2C_4	H_2CCHOH	C_8H^-	
PN	C_3	H^{3+}	HCCN	C_4Si	C_2H_4	C_6H^-	C_3H_6	
SO	C_2H	H_2D^+, HD^{2+}	$HCNH^+$	*l*-C_3H_2	CH_3CN	CH_3NCO	CH_3CH_2SH ?	
SO^+	C_2O	SiCN	HNCO	*c*-C_3H_2	CH_3NC	HC_5O	CH_3NHCHO ?	
SiN	C_2S	AlNC	HNCS	CH_2CN	CH_3OH	8 atoms	10 atoms	
SiO	CH_2	SiNC	$HOCO^+$	CH_4	CH_3SH	CH_3C_3N	CH_3C_5N	

http://astrochymist.org/astrochymist_ism.html

“Exotic” Molecules in the ISM



Source: Eric Herbst

An Example of a prebiotic molecule found in the ISM

THE ASTROPHYSICAL JOURNAL LETTERS

DETECTION OF E-CYANOMETHANIMINE TOWARD SAGITTARIUS B2(N) IN THE GREEN BANK TELESCOPE PRIMOS SURVEY

Daniel P. Zaleski[1], Nathan A. Seifert[1], Amanda L. Steber[1], Matt T. Muckle[1], Ryan A. Loomis[1], Joanna F. Corby[2], Oscar Martinez, Jr.[3,4], Kyle N. Crabtree[3,4], Philip R. Jewell[5], Jan M. Hollis[6]

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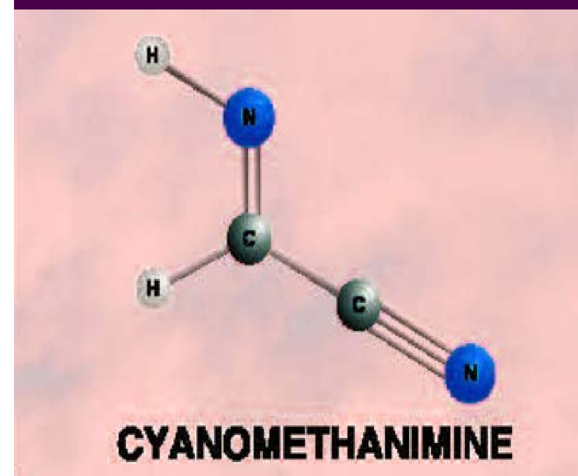
Published 2013 February 13 •

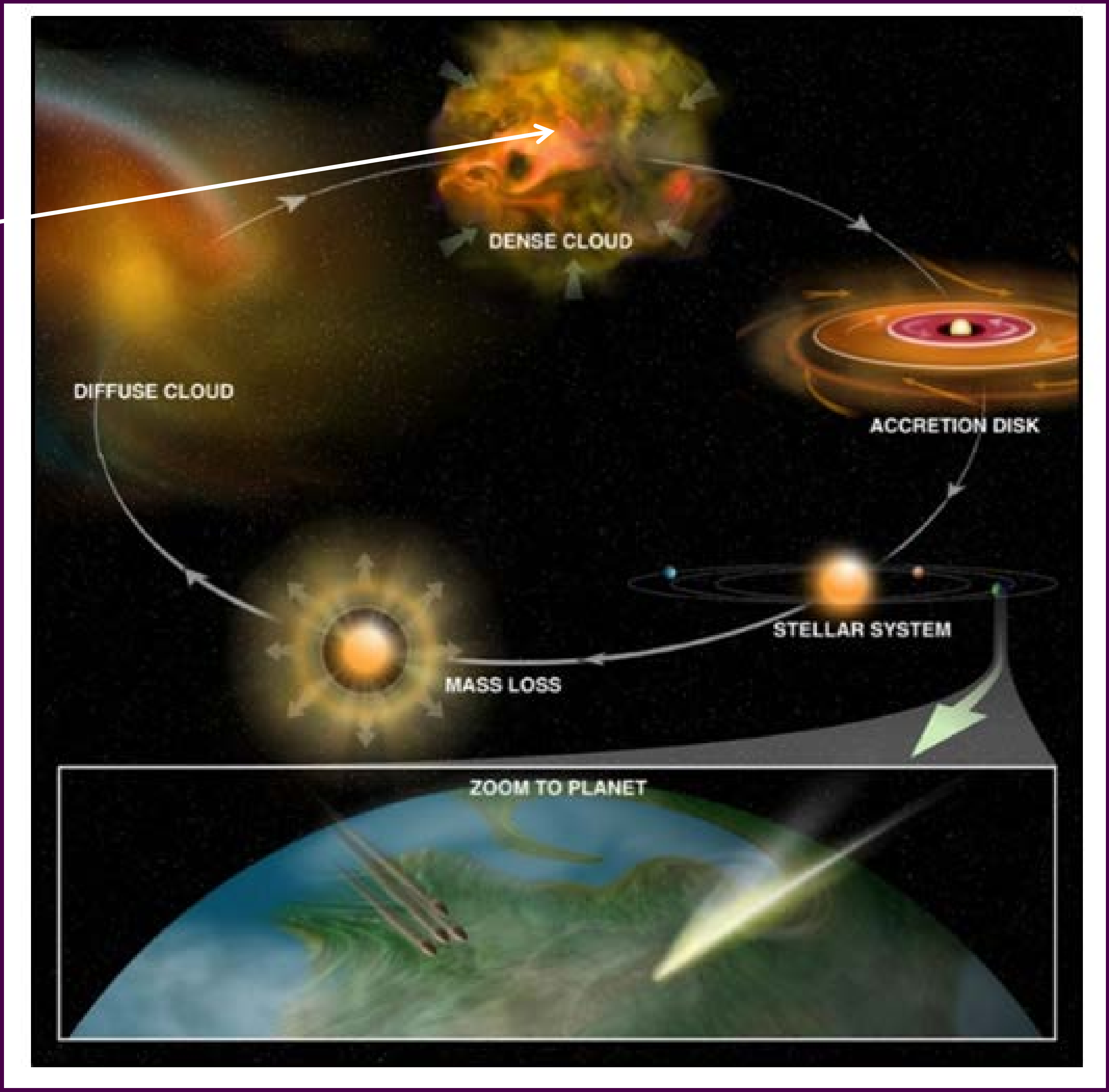
The Astrophysical Journal Letters, Volume 765, Number 1



