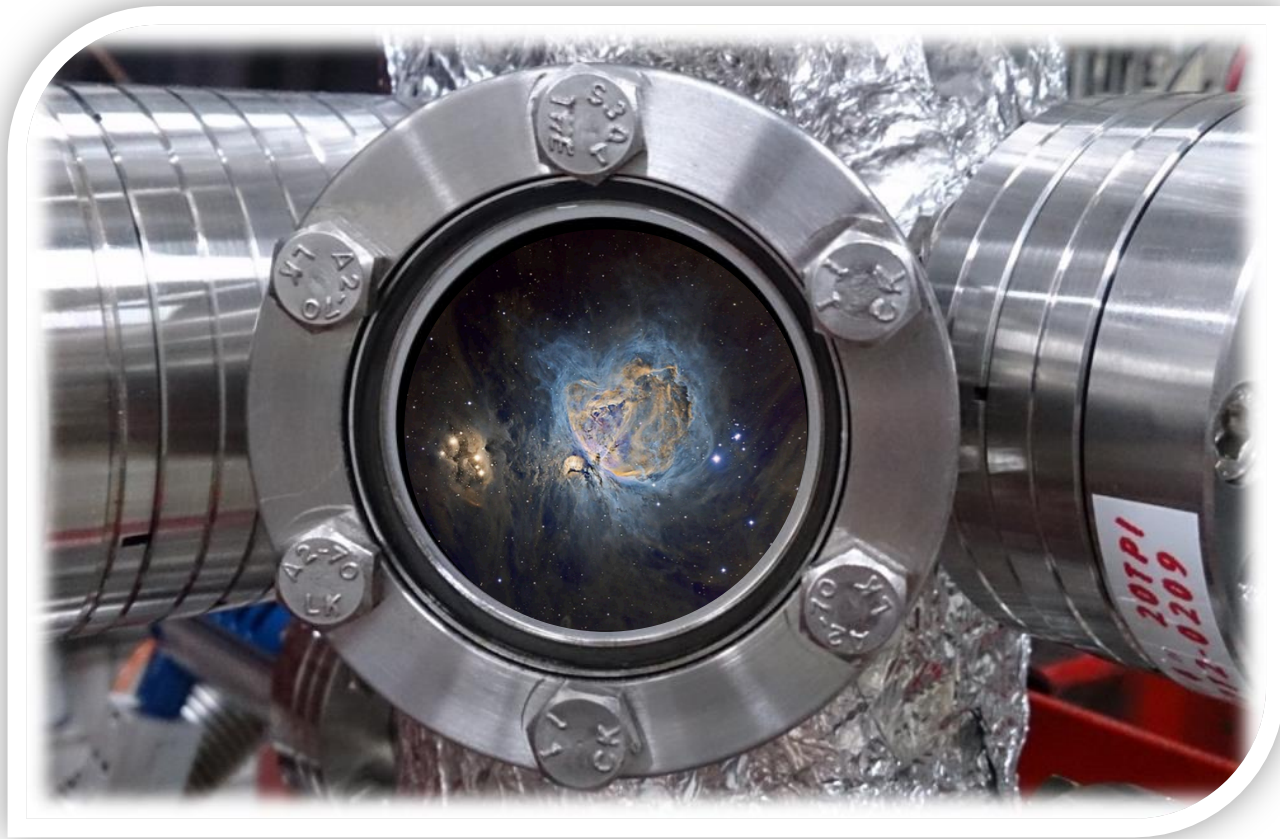


在實驗室裡遇見彗星



陳俞融

國立中央大學物理系

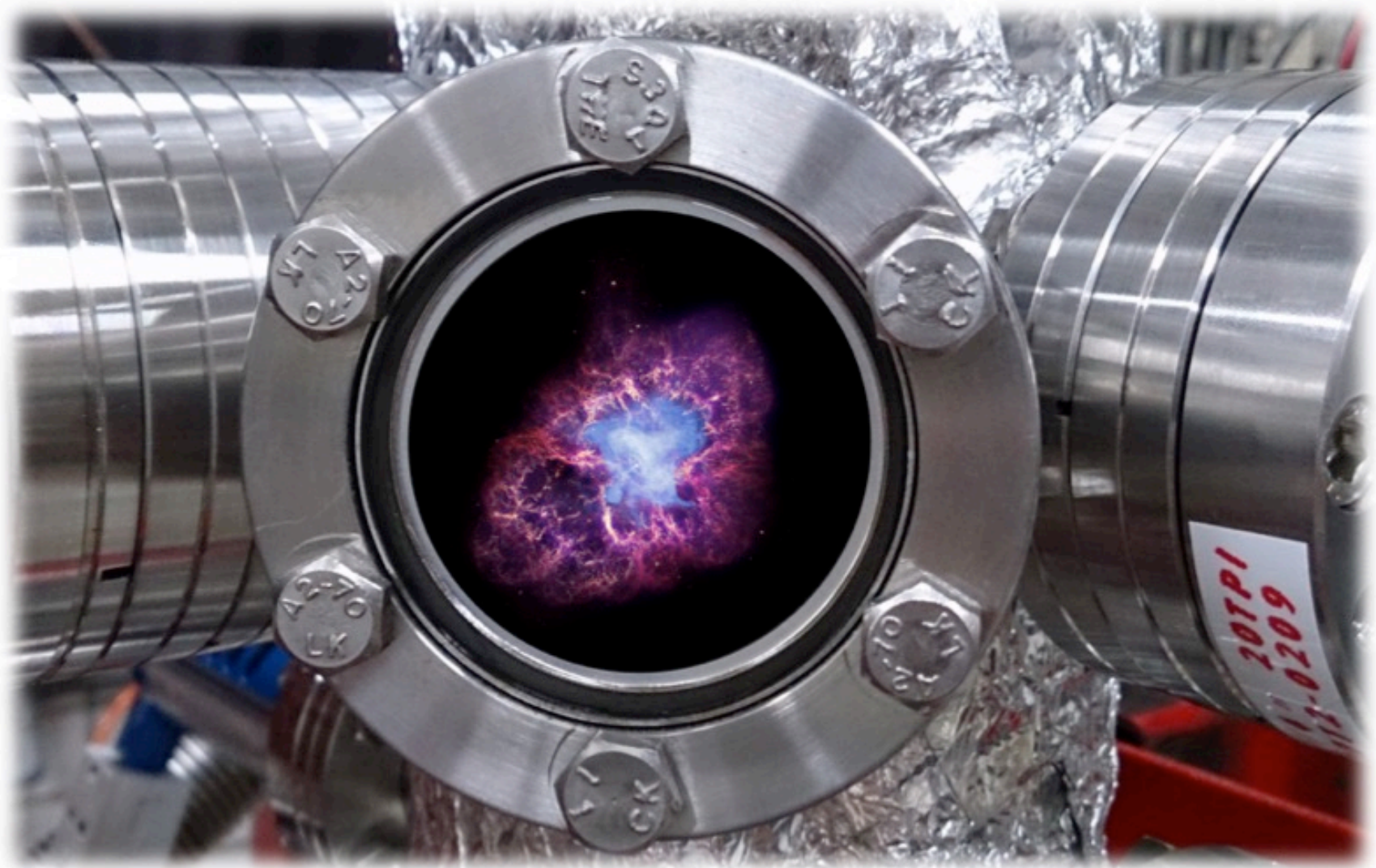
光子作用與光譜分析實驗室



國立中央大學

National Central University

什麼是實驗室天文學？



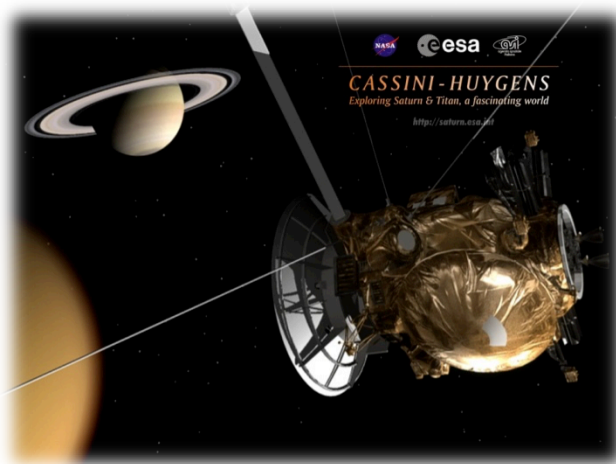
為什麼要有實驗室天文學？



1986 ESA
Giotto mission