Precursor of adenine, one of the four nucleobases of DNA

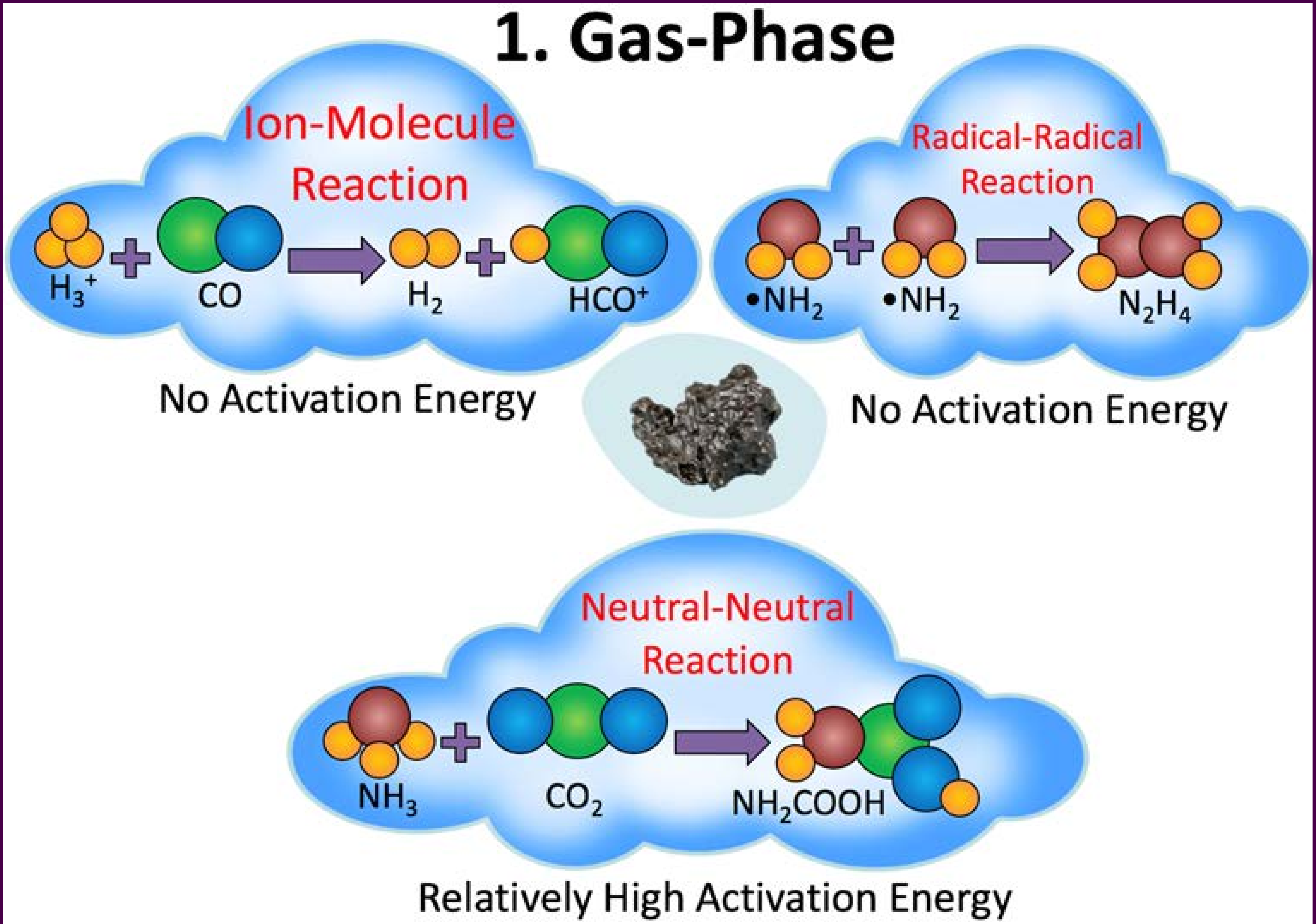
Cosmic Chemistry Cycle

Pre-stellar core

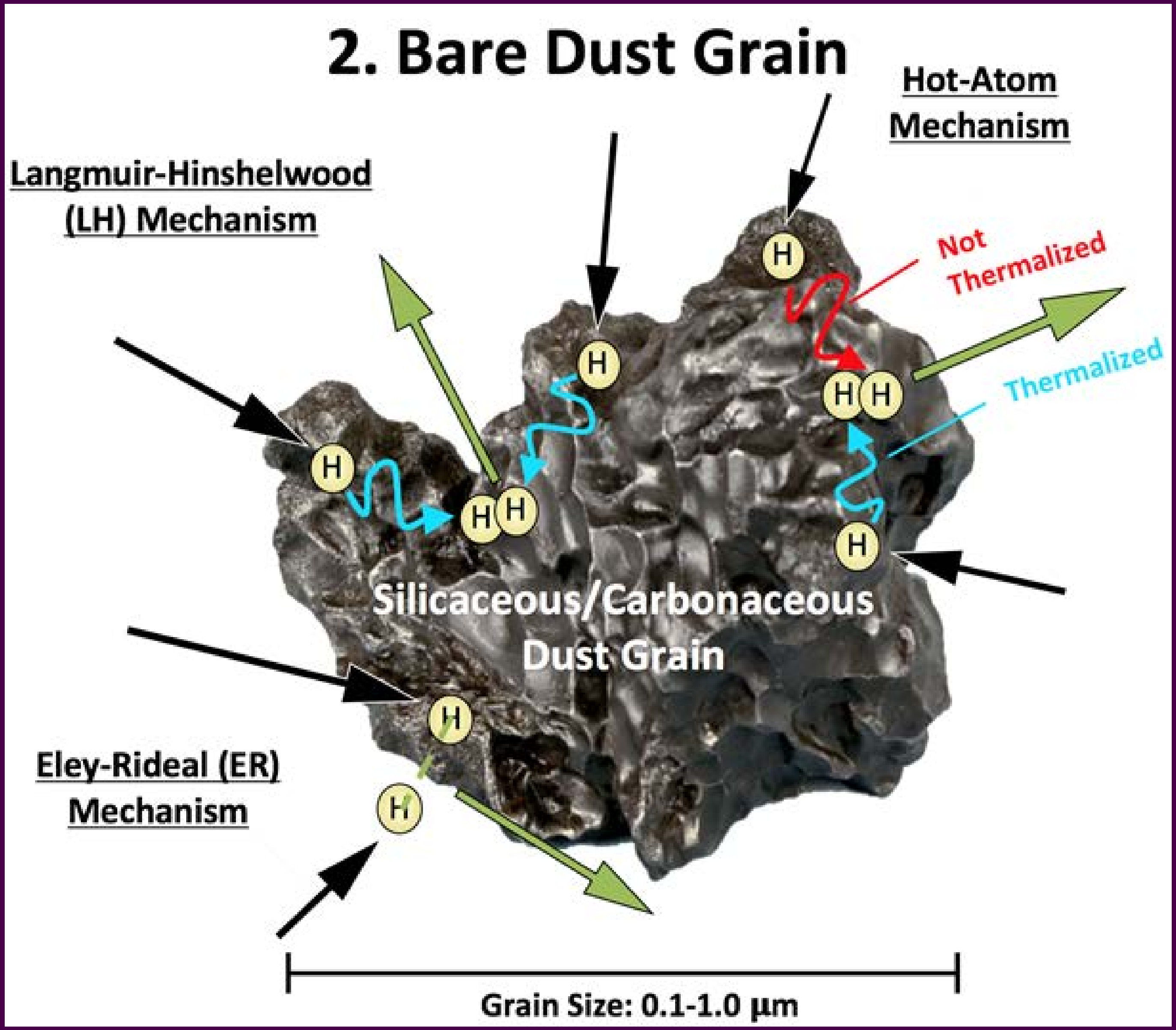


CREDIT: Bill Saxton, NRAO/AUI/NSF

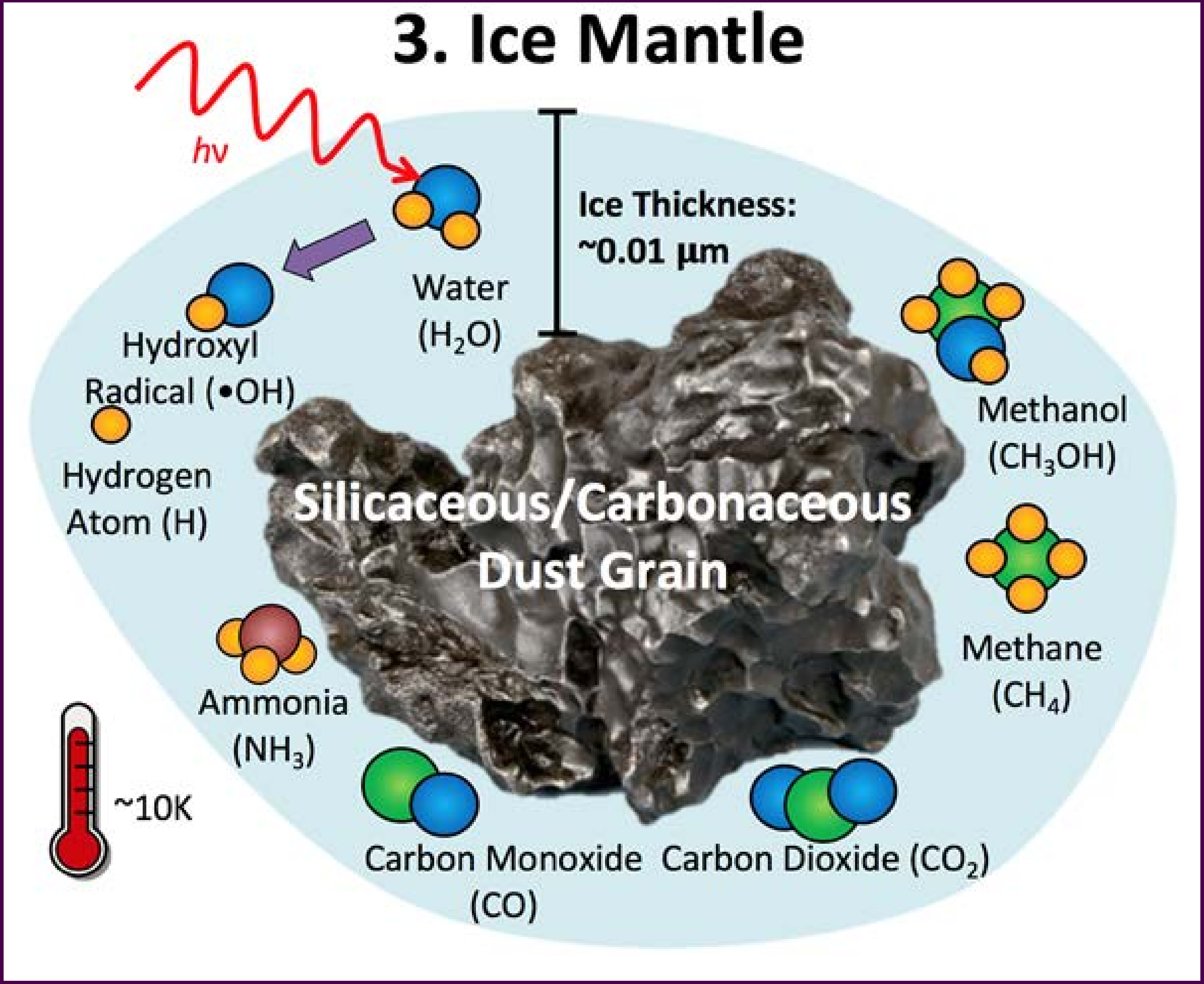
Three Environments for Astrochemistry



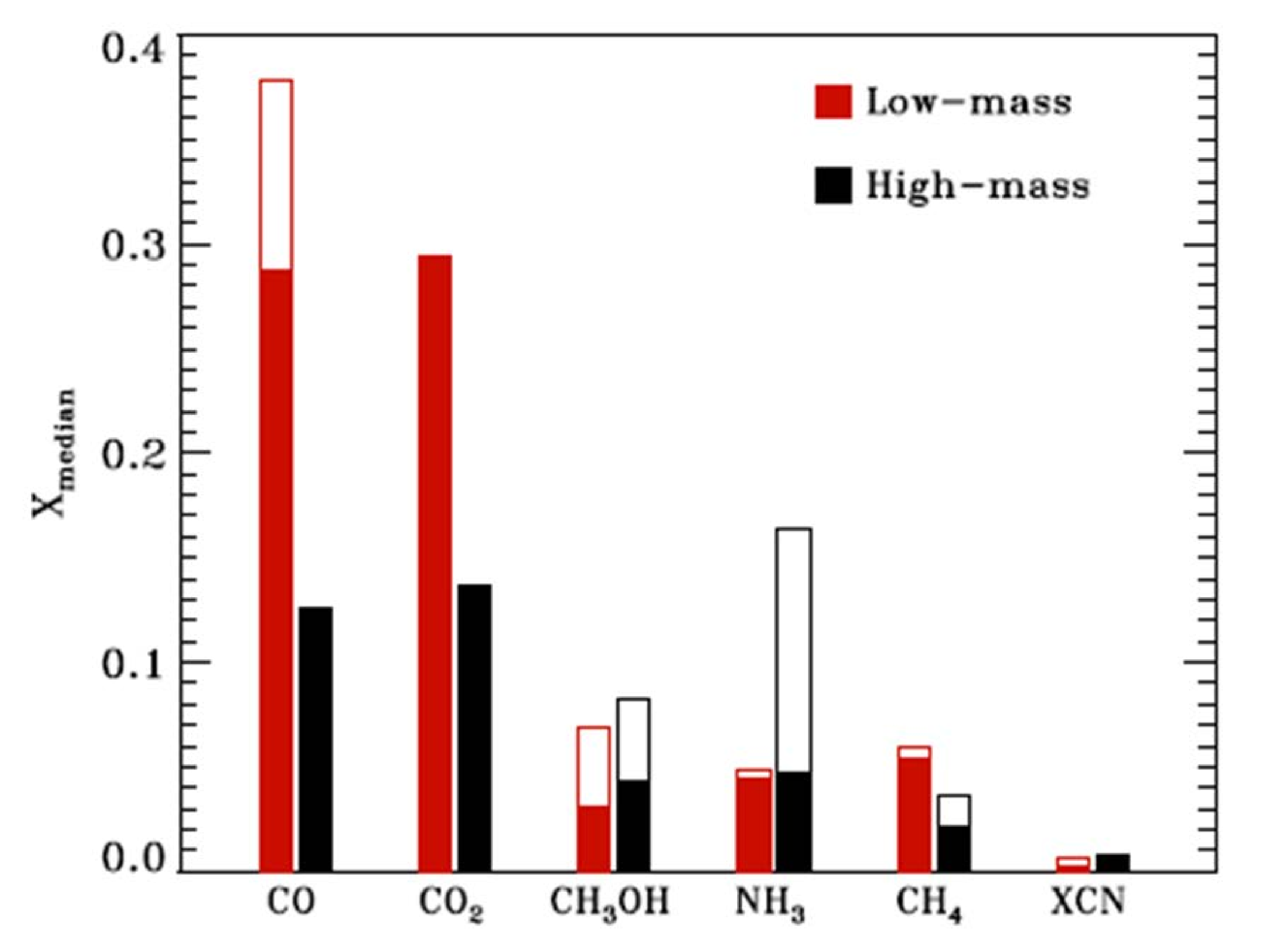
Three Environments for Astrochemistry



Three Environments for Astrochemistry

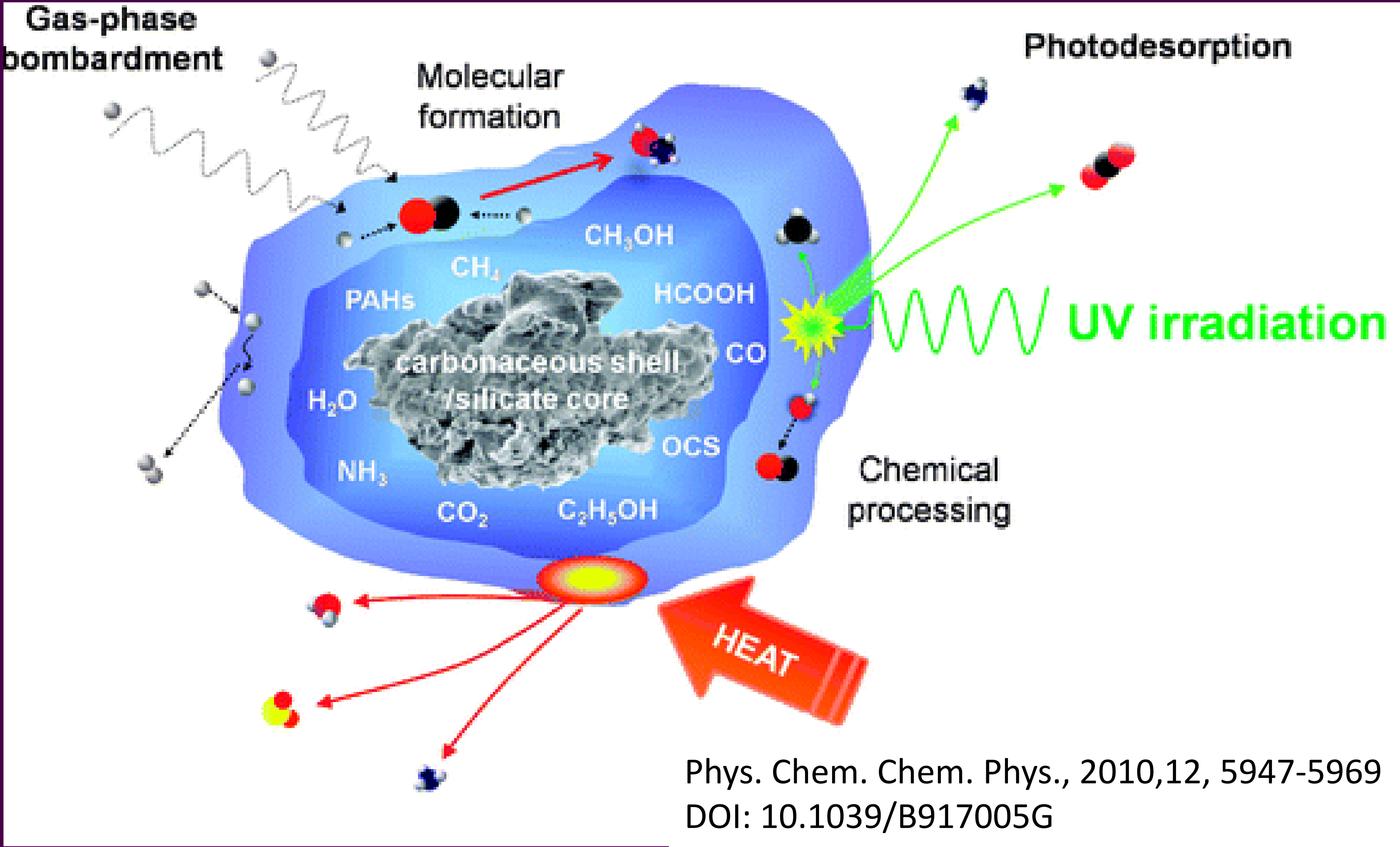


Molecular Composition of Interstellar Ices



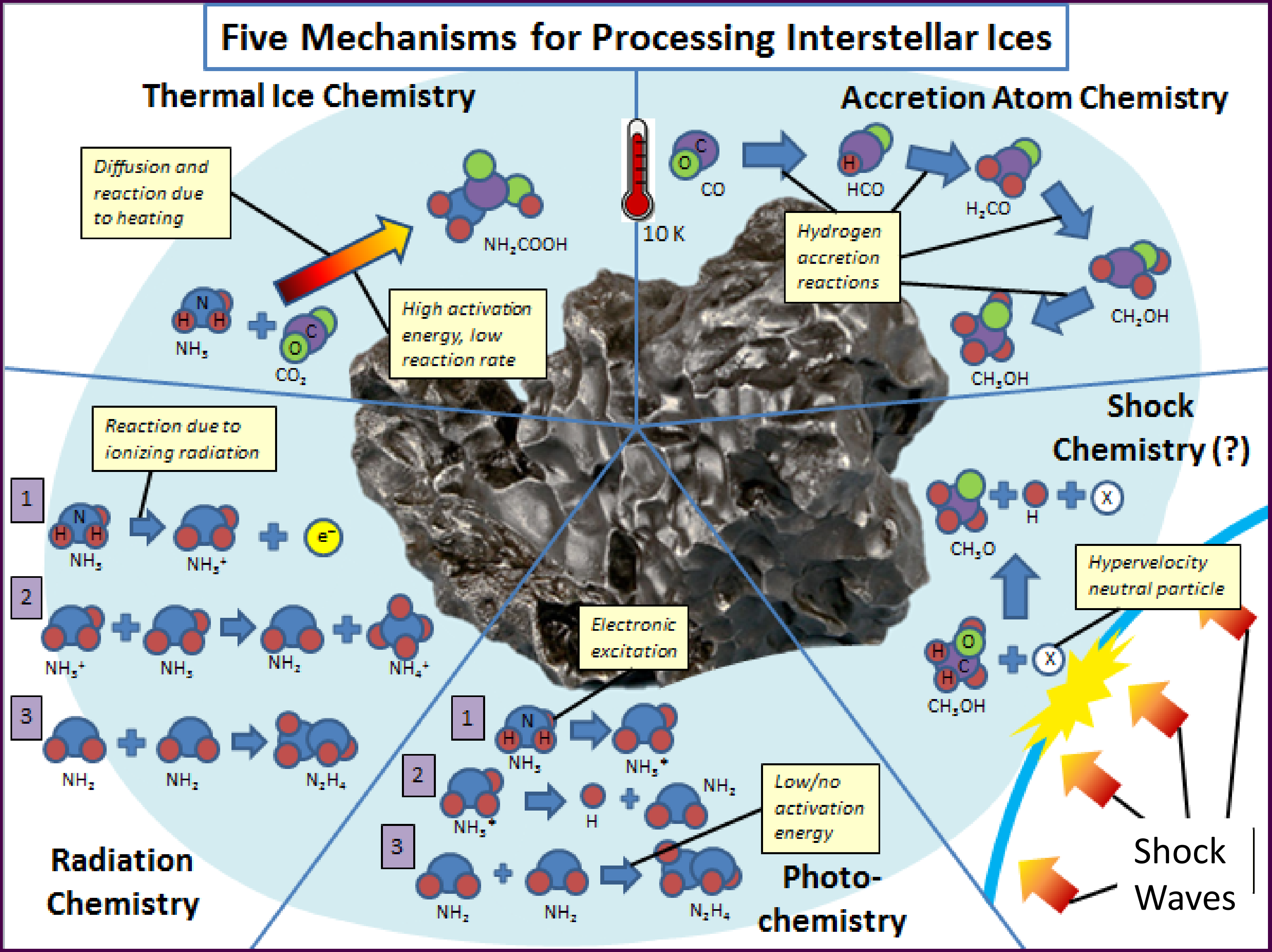
Öberg, K., et al. "The Spitzer Ice Legacy: Ice Evolution from cores to protostars." *The Astrophysical Journal* 740(2011): 16 pp.

Interstellar synthesis of prebiotic molecules: Widely Accepted Hypothesis



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

Five Mechanisms for Processing Interstellar Ices



Our Claim

We have performed the first direct comparison between photochemistry and radiation chemistry relevant to the energetic processing of interstellar ice analogs.

What is the difference between radiation chemistry and photochemistry?

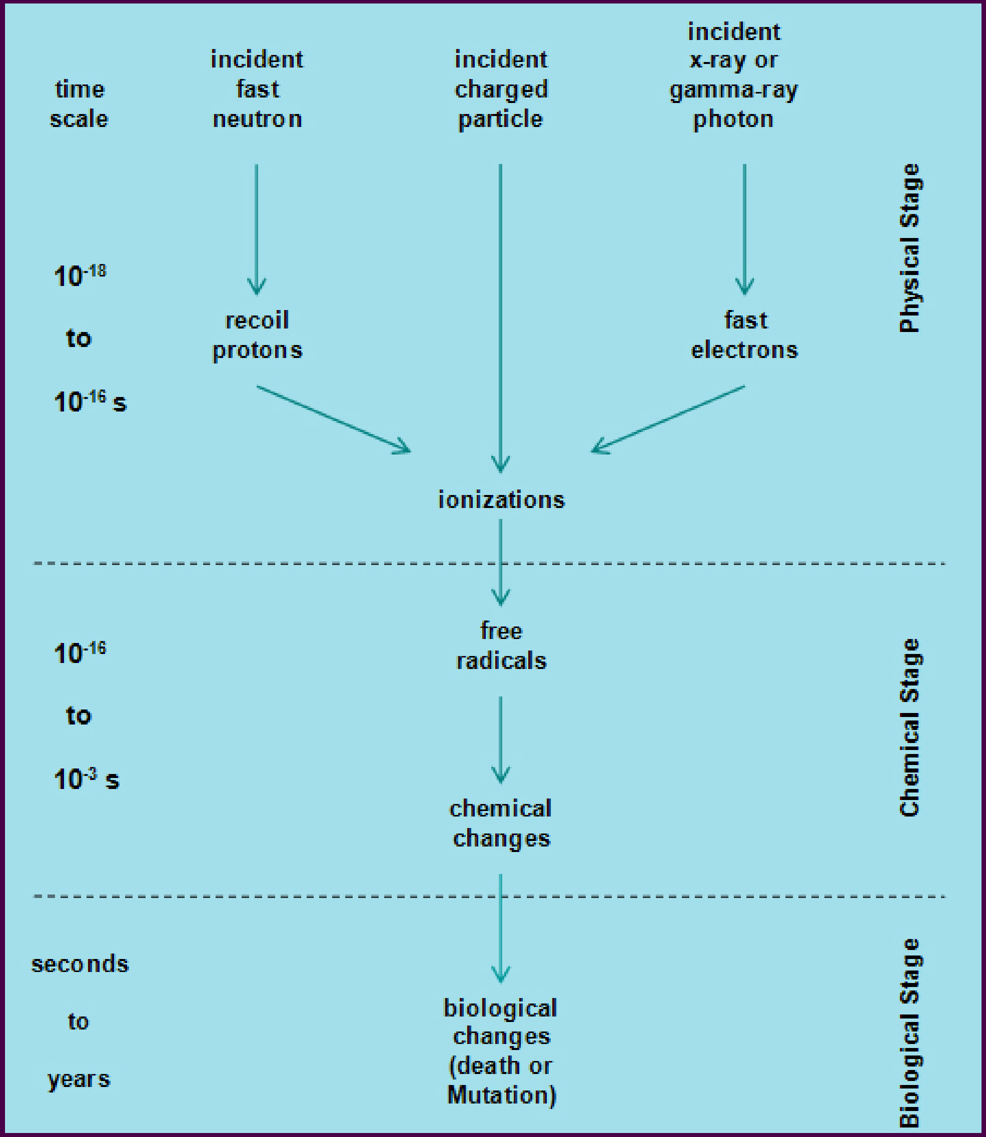
Radiation Chemistry

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.

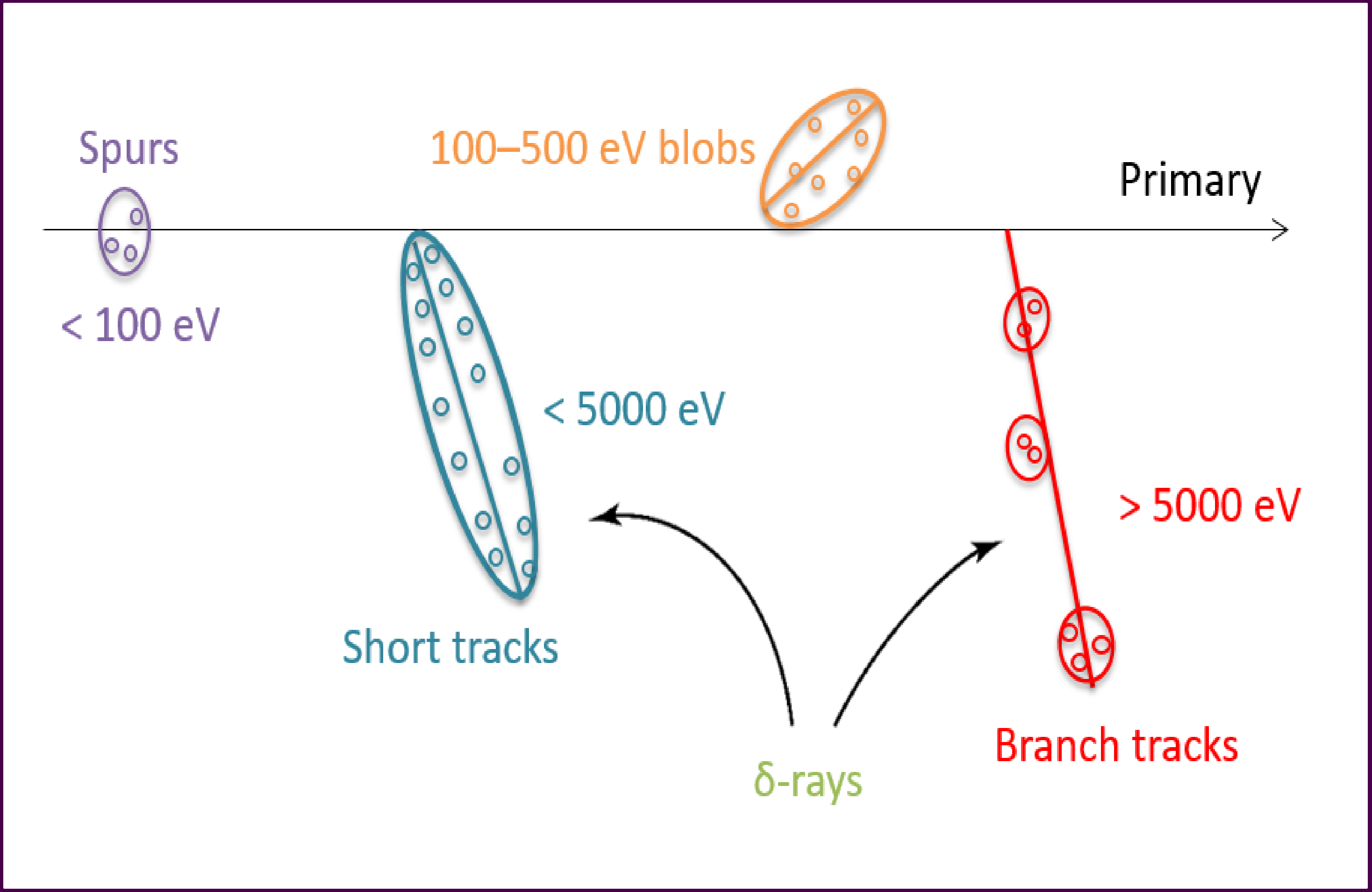
R.J. Woods, Basics of Radiation Chemistry, in: R.D.C. William J. Cooper, Kevin E. O'Shea

Time Scale of Radiation Chemistry



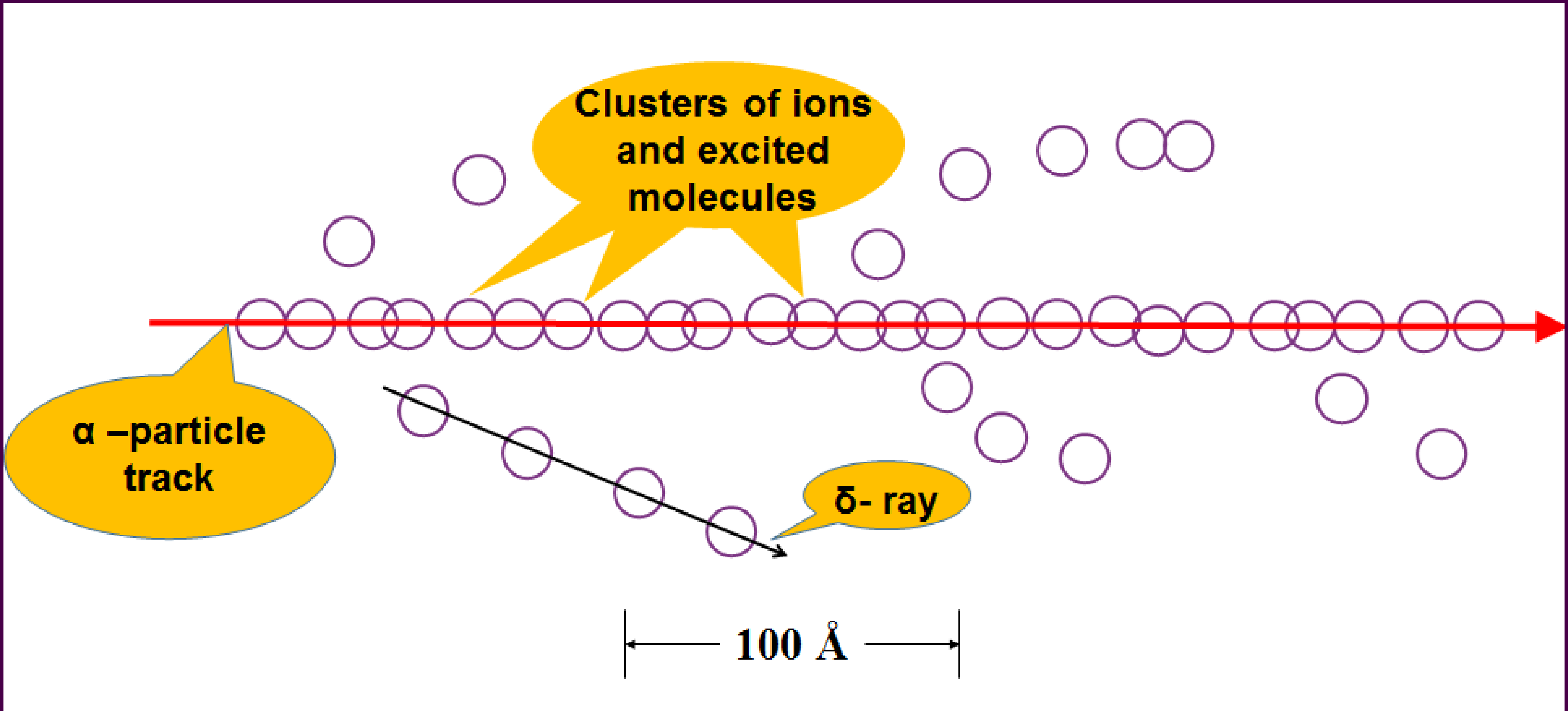
Encyclopedia Britannica

Distribution of Ion-pairs and Excitations in the Track of a Fast Electron in Water Low Linear Energy Transfer (LET)



A. Mozumber and J. L. Magee, *J. Chem. Phys.*, 1966, 45, 3332; M. Burton, Chem. Eng. News, 1969, 47, 86

Excitations in the track of an alpha-particle in water (High LET)



Alpha particles ~ 15 % of cosmic rays

Low vs. High LET Radiation Chemistry of Water

Low LET:

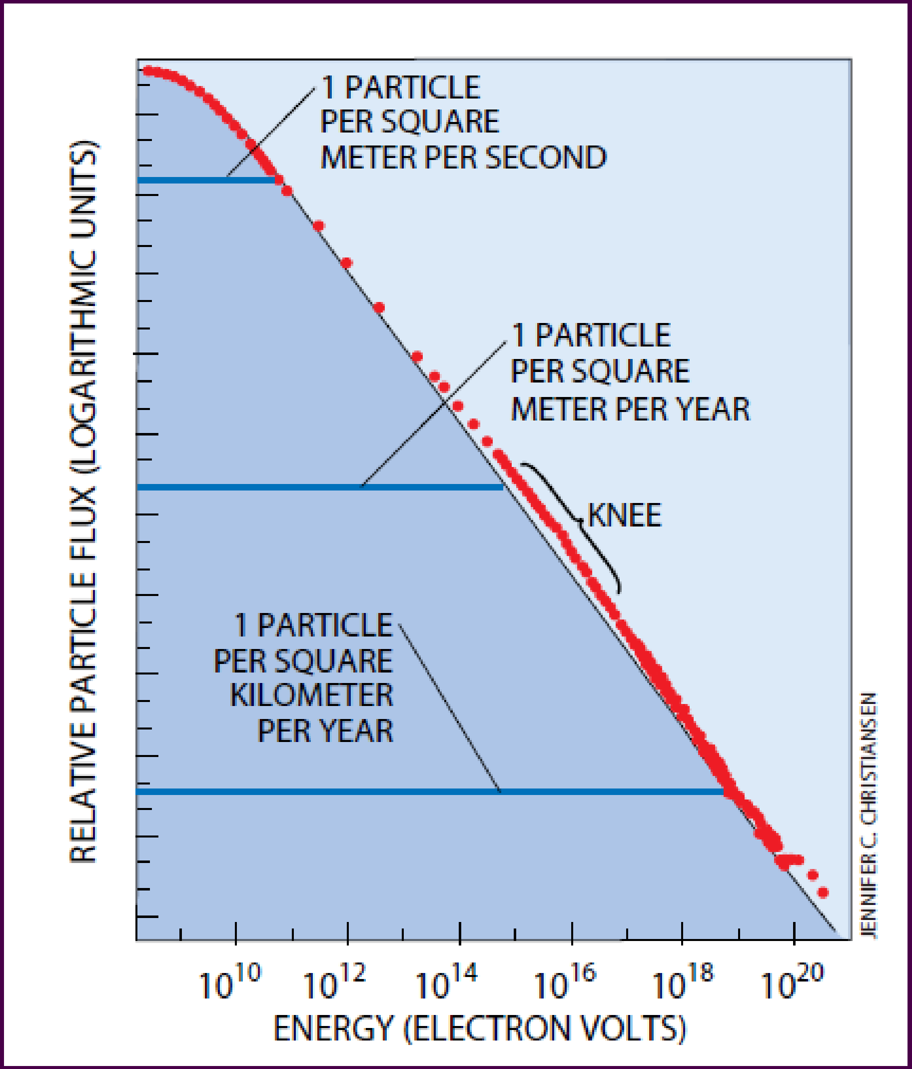
$$H_2O \rightsquigarrow 0.28\, e_{aq}^{-},\ 0.062\, H^{\bullet},\ 0.28\, {}^{\bullet}OH,\ 0.047\, H_2,\ 0.073\, H_2O_2,\ 0.28\, H_3O^{+}$$