Comet Halley



2005 NASA
Deep Impact
9P/Tempel 1



1997 ESA/NASA/ISA
Cassini mission
Saturn

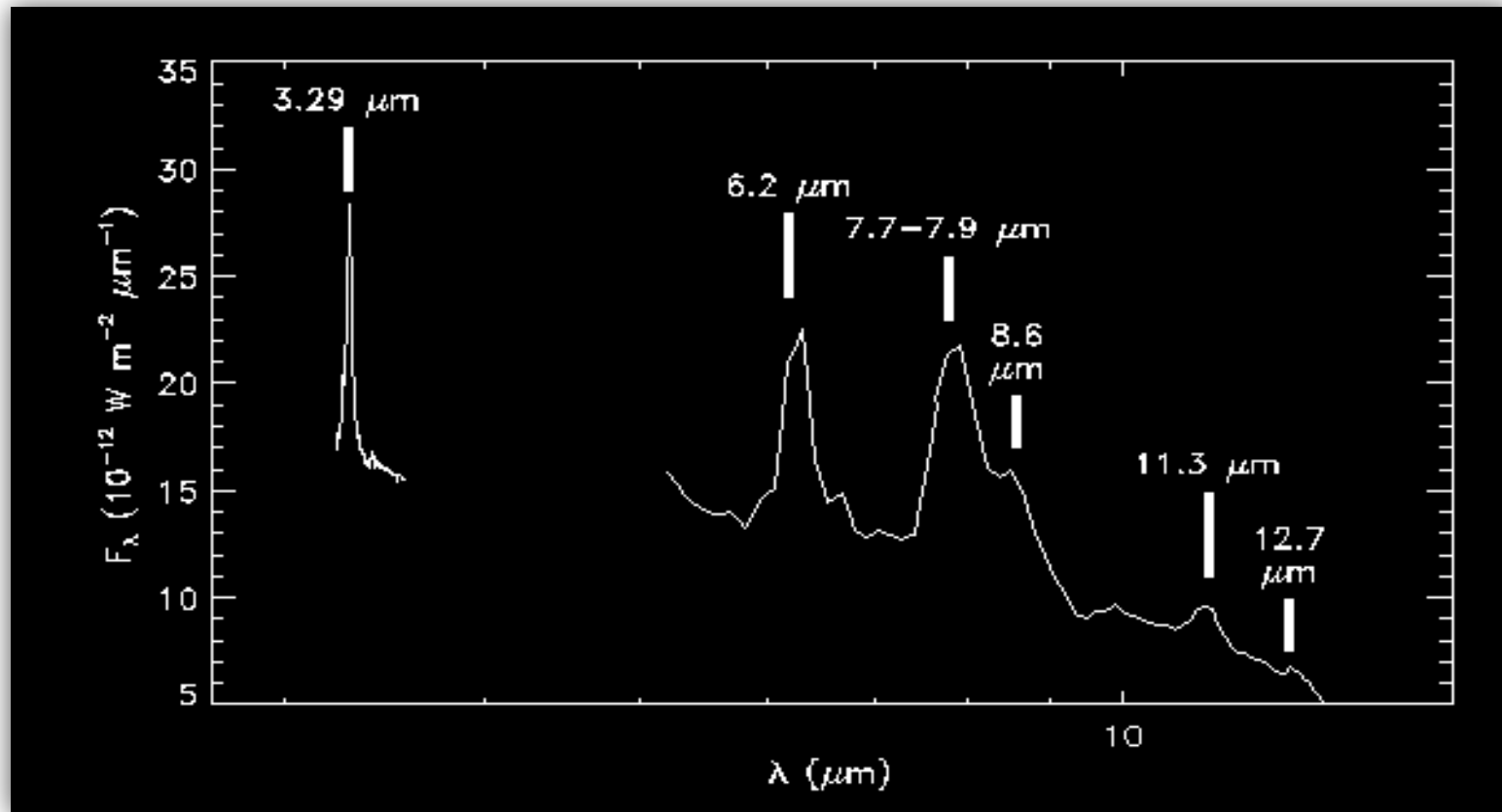


2004 ESA
Rosetta mission
Churyumov-Gerasimenko

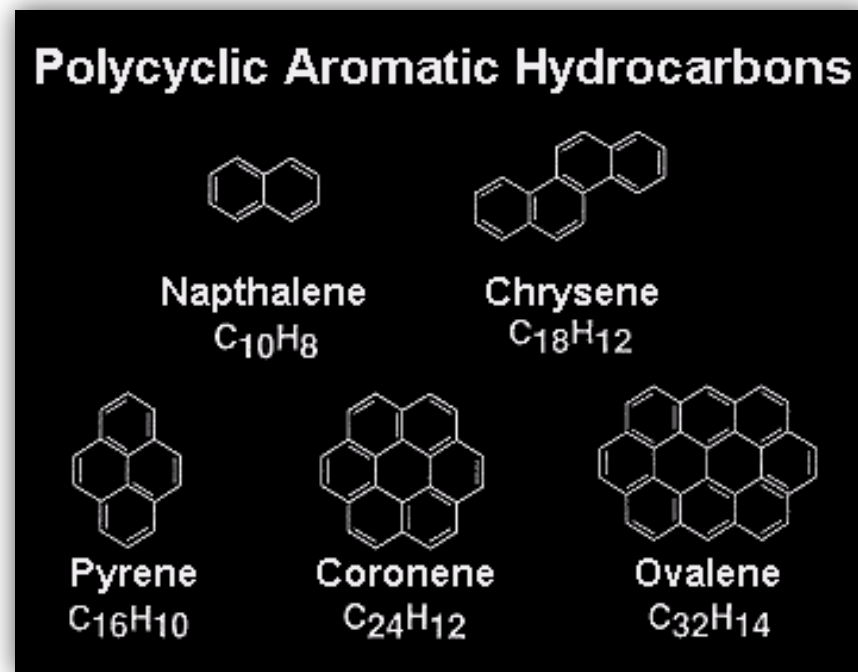
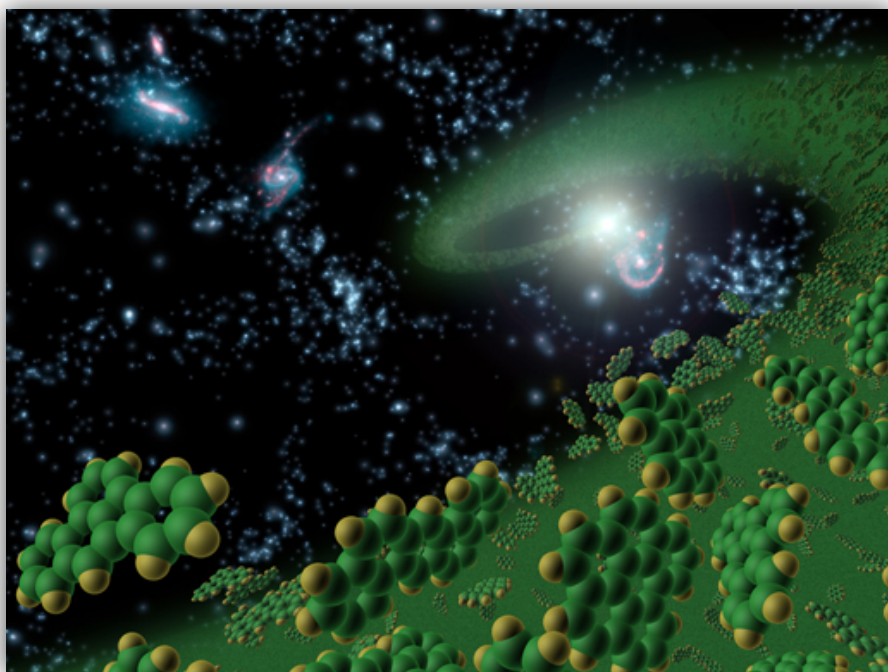


2013 ALMA
Star and planet formation

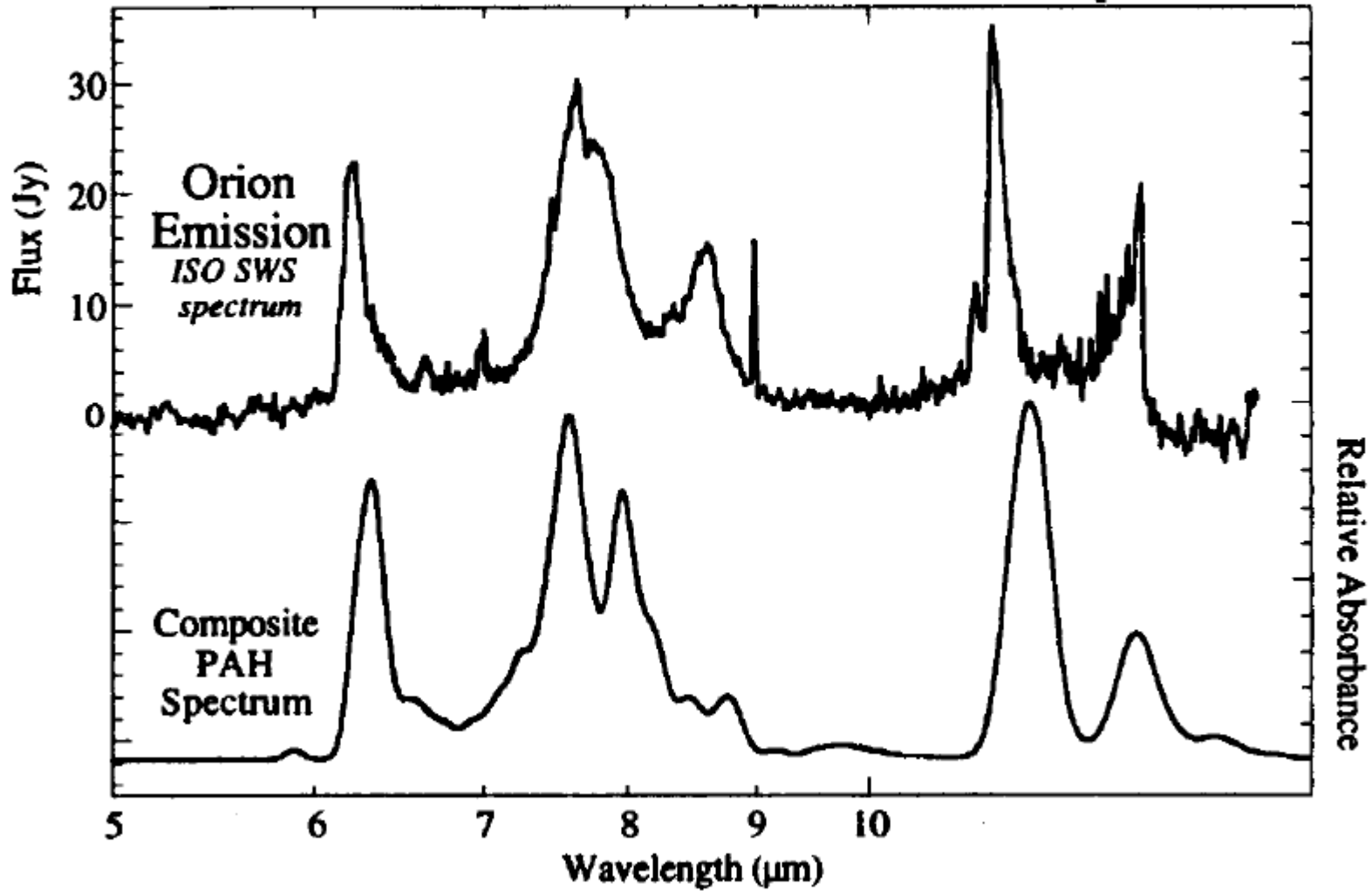
Unidentified Infrared Bands



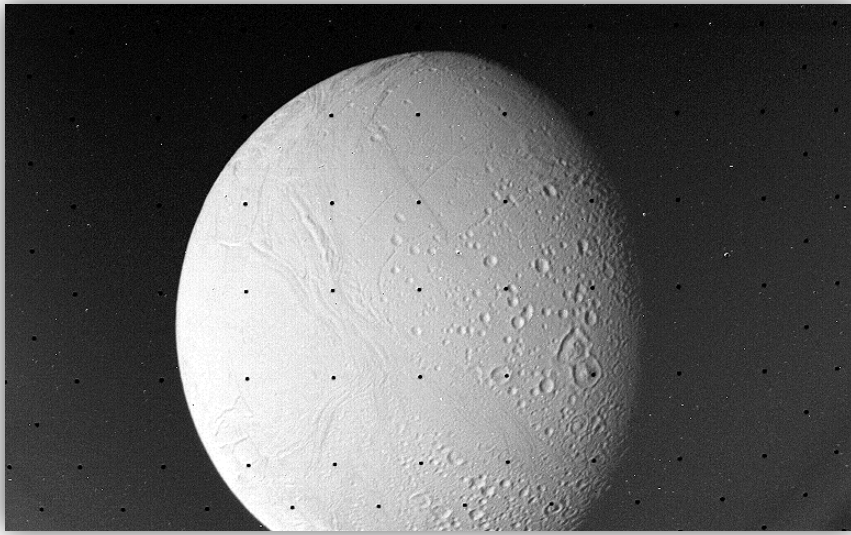
PAHs are among the most commonly proposed candidates for UIB



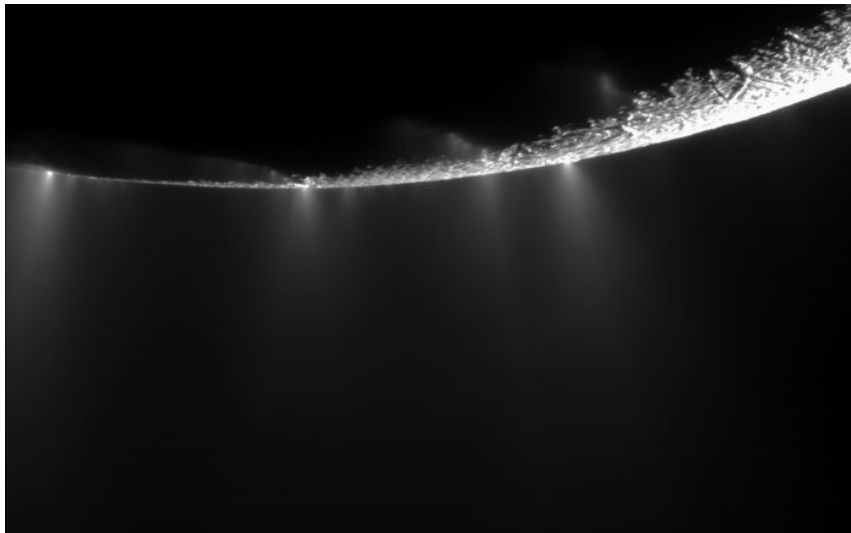
PAH Model of the Orion Infrared Emission Spectrum



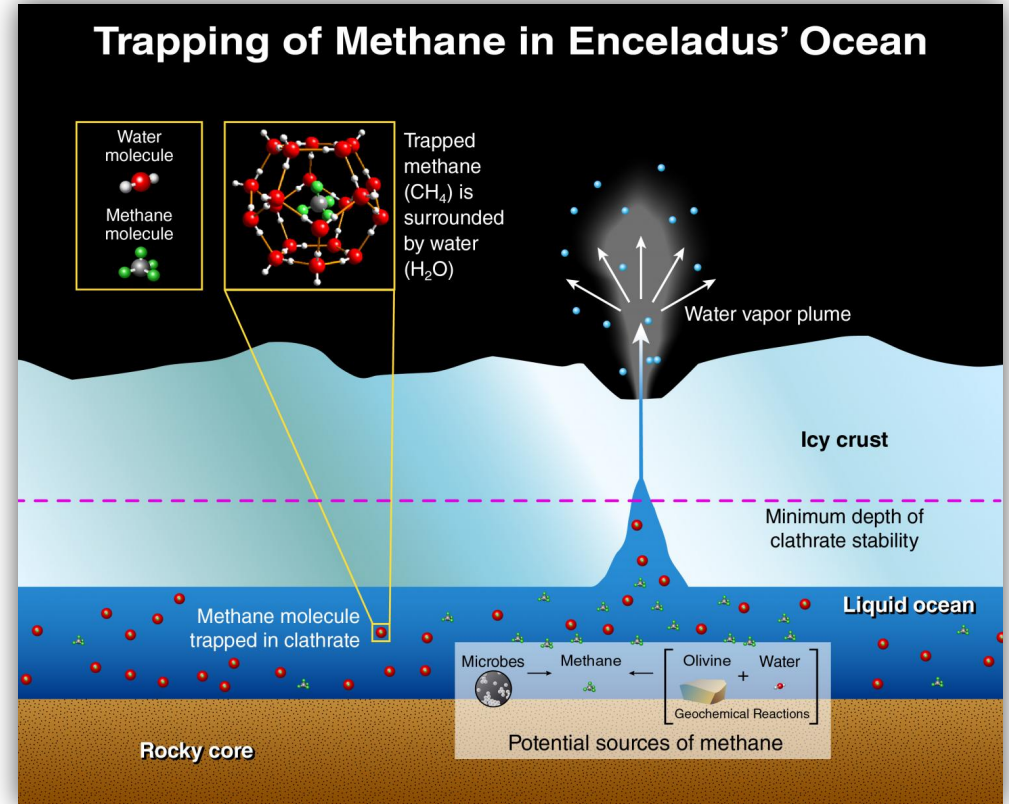
Hudgins & Allamandola 2002, NASA LAW



Voyager 2 image of Enceladus (1981)



Cassini, Enceladus plumes (2005)



Models for Interstellar Chemistry

Gas-Gas reaction

Processes are ion-molecule, neutral-neutral, charge exchange, radiative association, radiative recombination, dissociative recombination, CRP and FUV ionization and dissociation...etc.