High LET:

$$H_2O \rightsquigarrow 0.044\, e_{aq}^{-},\ 0.028\, H^{\bullet},\ 0.056\, {}^{\bullet}OH,\ 0.11\, H_2,\ 0.11\, H_2O_2,\ 0.044\, H_3O^{+}$$

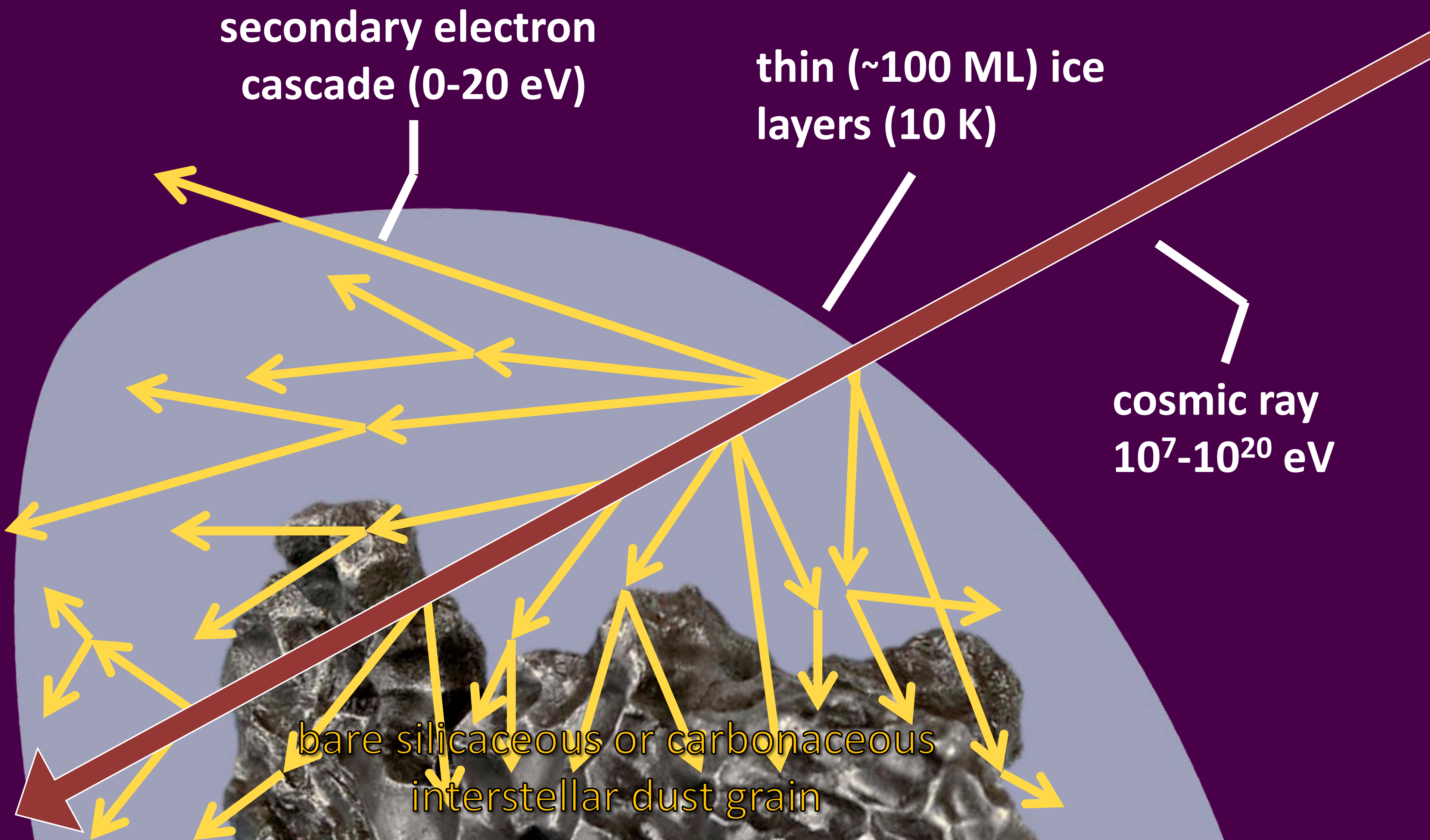
SOURCE: George V. BUXTON

Flux of Cosmic Rays Reaching Earth

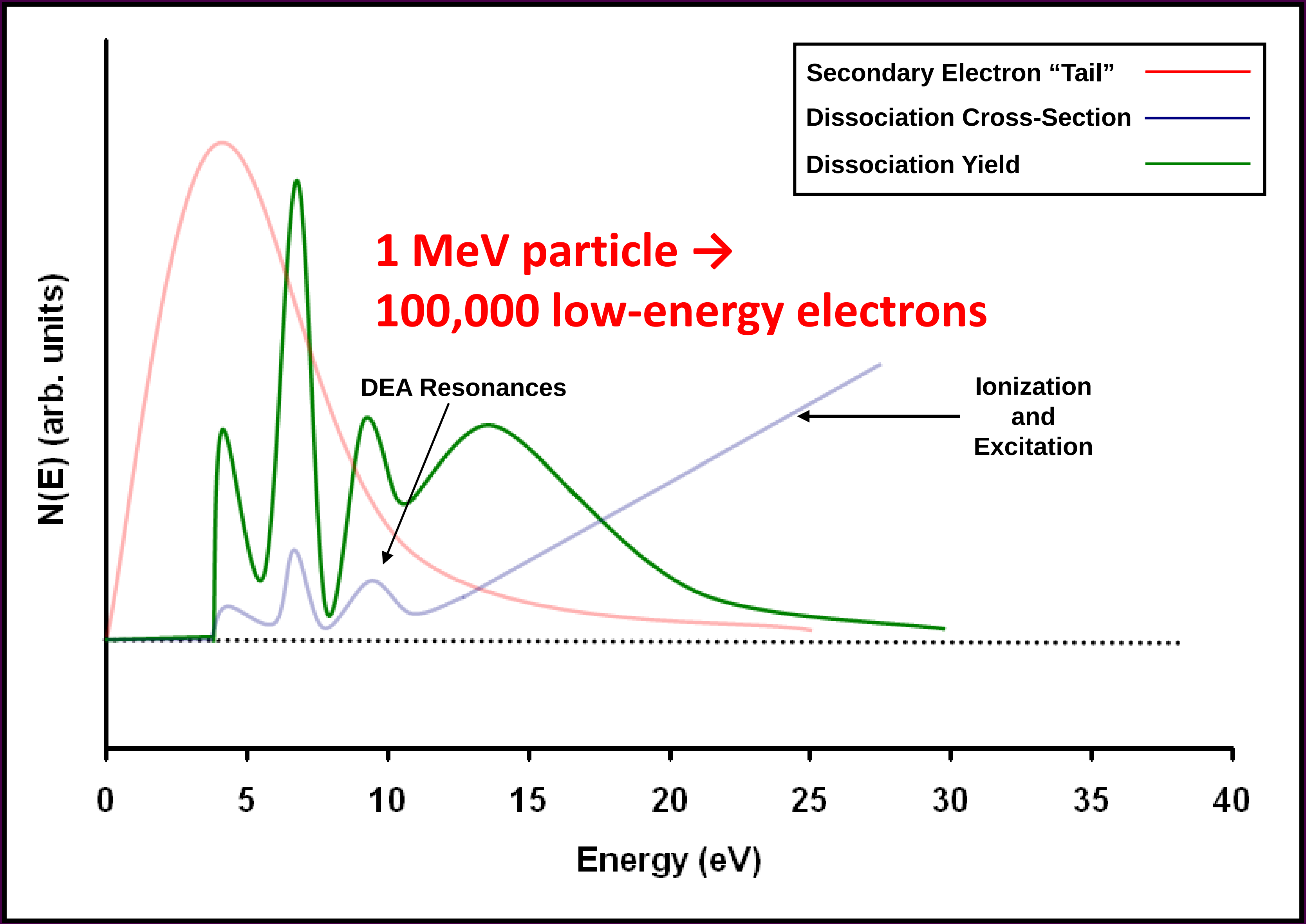


July 12, 2018: First identification of a cosmic ray source: TXS 0506+056

Formation of Secondary Electrons in Cosmic Ices and Dust Grains

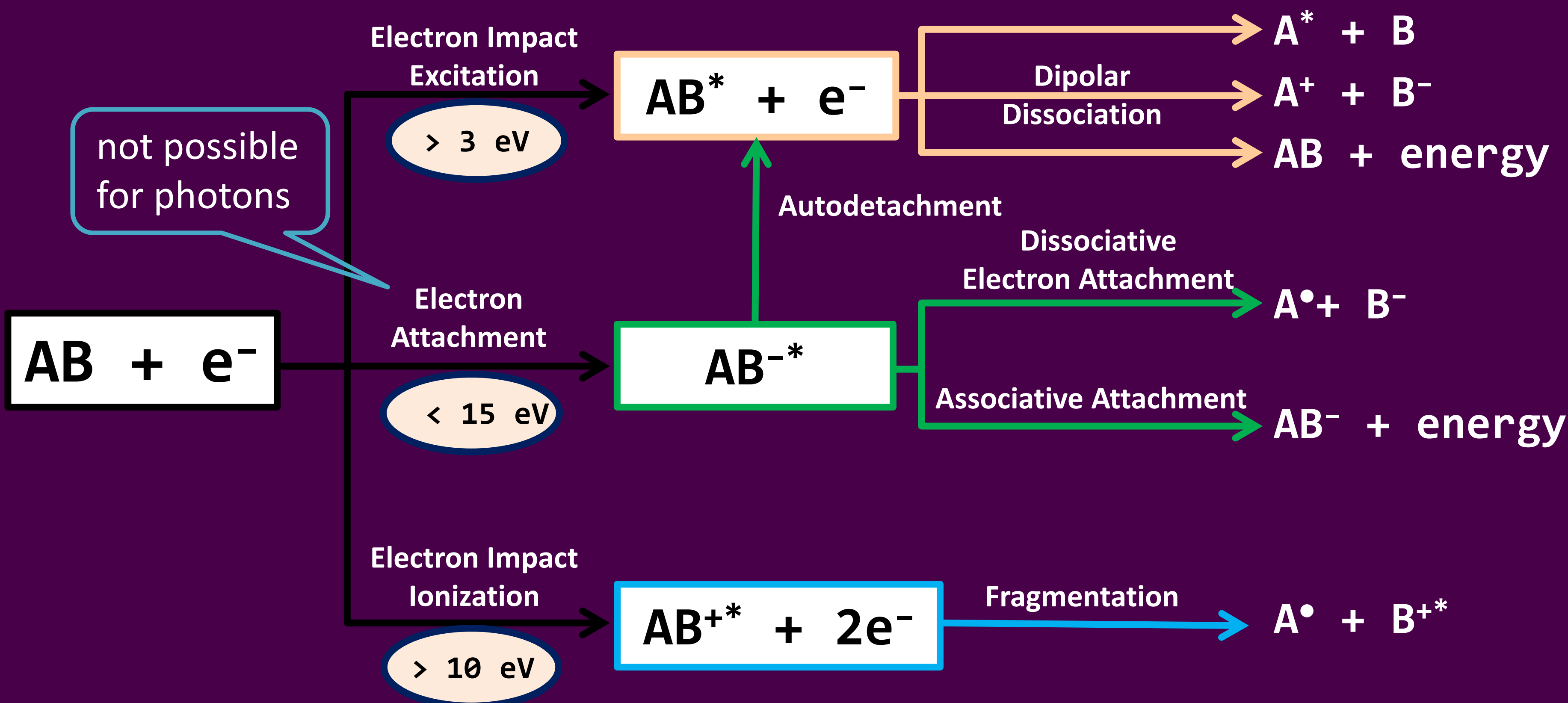


Importance of Low-Energy Electrons

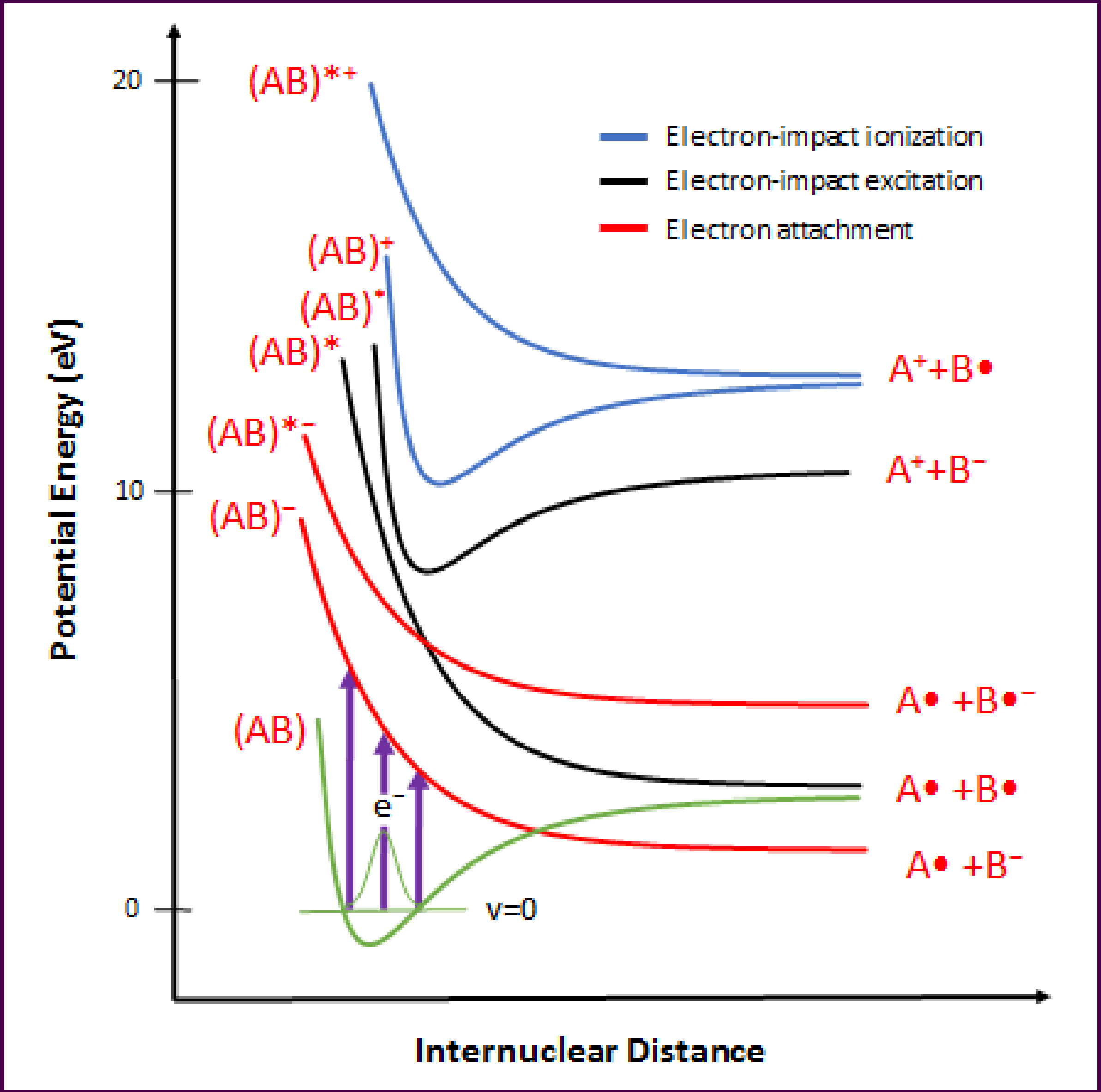


C. Arumainayagam et al., *Surface Science Reports* 65 (**2010**) 1–44.

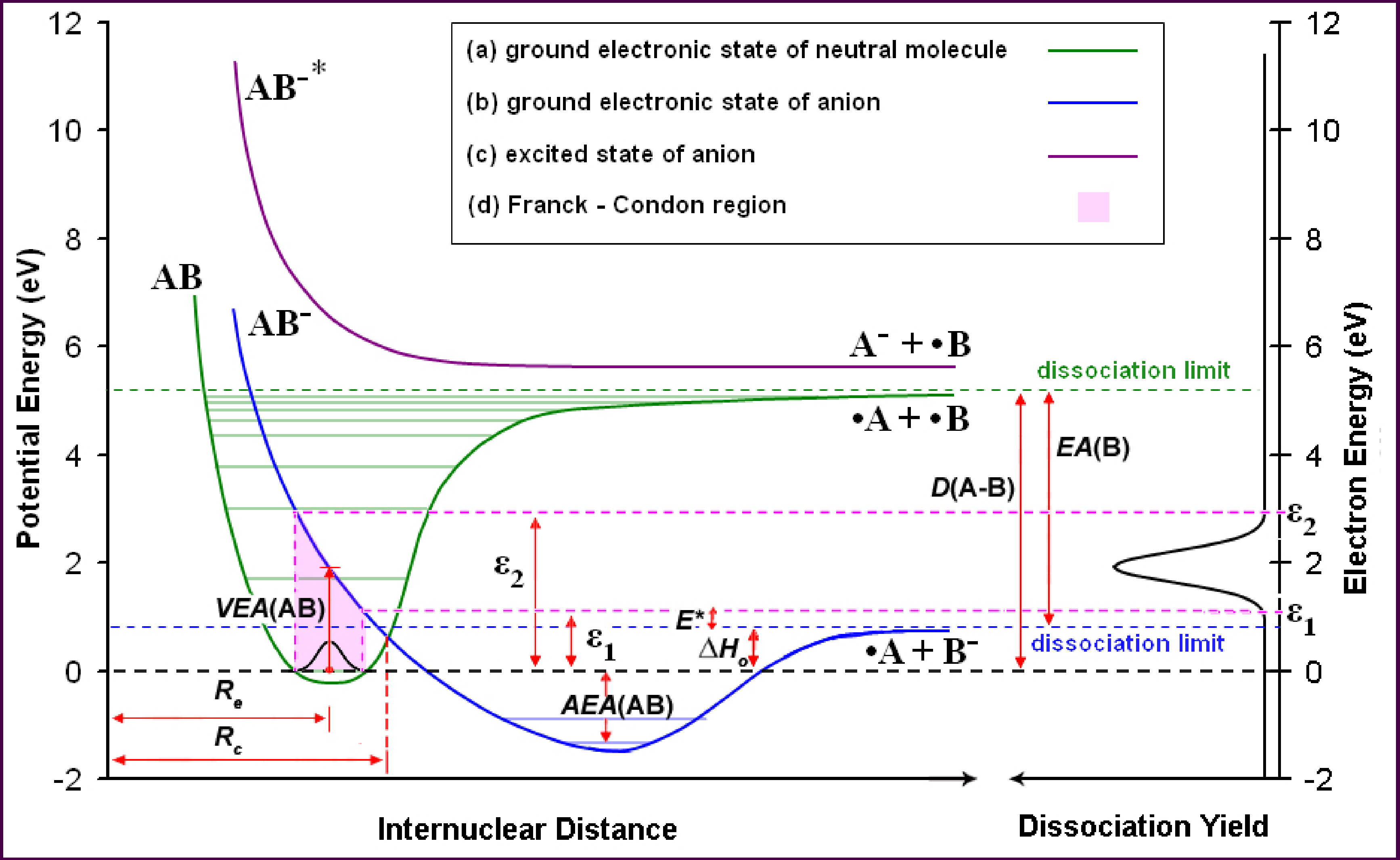
Electron-induced Dissociation Mechanisms