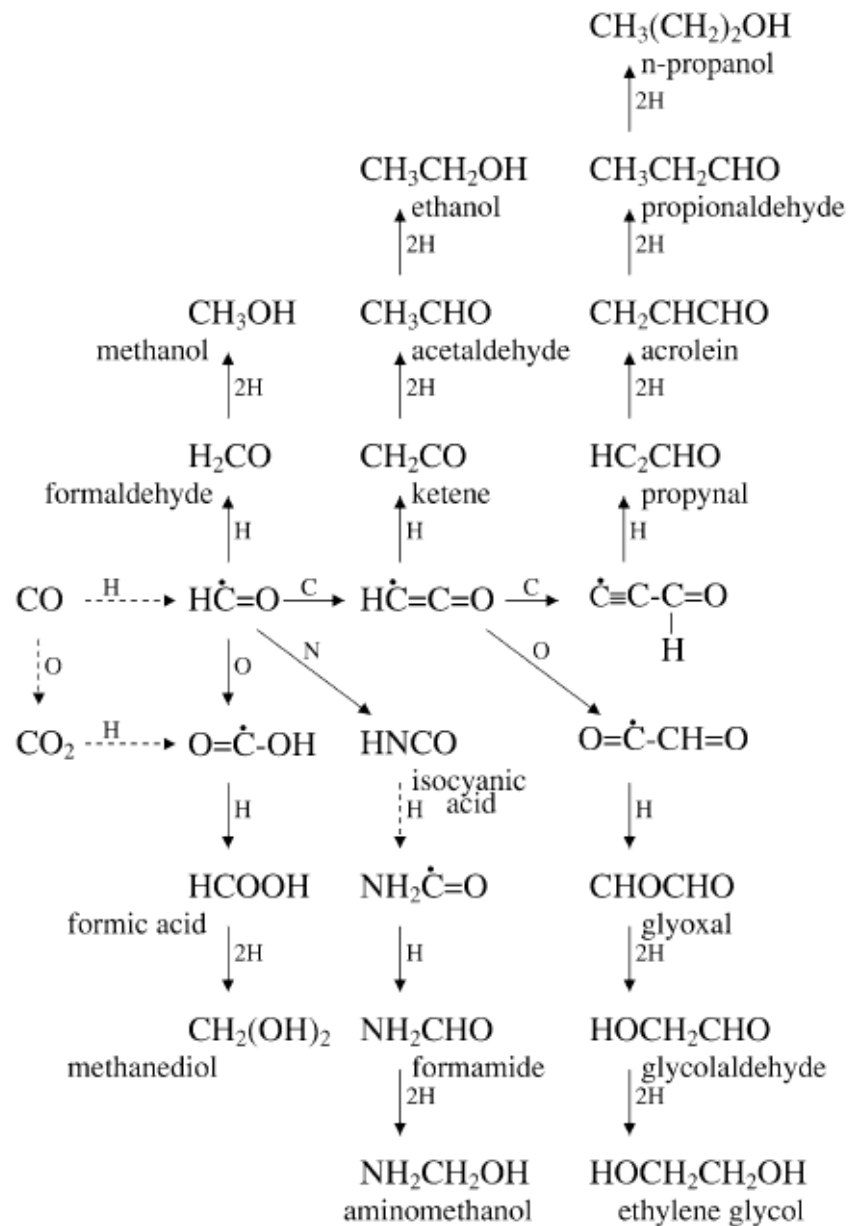
Gas-Surface reaction

Assumes molecules/atoms tunneling through potential wells of the surface sites and reaction barriers.

Gas-Surface Chemistry

Atom Addition Reactions

proposed by Tielens and Hagen (1982)



Models for Interstellar Chemistry

Gas-Gas reaction

Processes are ion-molecule, neutral-neutral, charge exchange, radiative association, radiative recombination, dissociative recombination, CRP and FUV ionization and dissociation...etc.

Gas-Surface reaction

Assumes molecules/atoms tunneling through potential wells of the surface sites and reaction barriers.

Grain Surface reaction

Includes *accretion* of neutral molecules onto the surfaces of amorphous silicate grains, *energetic sources irradiation* induced molecule-radical, radical-radical, atom-radical, atom-molecule, ion-radical, ion-atom, ion-molecule interaction/recombination, as well as thermal, CRP-driven and UV-desorption.

Grain Surface Chemistry

Energetic Sources Irradiation

Interstellar Medium (ISM)

99% is gas, 1% is dust

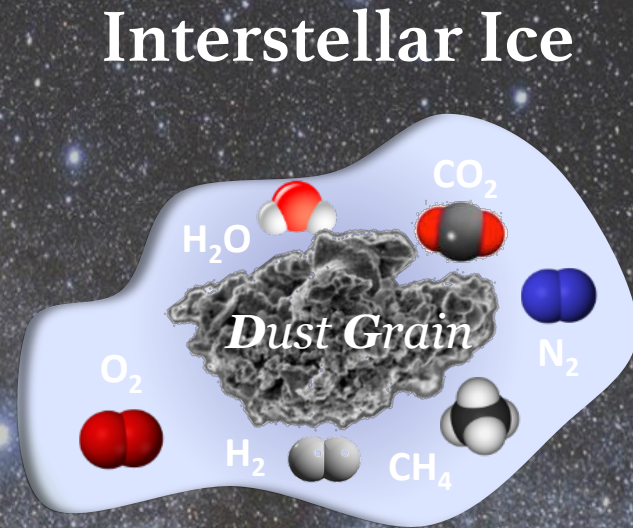
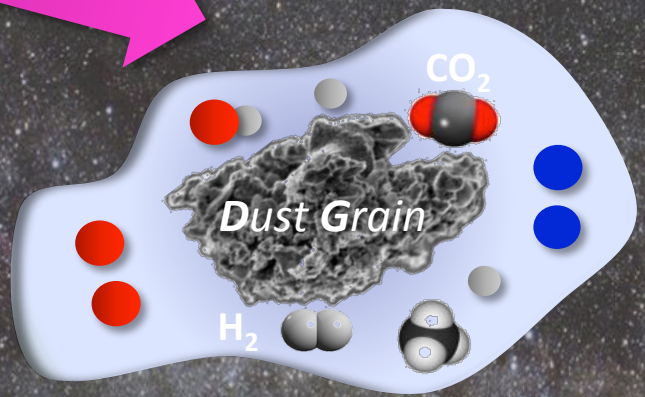