Electron-induced Dissociation Mechanisms



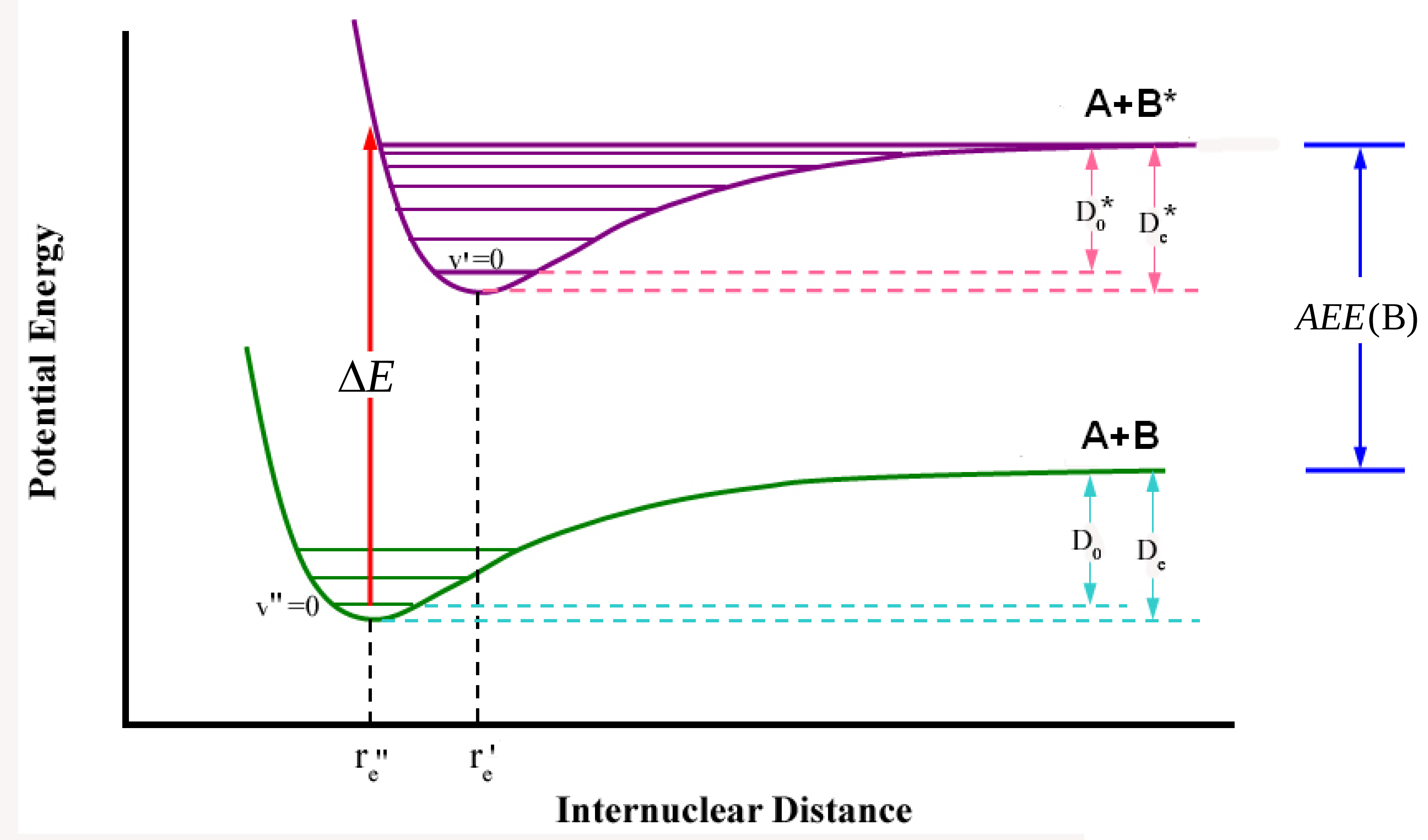
Breaking a 3.5 eV Bond with a 0 eV Electron



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

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

Photon-Induced Dissociation



Threshold Energy: $\Delta E = D_o(A - B) + AEE(B)$

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)

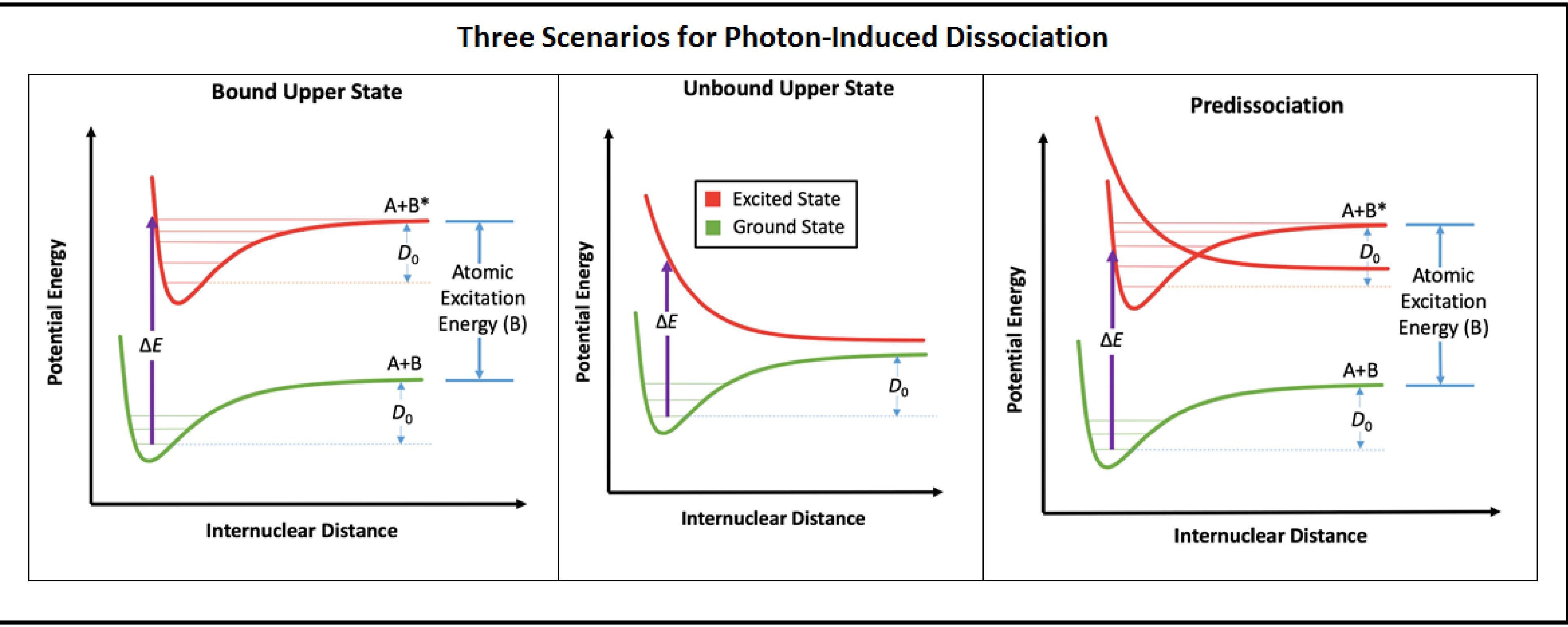
} no ionization; only excitation

- – vacuum-UV (6.2 –12.4 eV)

} ionization AND excitation

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

Photon-Induced Dissociation



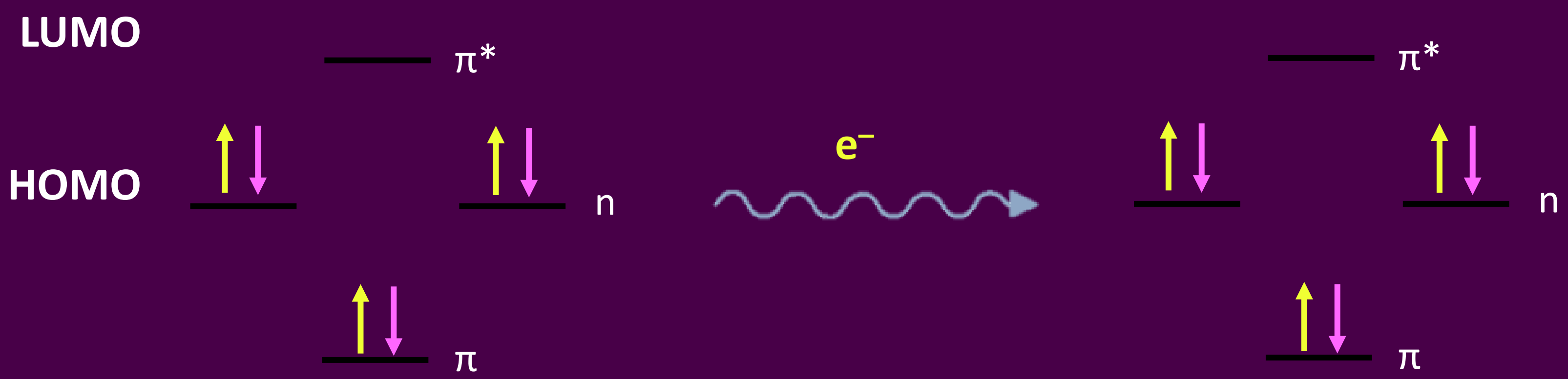
Reactions of a Photon-Excited Molecule

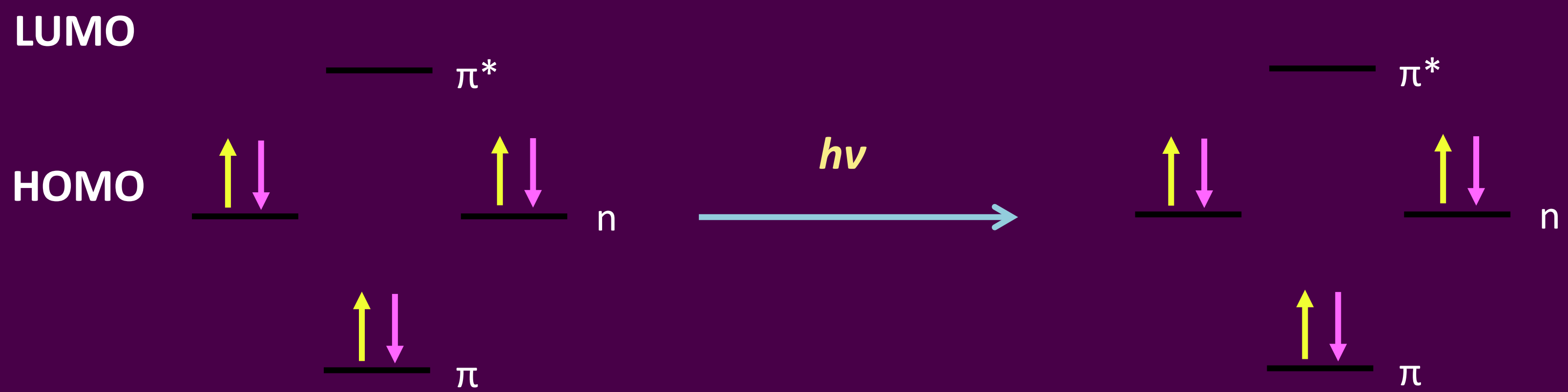
reaction pathway	name
$A{-}B{-}C^* \rightarrow A{-}B^\bullet + C^\bullet$	bond cleavage (photolysis) into free radicals
$A{-}B{-}C^* \rightarrow E + F$	photoisomerization followed by decomposition into stable molecules
$A{-}B{-}C^* + RH \rightarrow A{-}B{-}C{-}H + R^\bullet$	H-abstraction from a neighboring molecule
$A{-}B{-}C^* + D \rightarrow A{-}B{-}C + D^*$	photosensitization (energy transfer of all kinds)
$A{-}B{-}C^* + D \rightarrow A{-}B{-}C^+ + D^-$	photosensitization (electron transfer)

Photochemistry involves no production of secondary electrons.

Chemical Reviews, 115 (2015) 4218-4258.

Another Difference between Photons and Electrons



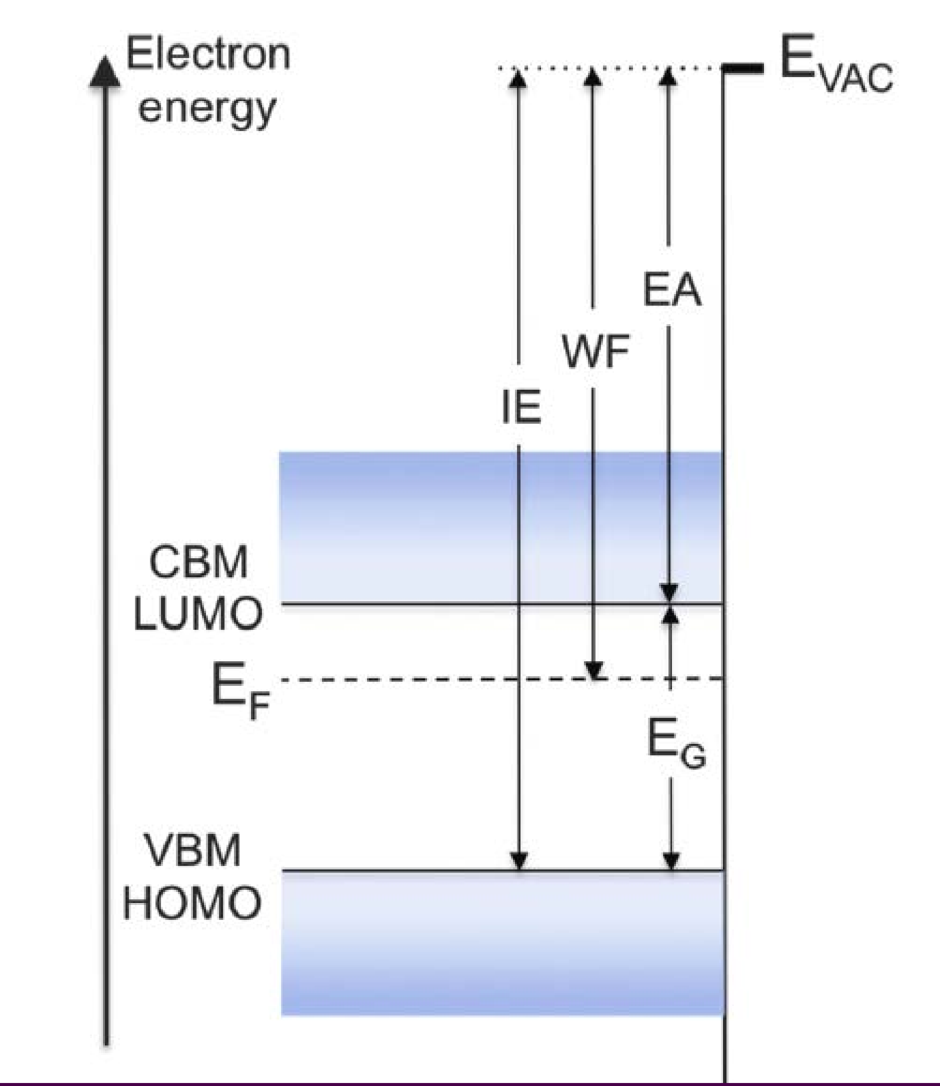


Photon-induced singlet to triplet transitions are nominally forbidden.

Condensed Phase Ionization Energy

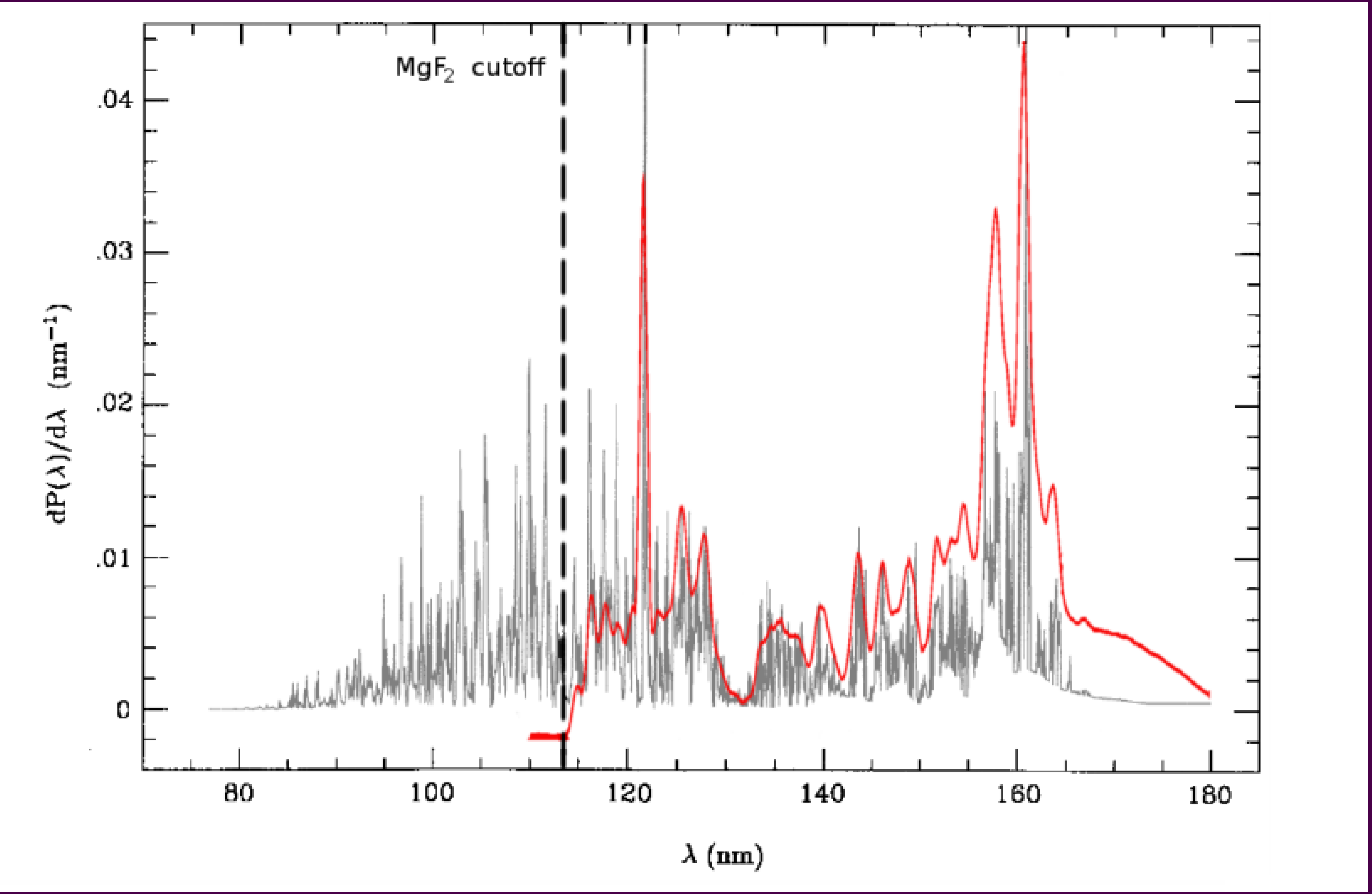
$$IE_{\substack{condensed\\ phase}} < IE_{\substack{gas\\ phase}}$$

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



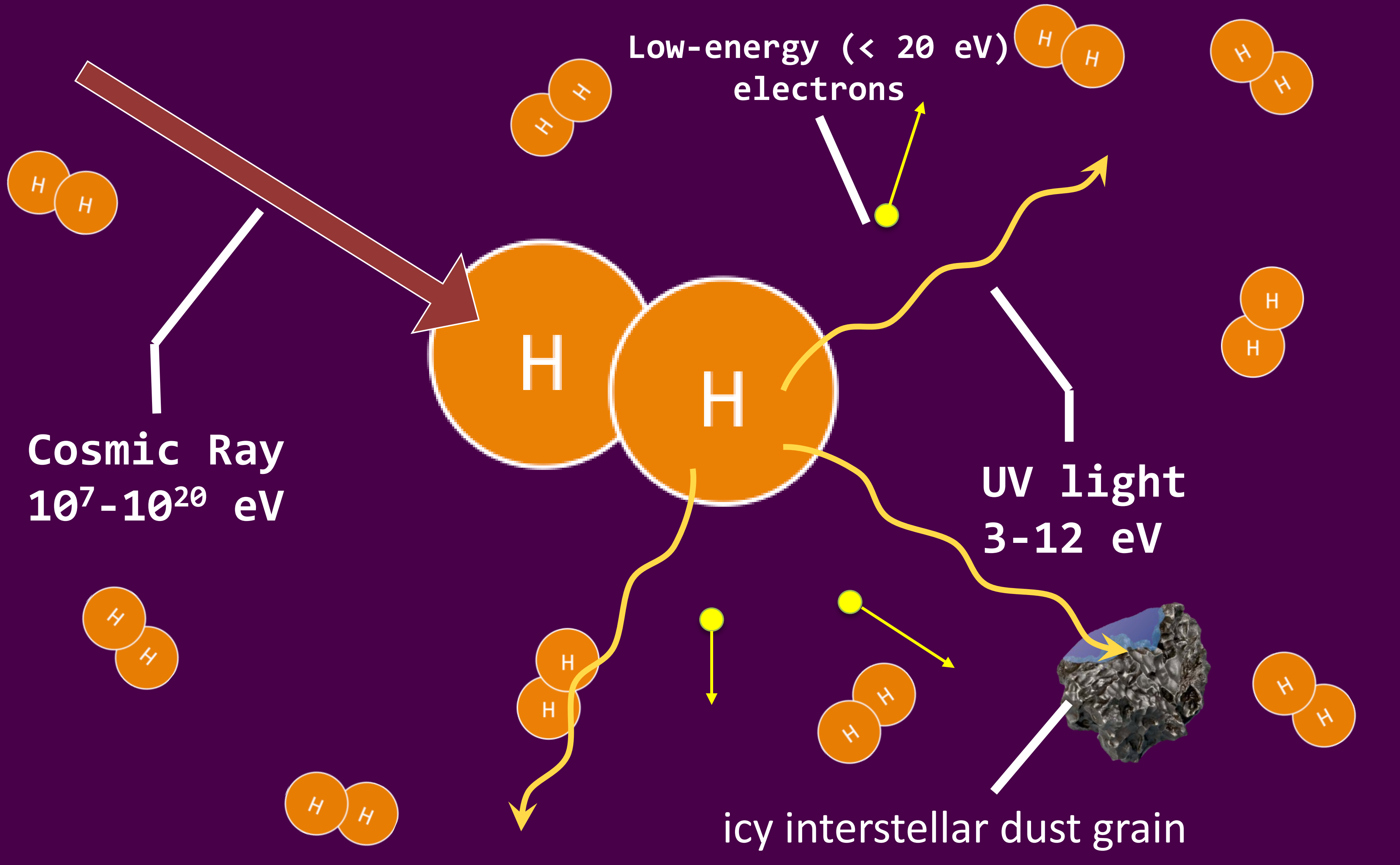
Mater. Horiz., 2016, 3, 7--10

VUV-emission spectrum of Microwave-discharge hydrogen-flow lamps (MDHL)

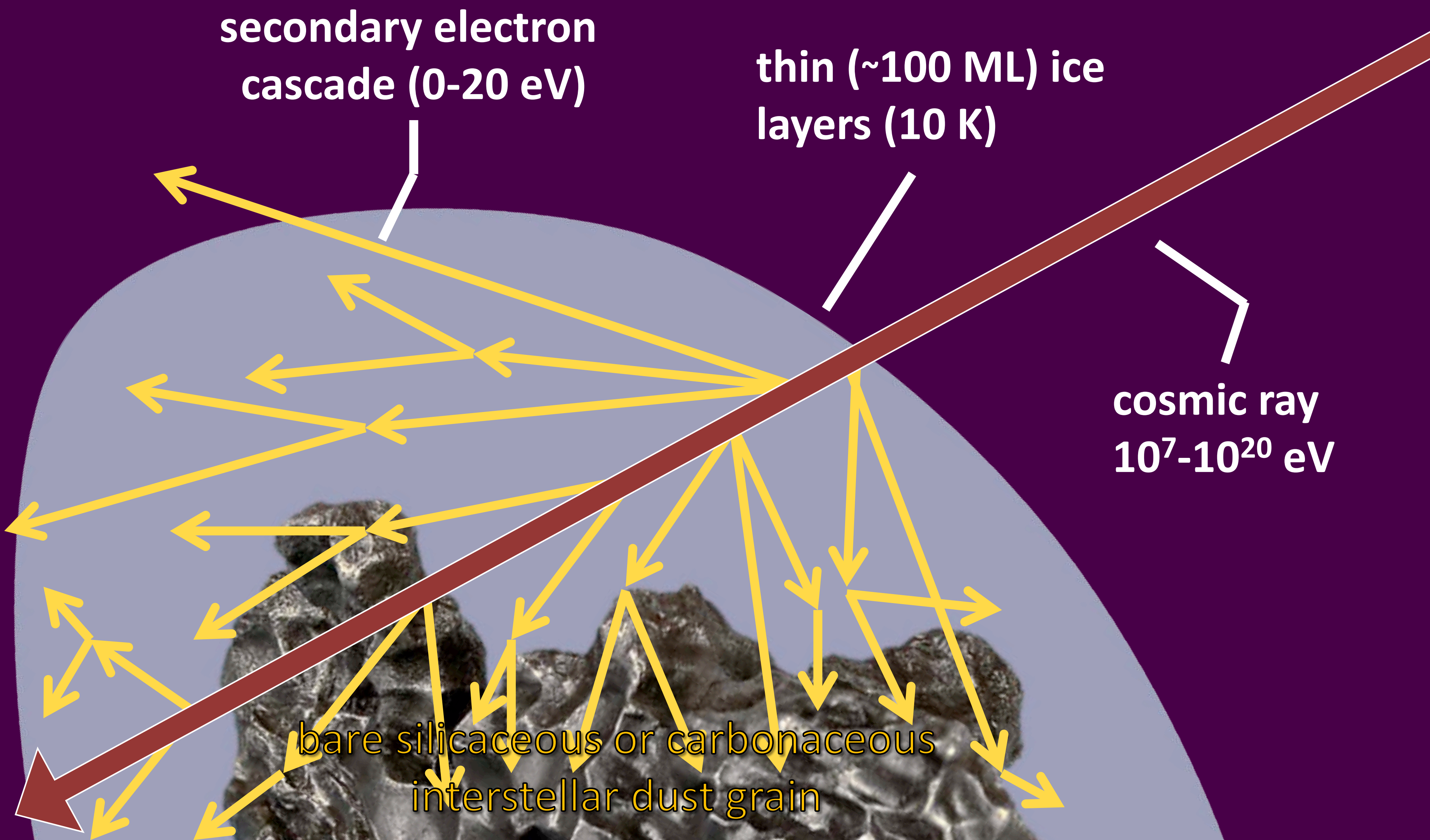


CREDIT: Gustavo Adolfo Cruz Diaz

UV light formation within dark, dense molecular clouds



Formation of Secondary Electrons in Cosmic Ices and Dust Grains



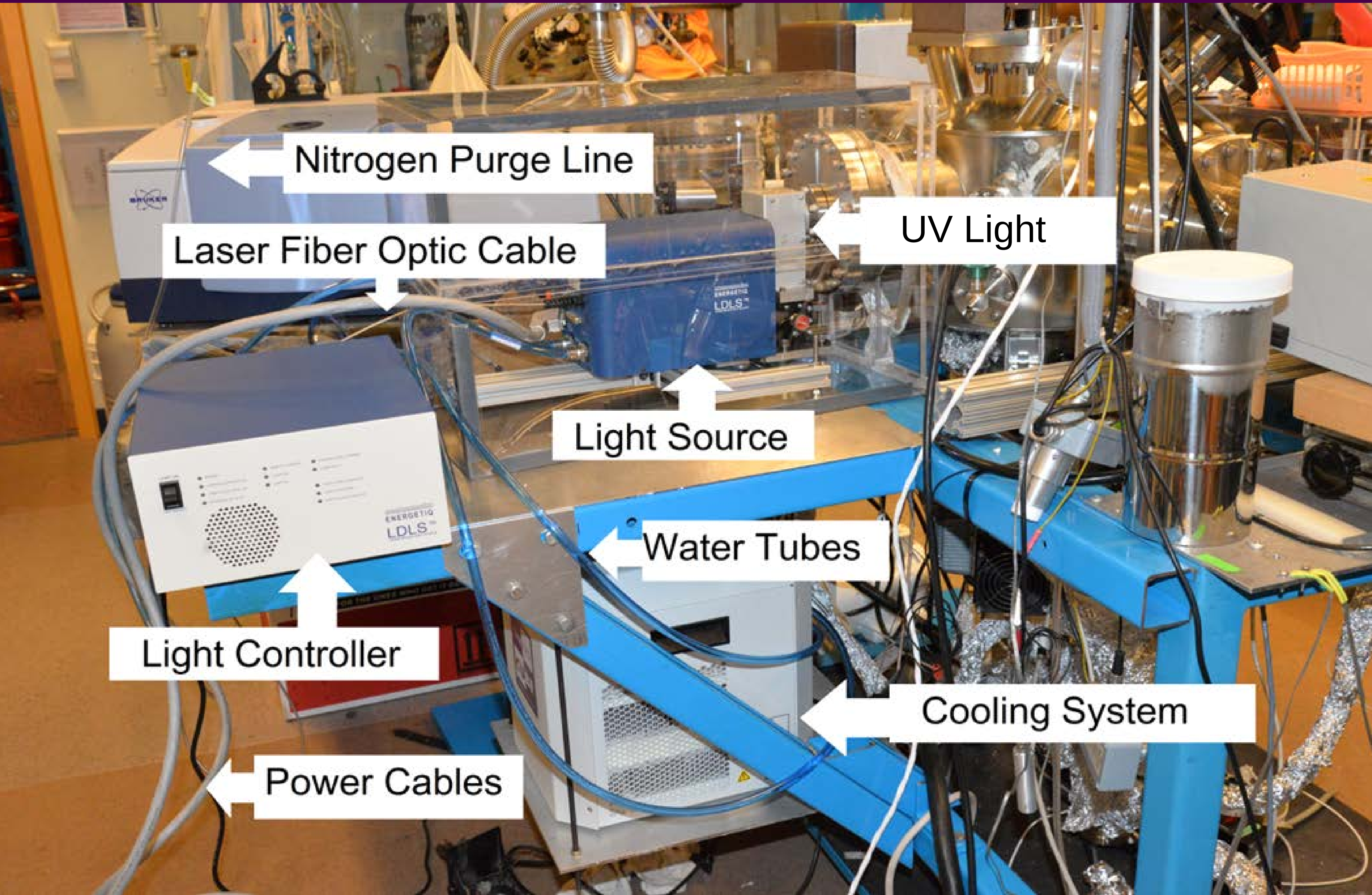
Previous Comparisons of Photochemistry and Radiation Chemistry Relevant to Astrochemistry

	Ice Material	Particle Radiation	Photon Energy	Technique	Conclusions
Hudson & Moore (2002)	N_2	0.8 MeV protons	10.6 eV	IR	N3-radical produced by ions but not photons
Gerakines et al. (2001)	$H_2O:CO_2:CH_3OH$, $H_2O:CO_2:CH_4$	0.8 MeV protons	10.2 eV	IR	Similar chemical products are observed in both cases
Gerakines et al. (2004)	HCN, $HCN:H_2O:NH_3$	0.8 MeV protons	11.3 eV	Mid-IR	Photon-induced dissociation led to higher destruction rates of HCN by a factor of 4
Caro et al. (2014)	$CH_3OH:NH_3$	620 MeV Zn^{26+} 19.6 MeV Ne^{6+}	10.6 eV	IR	Products formed depend only weakly on the type of irradiation

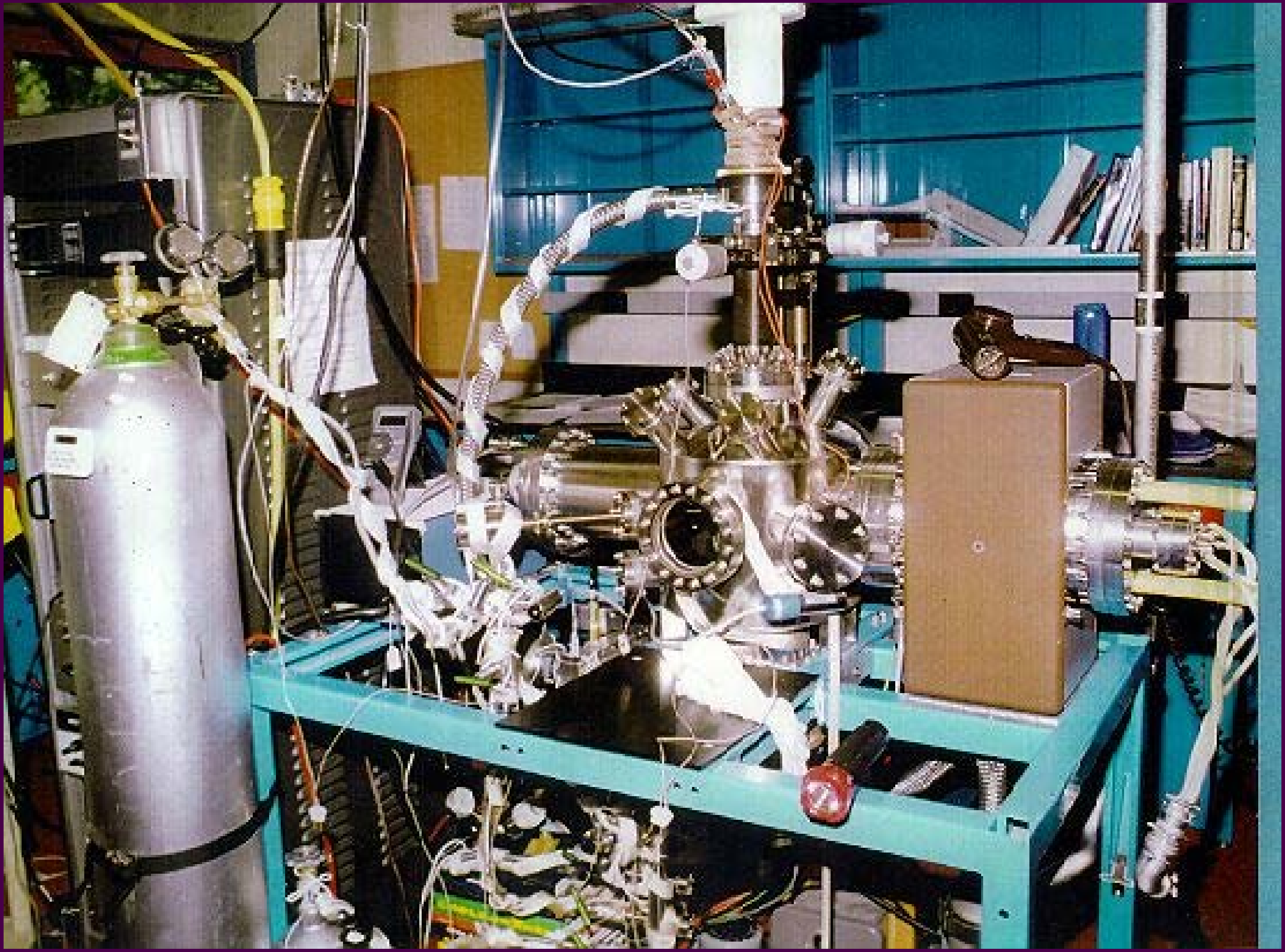
Our Claim

We have performed the first direct comparison between photochemistry and radiation chemistry relevant to the energetic processing of interstellar ice analogs.

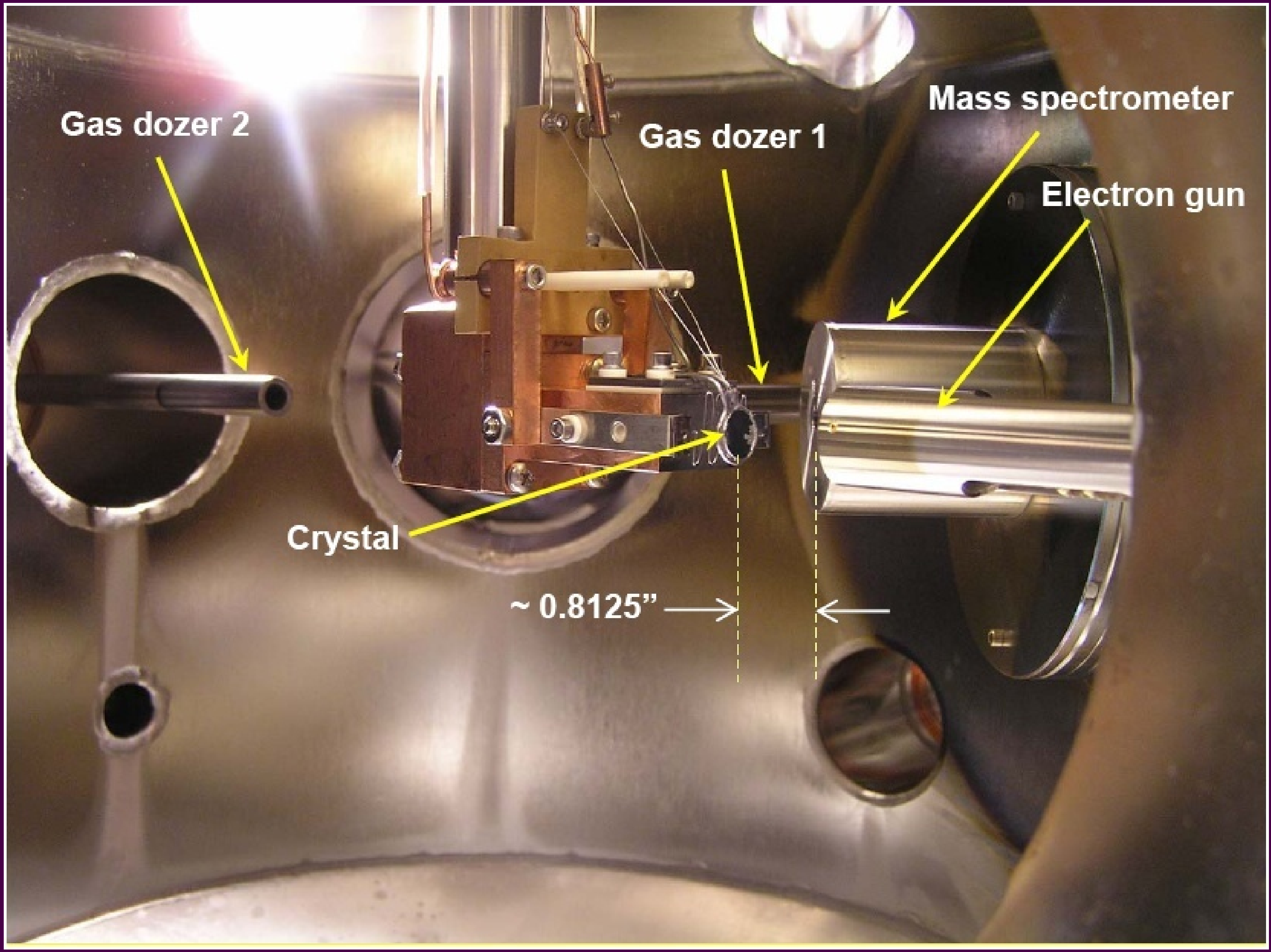
How do you create a little bit of heaven on earth?