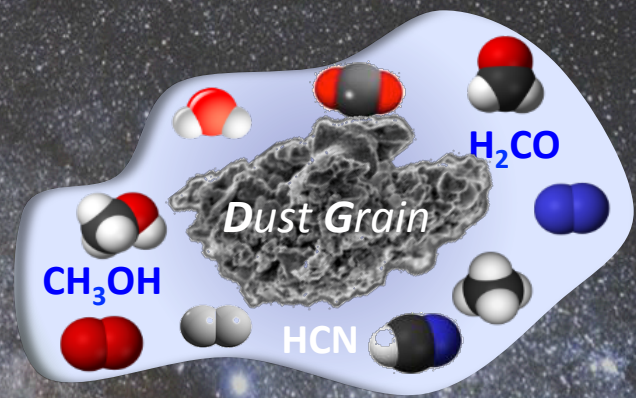
Photo-induced desorption

Photo-induced chemical reaction

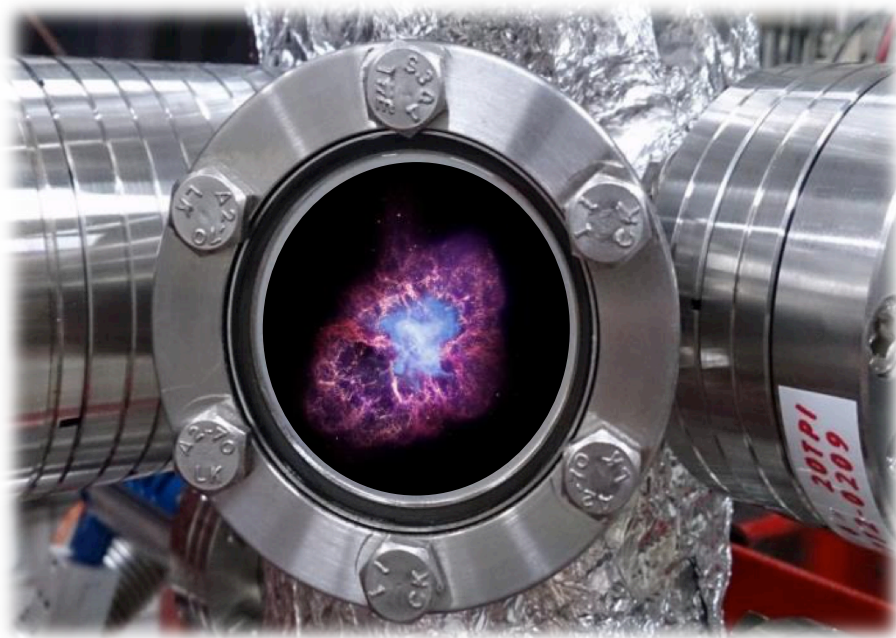
PHOTONS



COSMIC RAYS



How to Approach Interstellar Environment ?