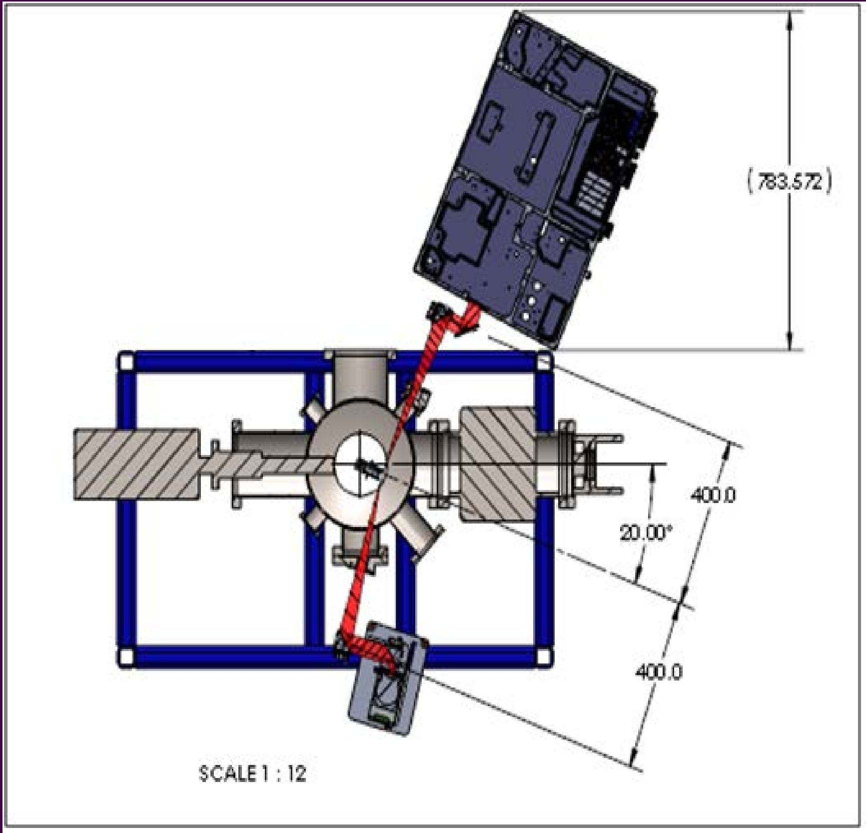
UHV Chamber at Wellesley College

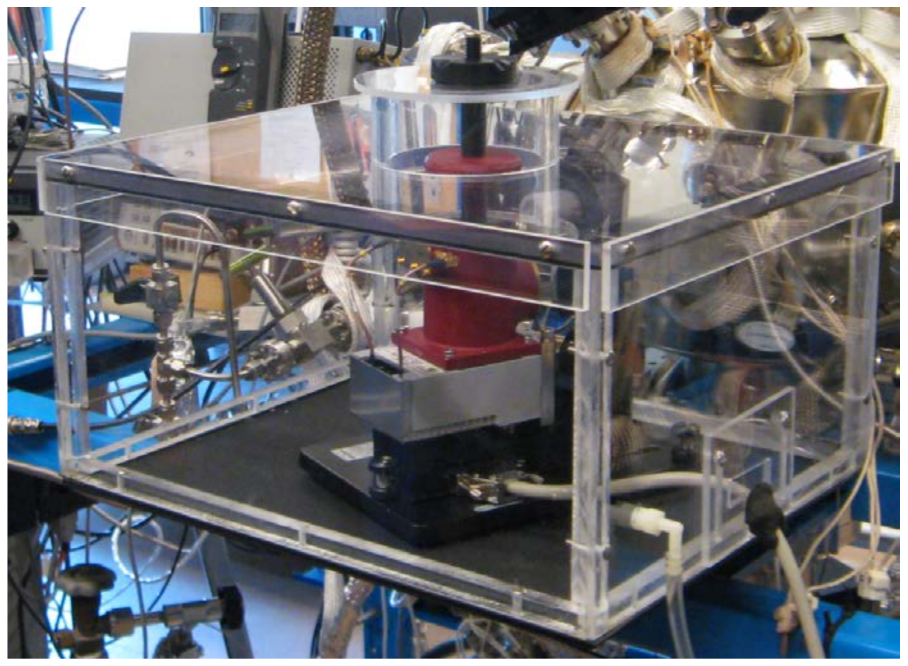


Inside of the UHV chamber

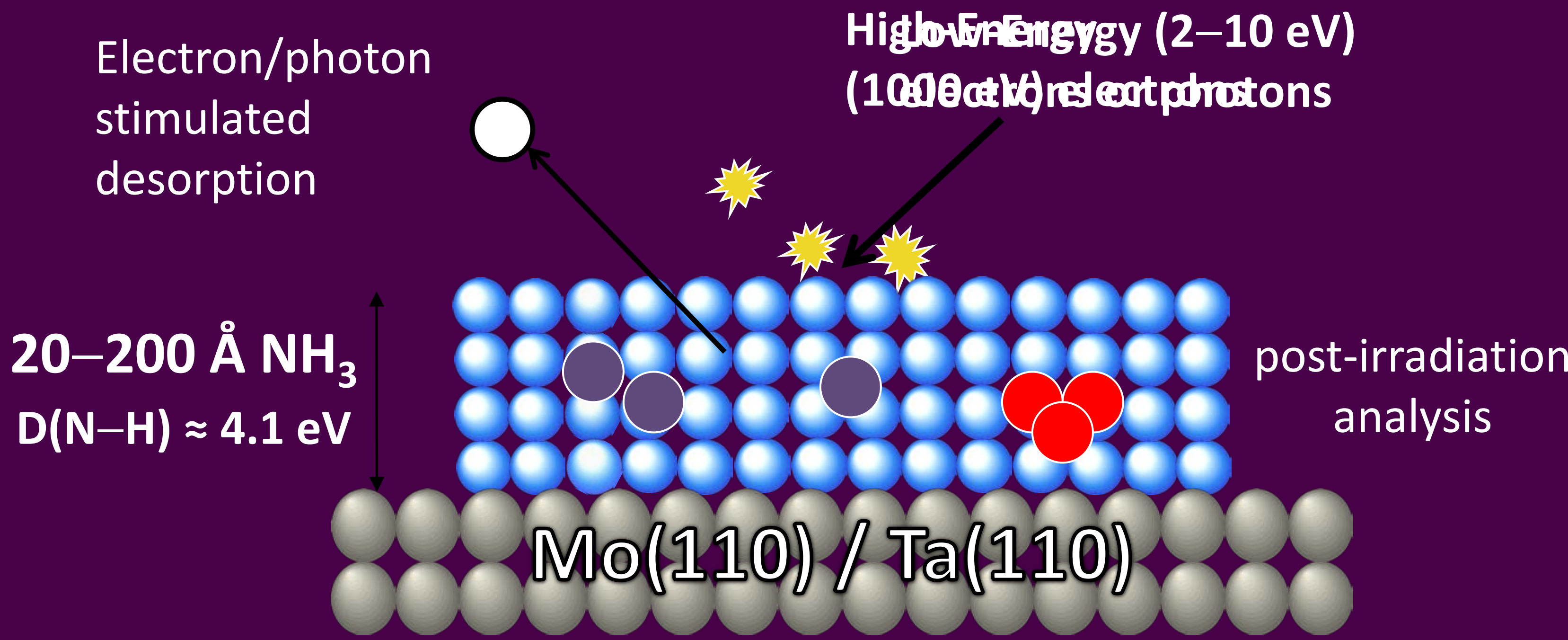


Infrared Reflectance Absorbance Spectroscopy (IRAS): Experimental Setup





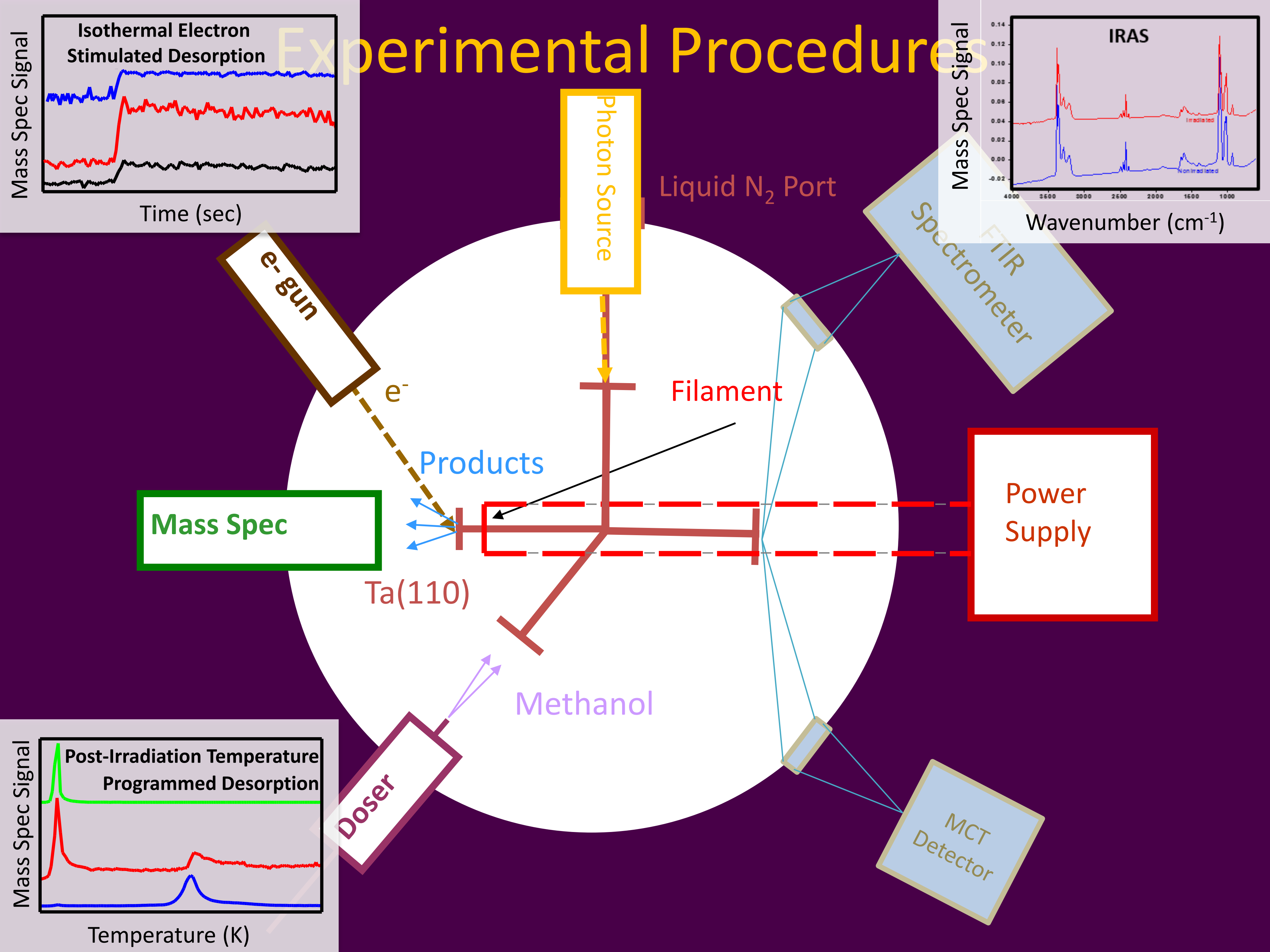
Experimental Procedures



$P = 1\times10^{-9}$ torr

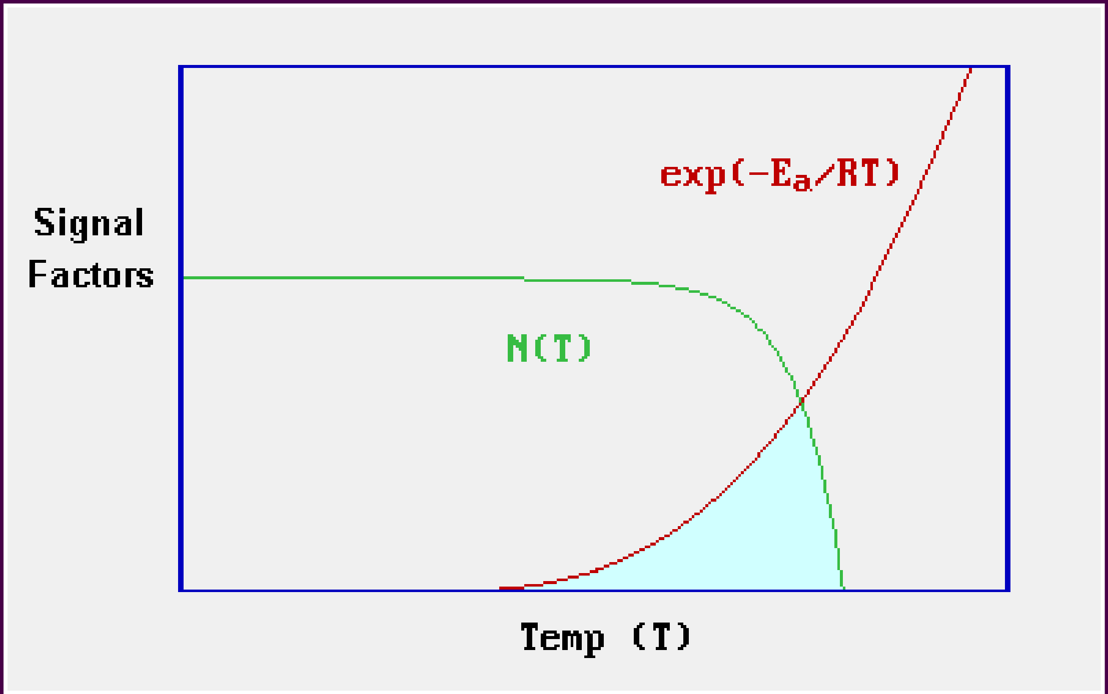
$T = 90$ K

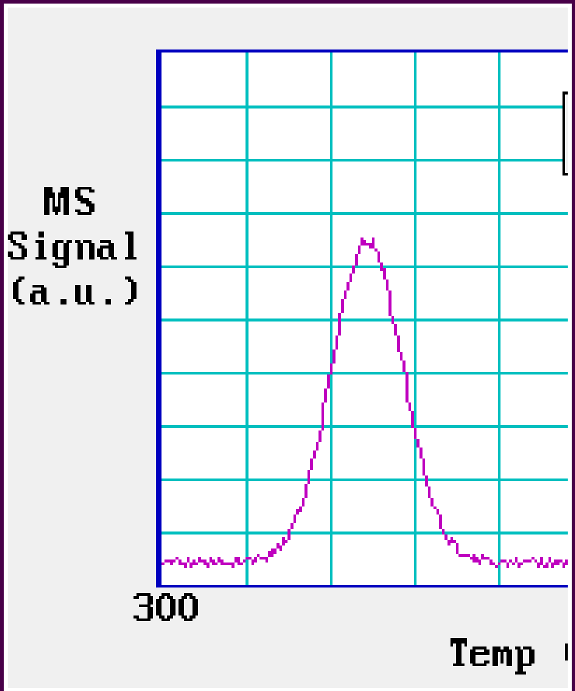
Experimental Procedures



Temperature-Programmed Desorption (TPD)

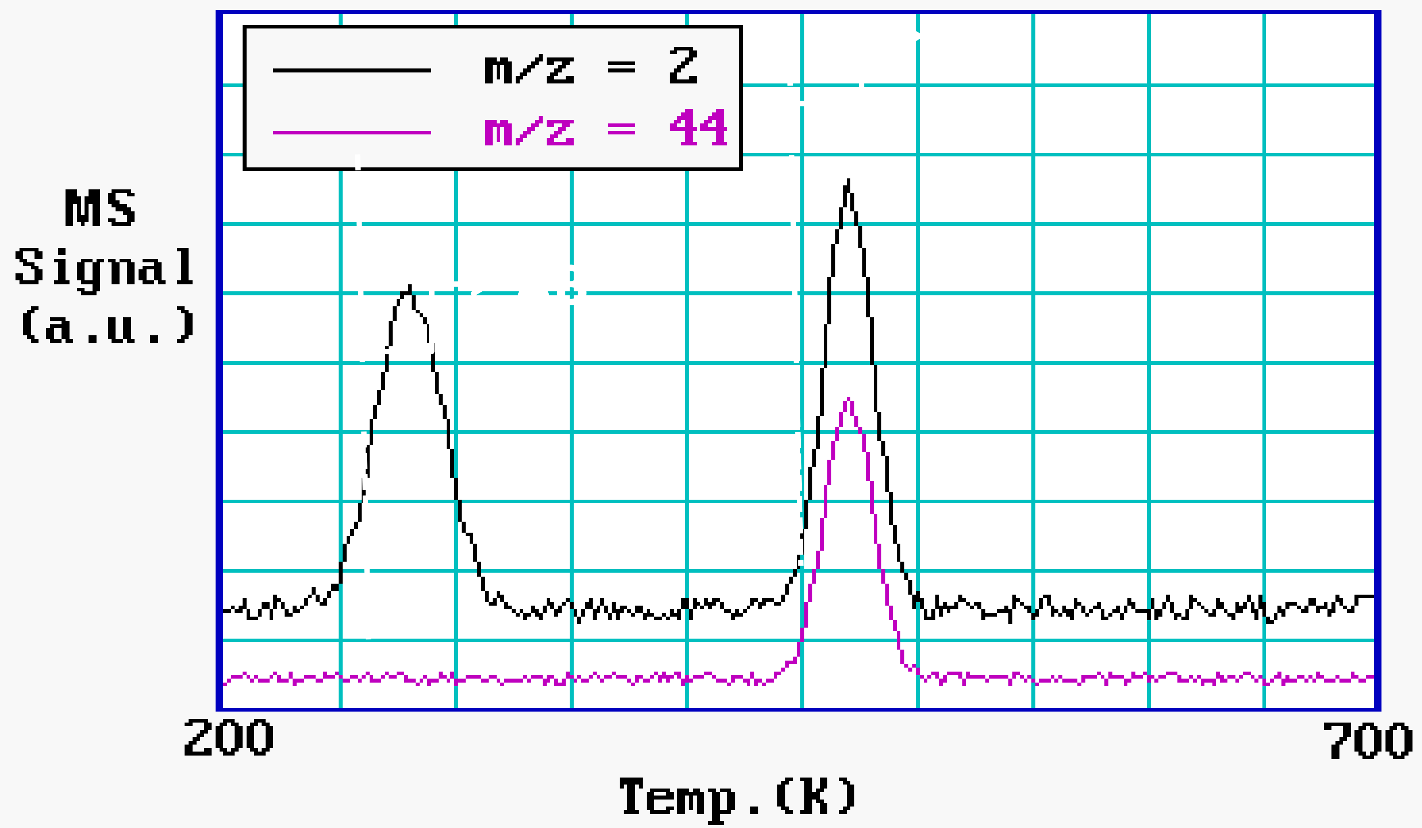
$$\text{MS signal} = R = kN = A\, e^{\frac{-E_a}{RT}} N$$





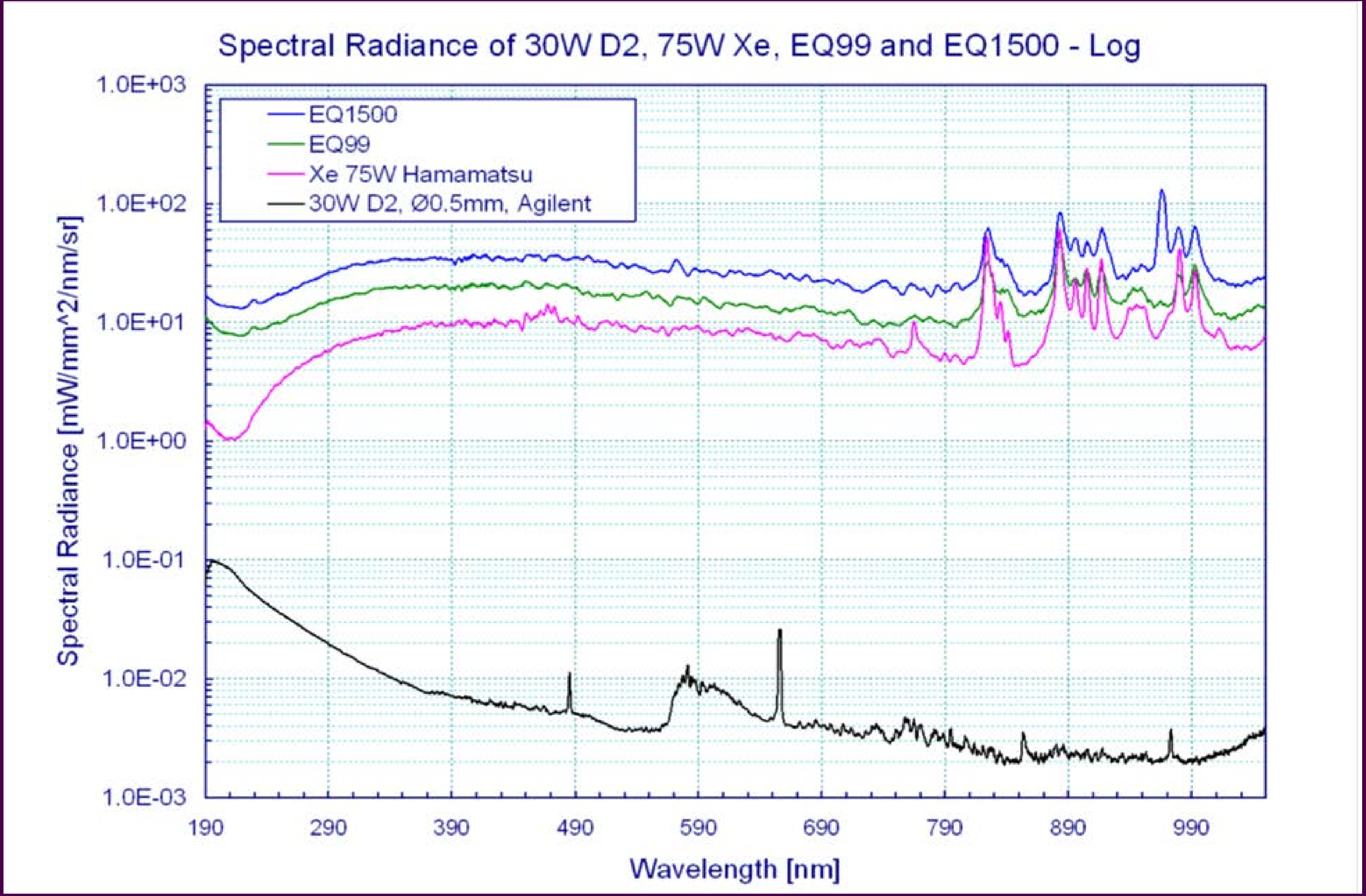
Figures: http://www.chem.qmul.ac.uk/surfaces/scc/scat5_6.htm

Tempature Programmed Desorption
How to Identify Desorption Peaks

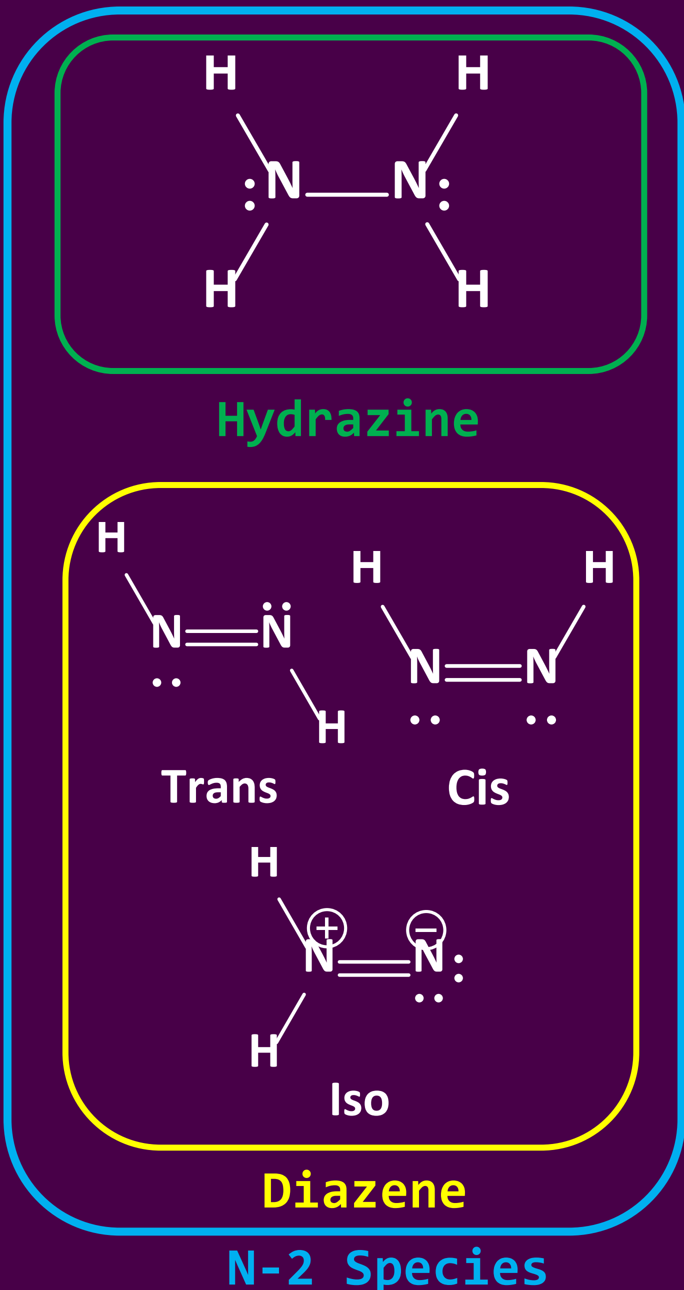


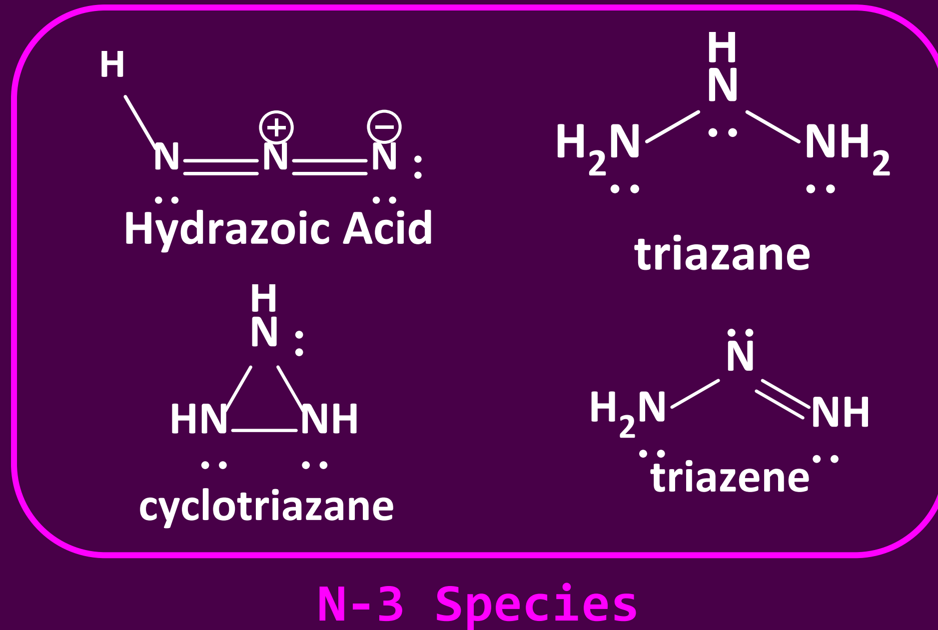
Figures: http://www.chem.qmul.ac.uk/surfaces/scc/scat5_6.htm