- Ultra High Vacuum
- Extreme Low Temperature
- Energy Source

Transmission FTIR

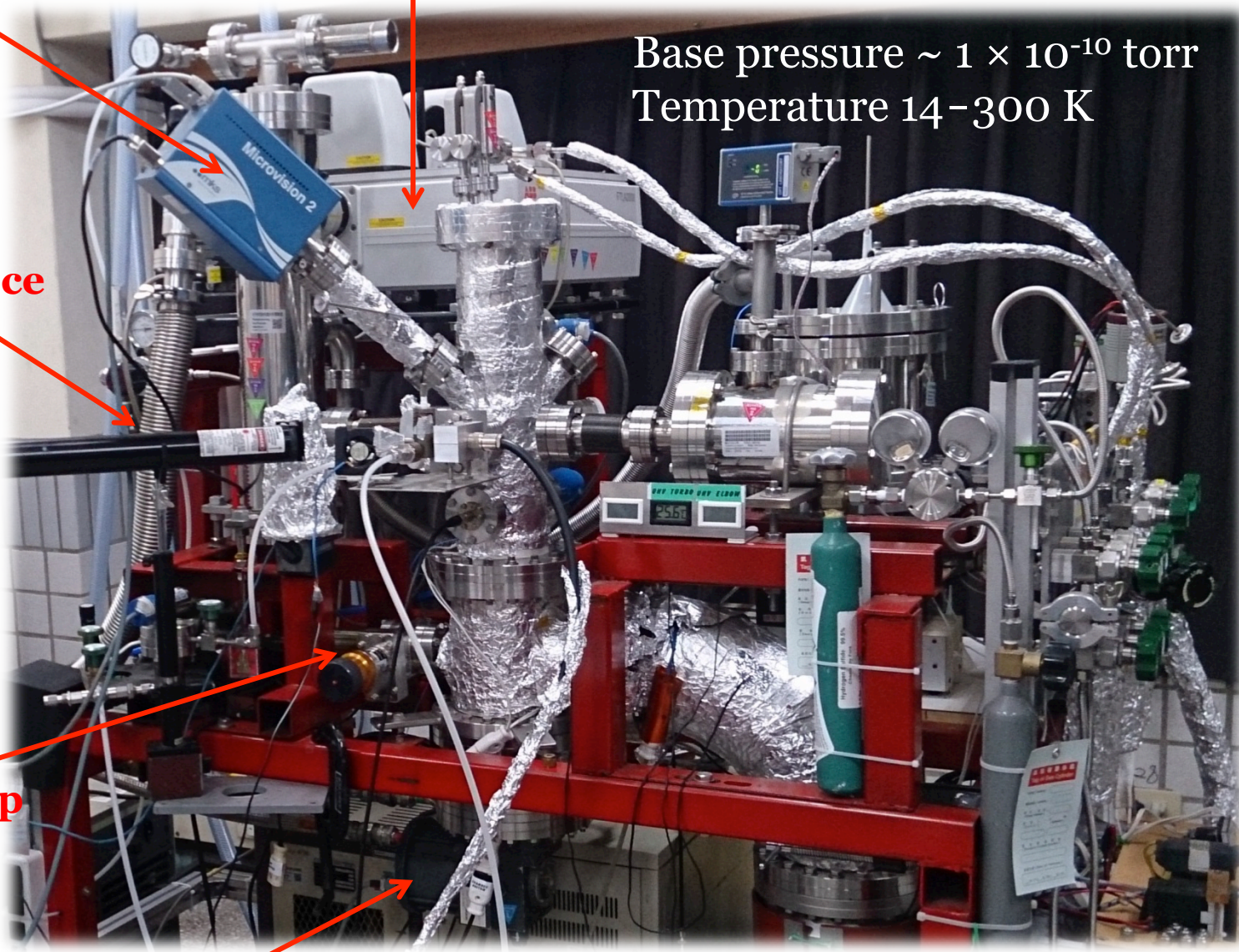
QMS

Base pressure $\sim 1 \times 10^{-10}$ torr
Temperature 14–300 K

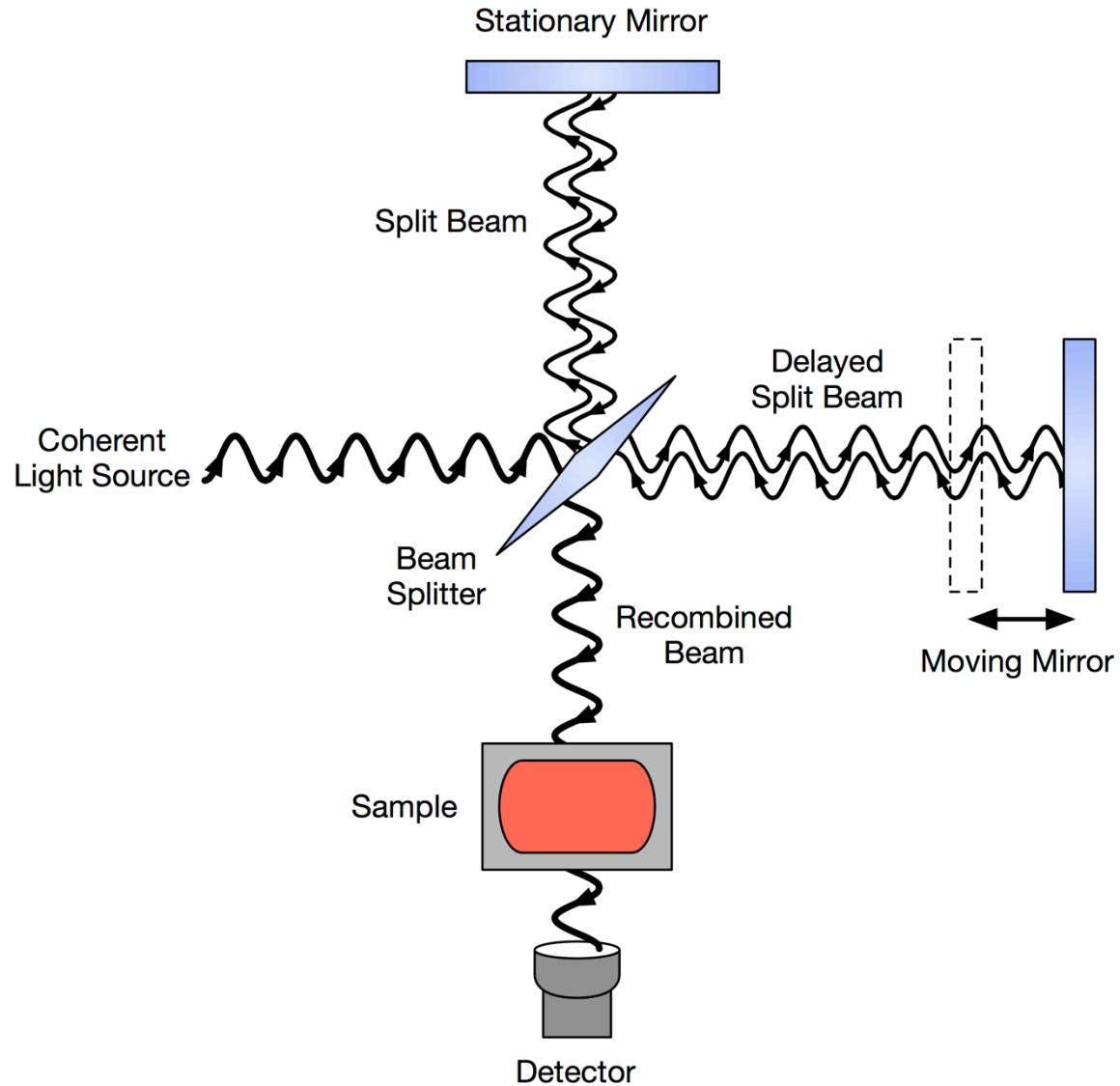
Laser
Interference
System

Getter Pump