Extremely Bright < 8 eV Photon Source: Laser-Driven Plasma: EQ 1500

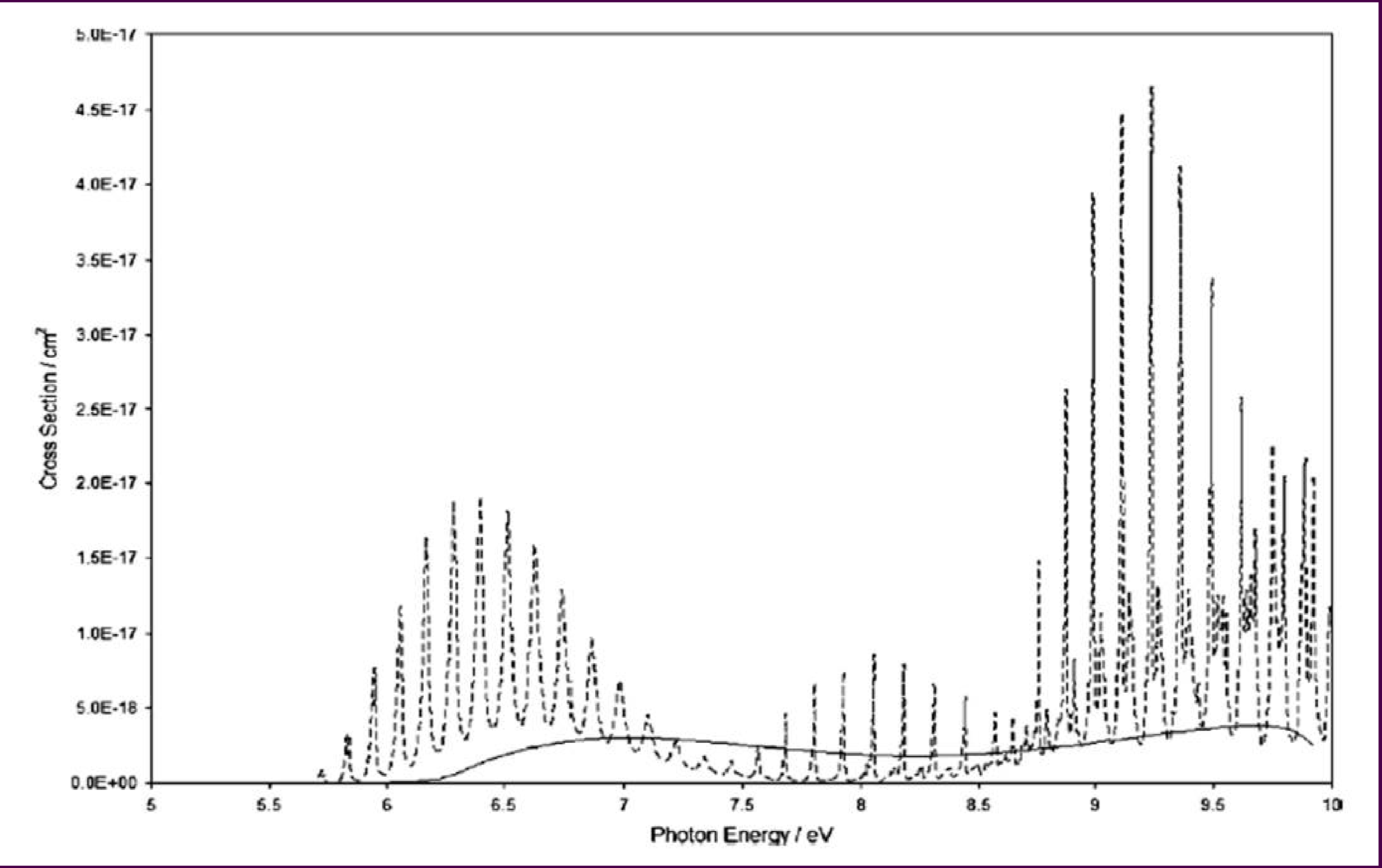


Possible Radiolysis/Photolysis Products of Ammonia



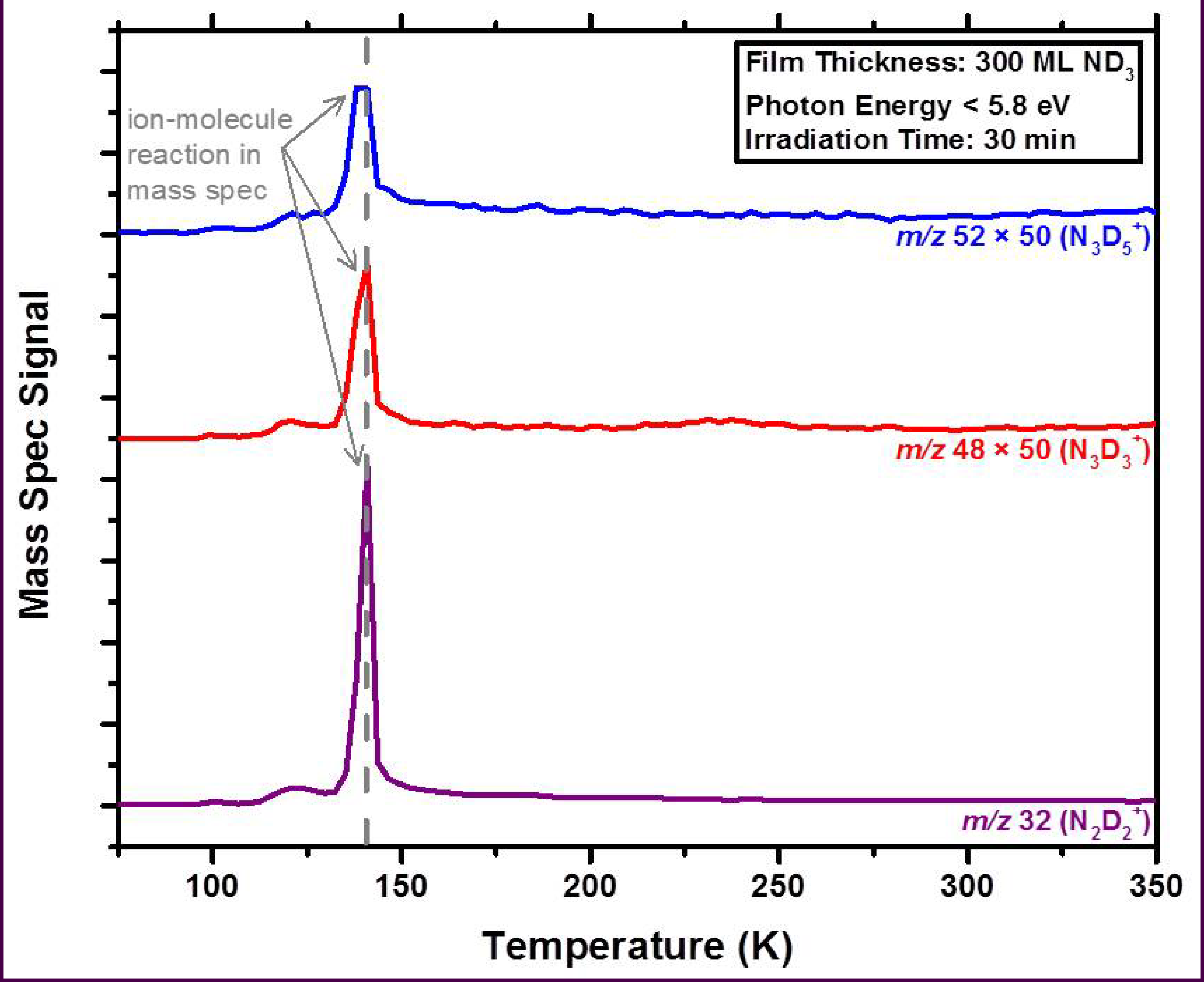


UV Absorption Spectrum of Condensed Ammonia



Mason, N.J. et. al, *Faraday Discussions*, 2006.

Lower-Energy (< 6 eV) Photons: No Photolysis Products



Mean Free Path Calculation for a 7 eV Photon

$$\lambda = \frac{1}{n\sigma}$$

$$= \frac{1}{(\text{number of molecules per cm}^3)(\text{photon absorption cross section in cm}^2)}$$

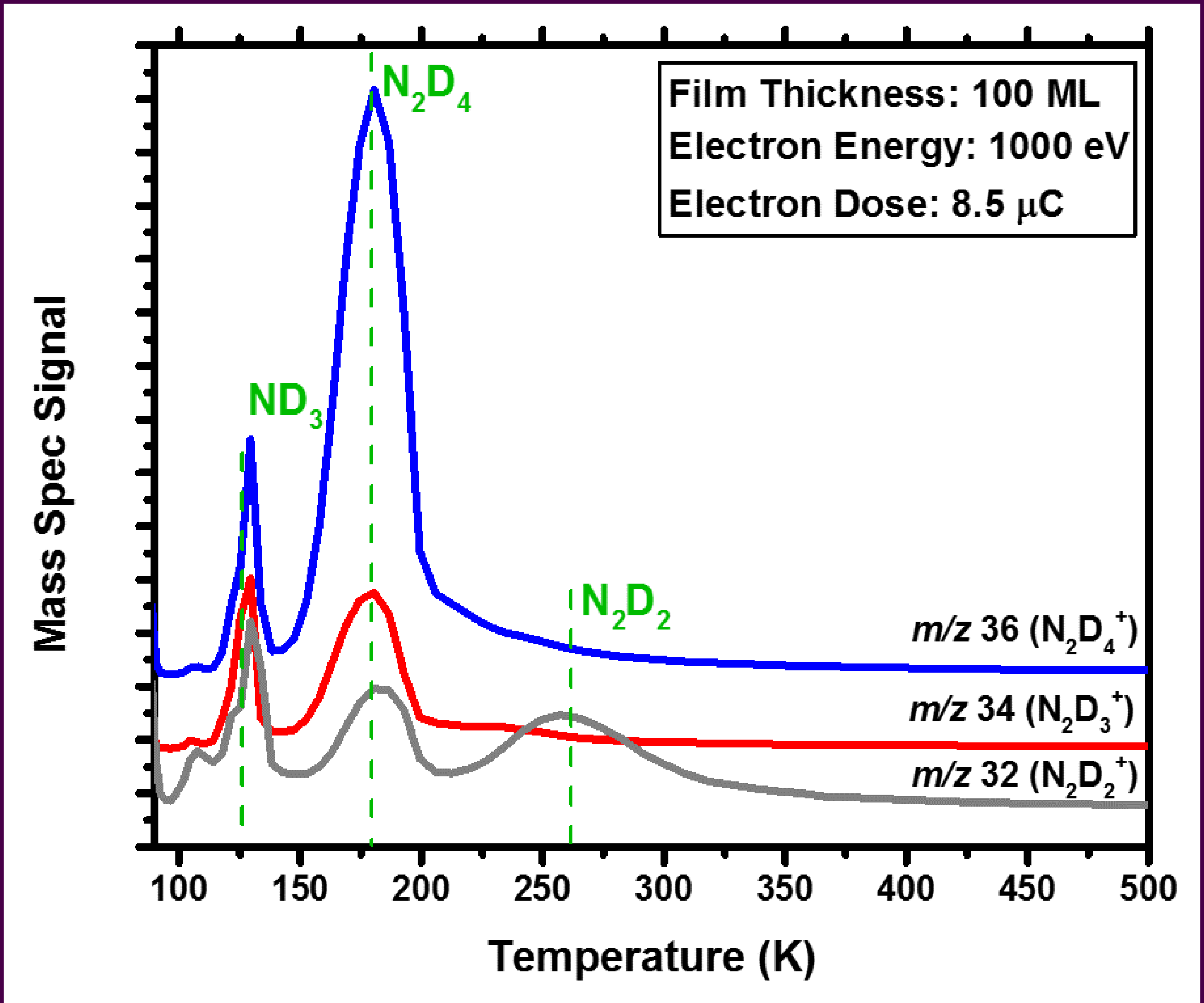
$$= \frac{1}{\left(\frac{\text{density in g/cm}^3}{\text{molar mass in g/mole}}\right)\left(\begin{matrix}\text{number of molecules}\\ \text{per mole}\end{matrix}\right)\left(\begin{matrix}\text{photon absorption}\\ \text{cross section in cm}^2\end{matrix}\right)}$$

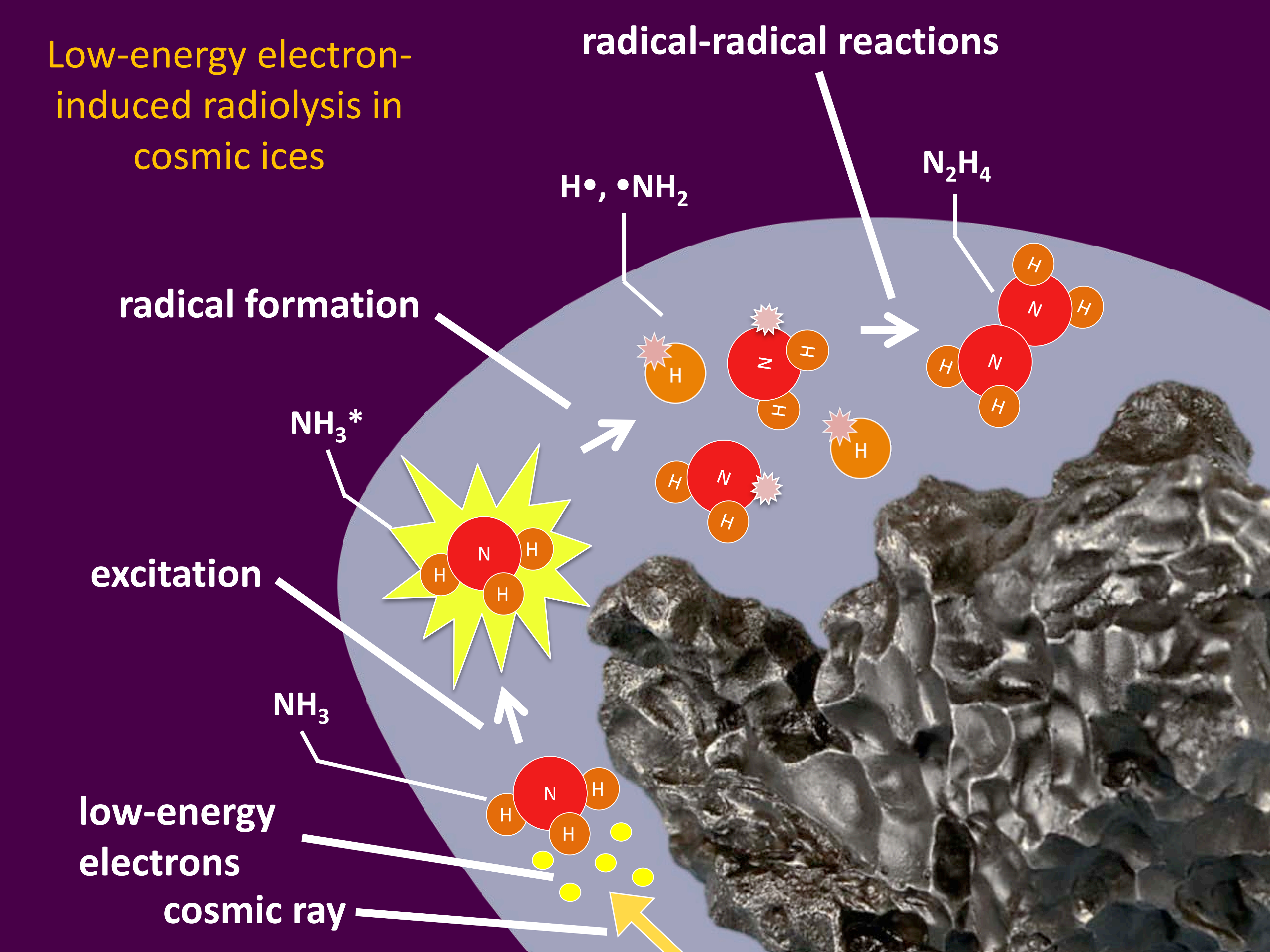
$$= \frac{1}{\left(\frac{0.68\ \text{g/cm}^3}{17\ \text{g/mole}}\right)(6.02\times 10^{23}/\text{mole})(2\times 10^{-18}\,\text{cm}^2)}$$

$$= 0.2\ \text{microns}$$

Most, if not all, of the ice mantle surrounding dust grains will be susceptible to photochemistry

Detection of Hydrazine and Diazene at High Incident Electron Energies

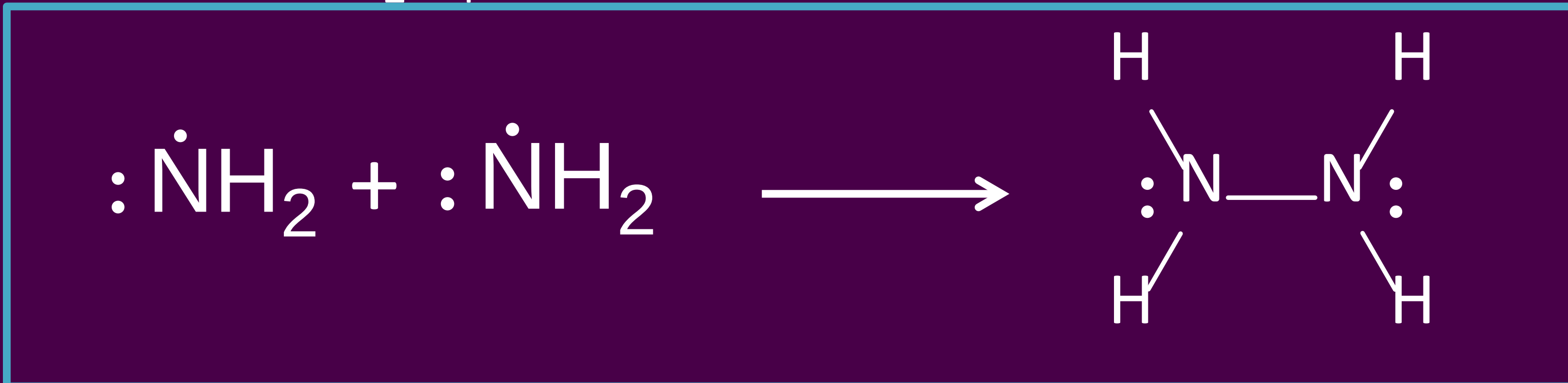




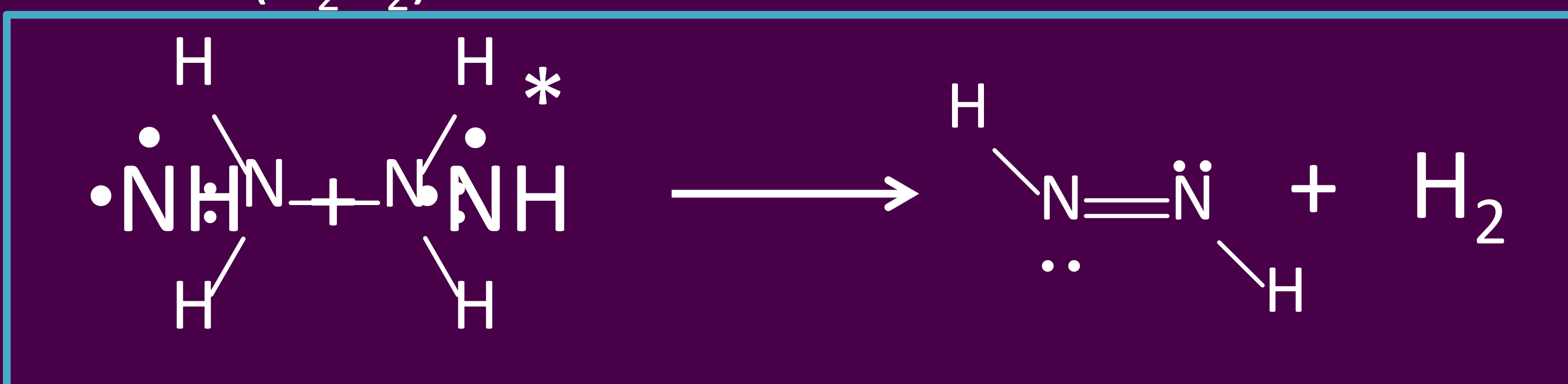
Low-energy electron-induced radiolysis in cosmic ices
radical-radical reactions
N2H4
H•, •NH2
radical formation
NH3*
excitation
NH3
low-energy electrons
cosmic ray

Proposed Mechanisms of Hydrazine and Diazene from Ammonia via Radiation Chemistry

Hydrazine (N_2H_4)

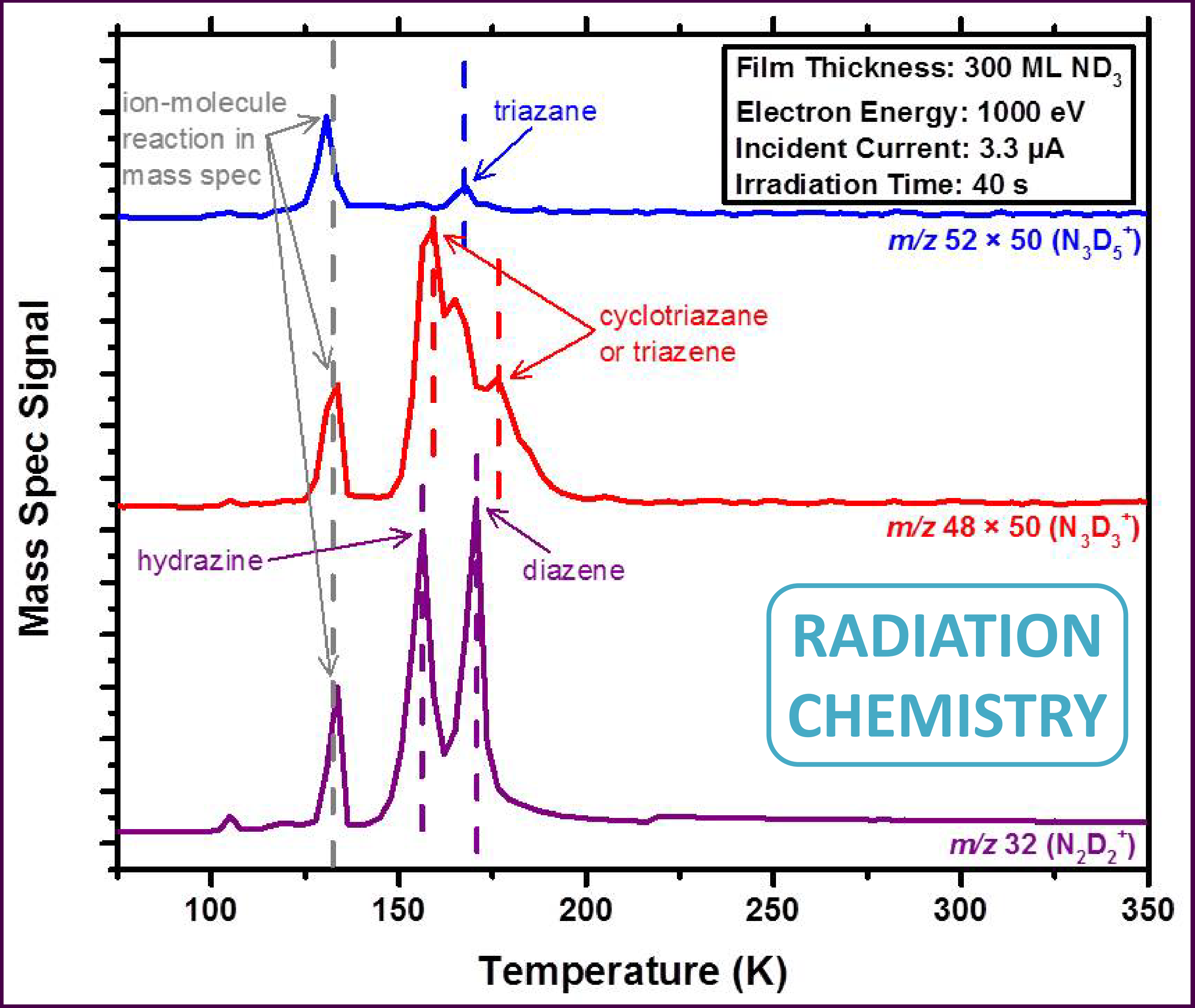


Diazene (N_2H_2)

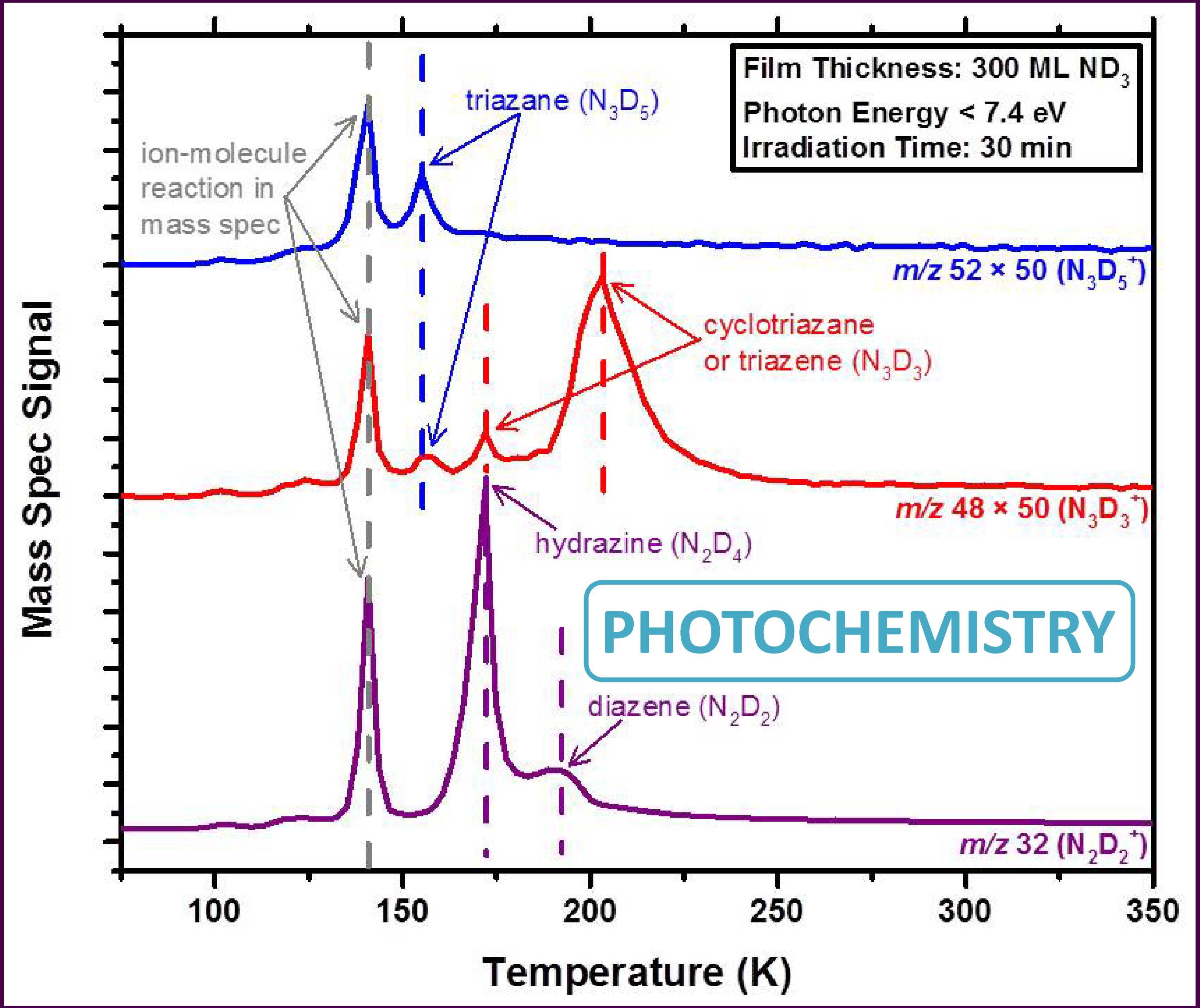


Zheng, W. et al. *The Astrophysical Journal*. 674:1242-1250, 2008 February 20

Products of High Energy Electrons From Condensed Ammonia



Products of Low-Energy Photons From Condensed Ammonia



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.

Energetics of Ammonia Photolysis

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Condensed-Phase Photochemistry in the Absence of Radiation Chemistry

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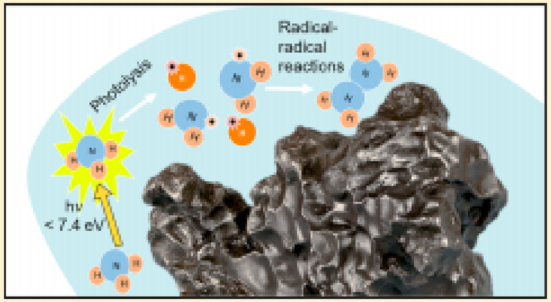
ABSTRACT: We report postirradiation photochemistry studies of condensed ammonia using photons of energies below condensed ammonia's ionization threshold of ~9 eV. Hydrazine (N_2H_4), diazene (also known as diimide and diimine; N_2H_2), triazane (N_3H_5), and one or more isomers of N_3H_3 are detected as photochemistry products during temperature-programmed desorption. Product yields increase monotonically with (1) photon fluence and (2) film thickness. In the studies reported herein, the energies of photons responsible for product formation are constrained to less than 7.4 eV. Previous post-irradiation photochemistry studies of condensed ammonia employed photons sufficiently energetic to ionize condensed ammonia and initiate radiation chemistry. Such studies typically involve ion−molecule reactions and electron-induced reactions in addition to photochemistry. Although photochemistry is cited as a dominant mechanism for the synthesis of prebiotic molecules in interstellar ices, to the best of our knowledge, ours is one of the first astrochemically relevant studies that has found unambiguous evidence for condensed-phase chemical synthesis induced by photons in the absence of ionization.



KEYWORDS: *astrochemistry, ammonia, interstellar medium, nonionizing, photons, ice*

Role of low-energy electrons in the synthesis of prebiotic molecules

THE JOURNAL OF CHEMICAL PHYSICS **148**, 164702 (2018)

Glycine formation in CO_2:CH_4:NH_3 ices induced by 0-70 eV electrons

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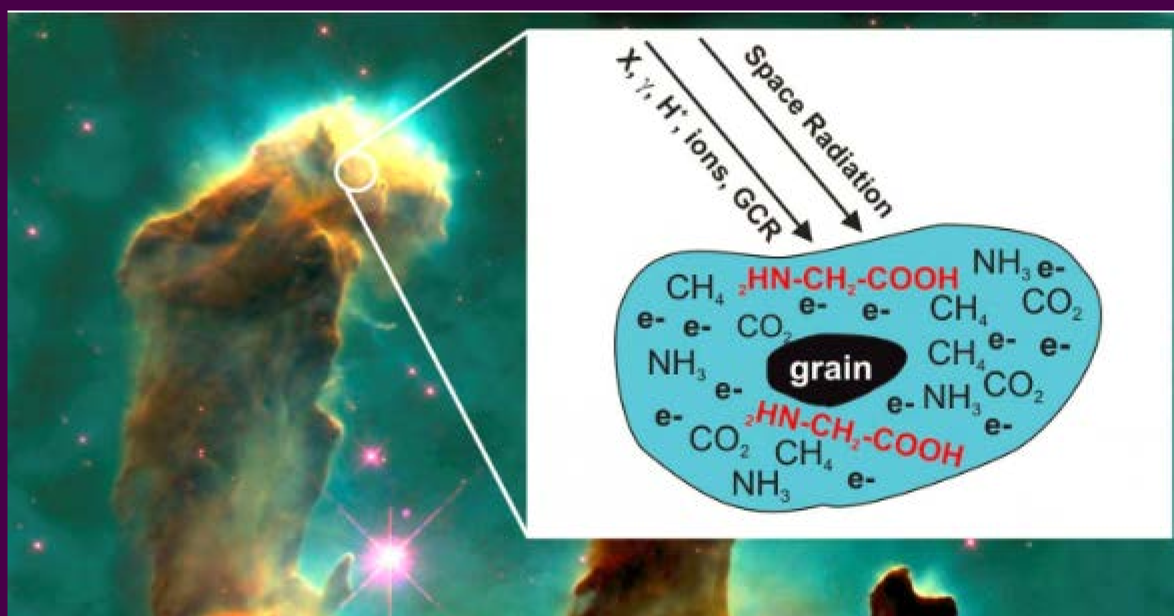
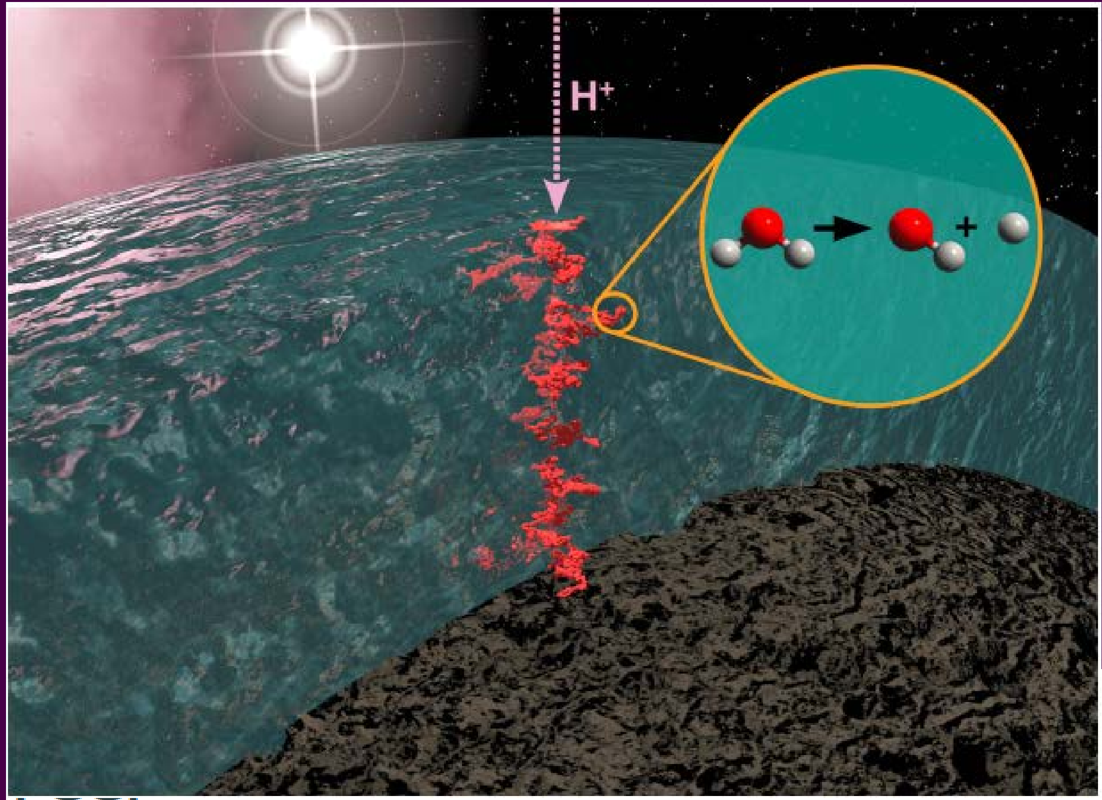


https://www.eurekalert.org/multimedia/pub/168851.php



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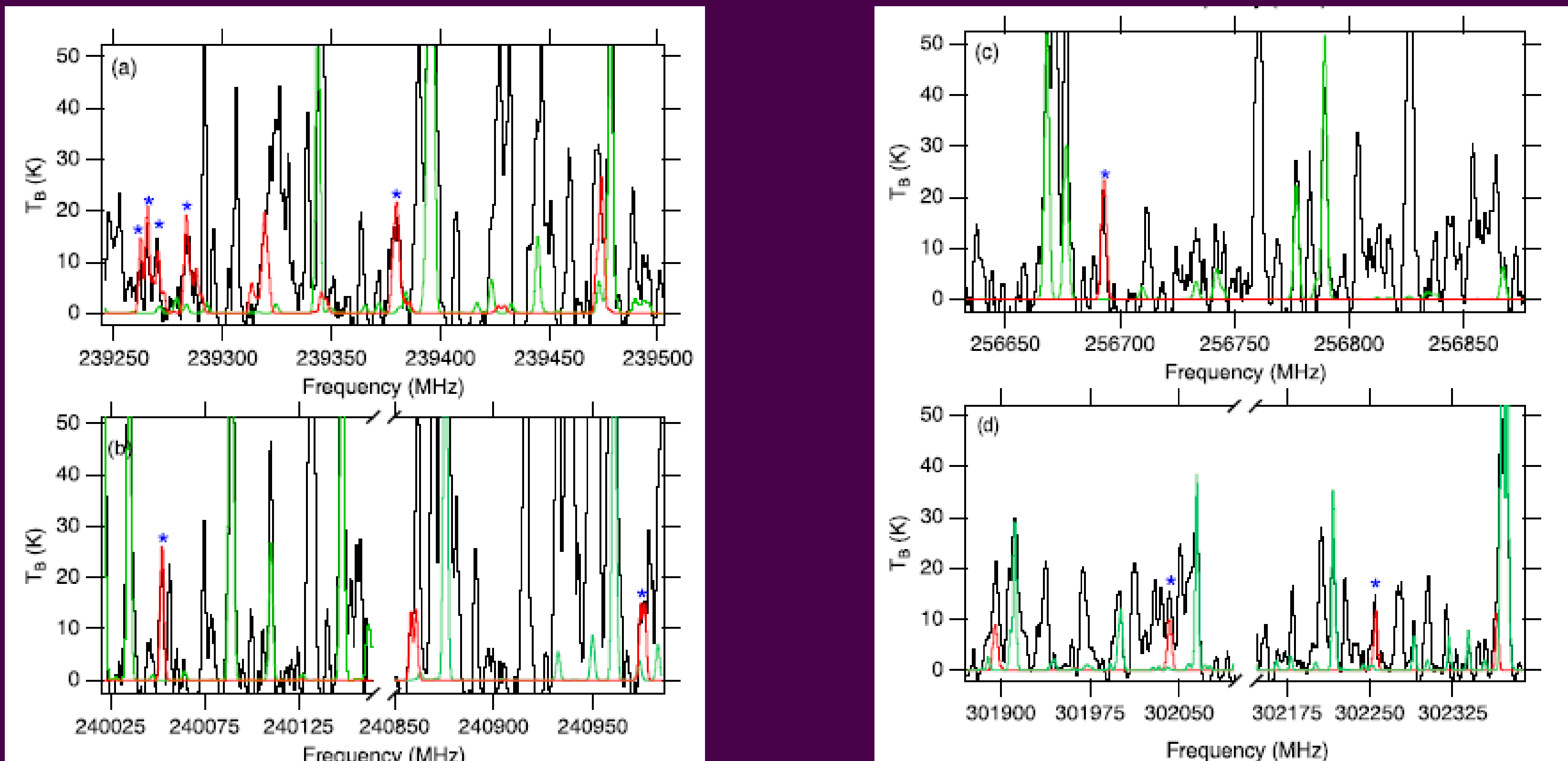
Cite this: *Phys. Chem. Chem. Phys.*, 2018, **20**, 5359

A general method for the inclusion of radiation chemistry in astrochemical models

Christopher N. Shingledecker *[a] and Eric Herbst[ab]

December 2017: Identification of Methoxy methanol in the ISM [~10 quadrillion miles away]



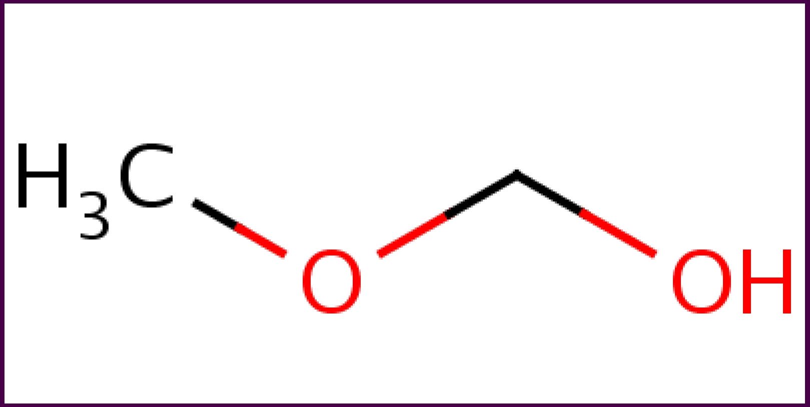
Black: Overall microwave spectrum of NGC 6334I

Red: Simulated rotational spectrum of methoxymethanol

Green: Simulations of species that are major contributors to the overall spectrum

Brett A. McGuire *et al* 2017 *ApJL* **851** L46; James O. Chibueze *et al* 2014 *ApJ* **784** 114

First Detection of Methoxymethanol as a Photolysis Product of Condensed Methanol



Conclusions

- Photochemistry (excitation) vs. Radiation chemistry (excitation + electron attachment + ionization)

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- First <u>direct</u> comparison between photochemistry and radiation chemistry.

Conclusions

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- Laboratory studies of interstellar ice analogs
- First <u>direct</u> comparison between photochemistry and radiation chemistry.
- Low-energy (< 20 eV) electrons likely drive interstellar ice chemistry.

Conclusions

- Photochemistry (excitation) vs. Radiation chemistry (excitation + electron attachment + ionization)
- Laboratory studies of interstellar ice analogs
- First direct comparison between photochemistry and radiation chemistry.
- Low-energy (< 20 eV) electrons likely drive interstellar ice chemistry.
- Need quantitative wavelength-dependent photochemistry studies of ice analogs

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Dr. Petra Swiderek, University of Bremen
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