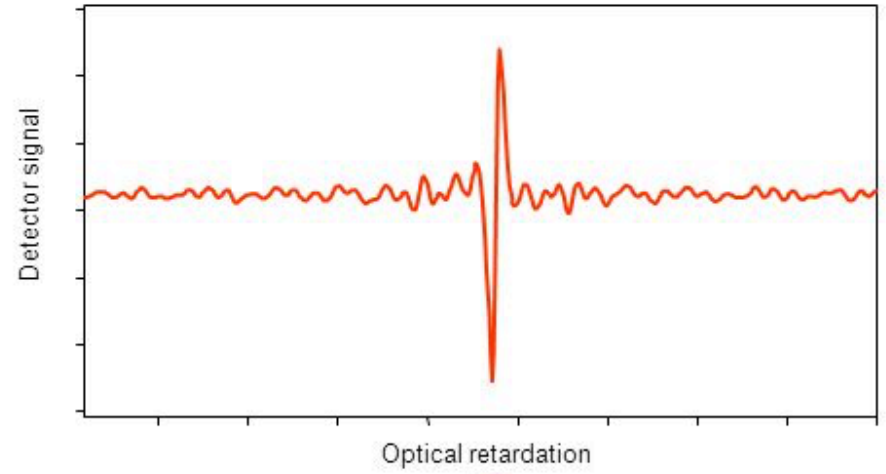
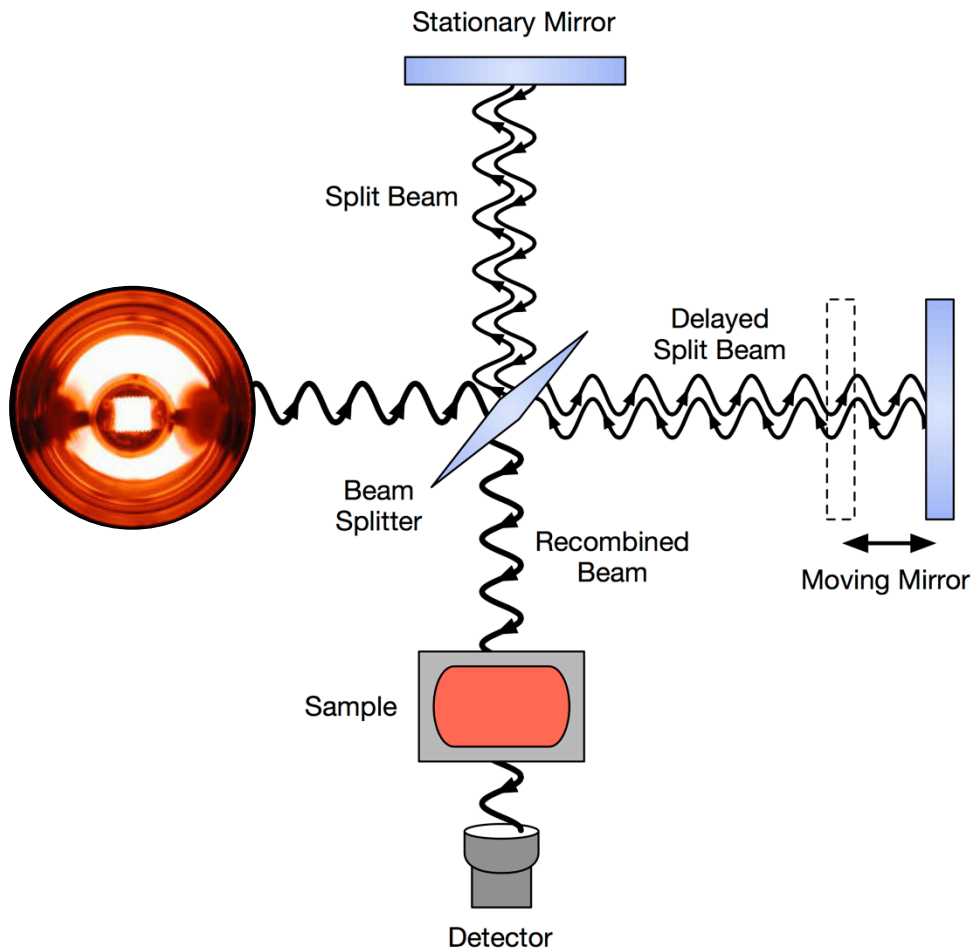
He Closed-Cycle Cryostat



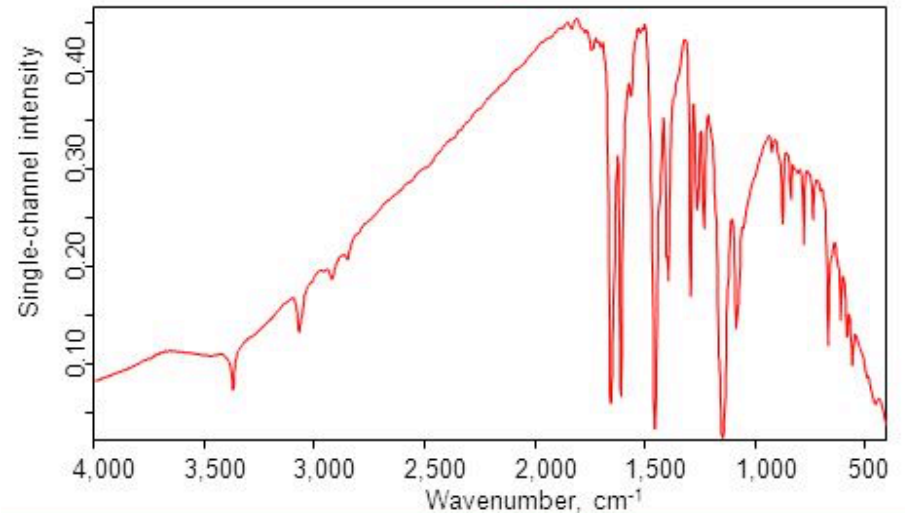
Fourier Transform Infrared Spectrometry



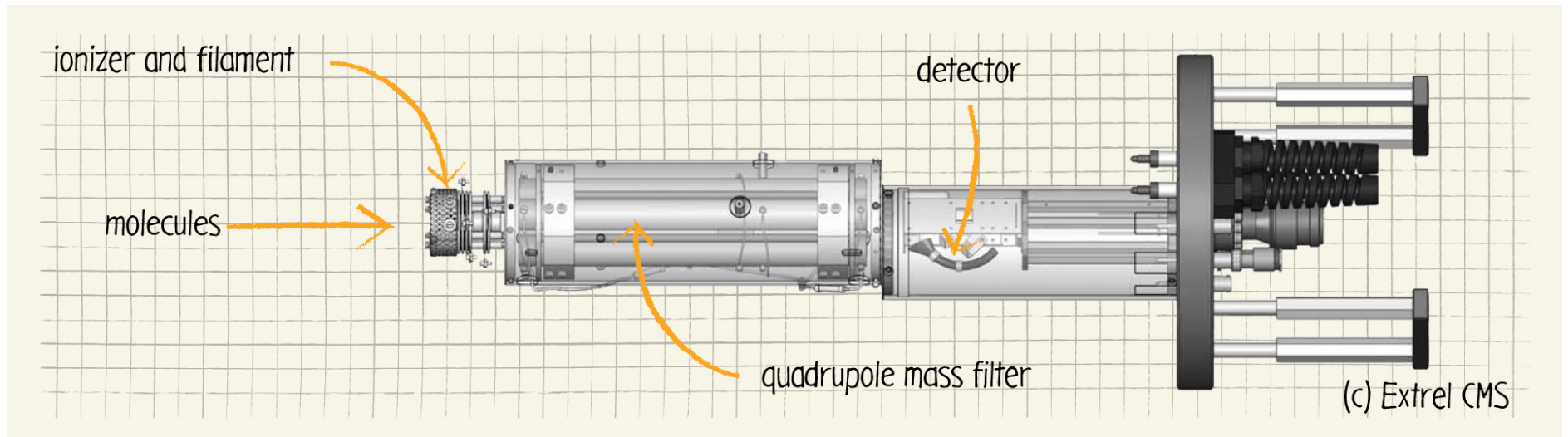
Fourier Transform Infrared Spectrometry



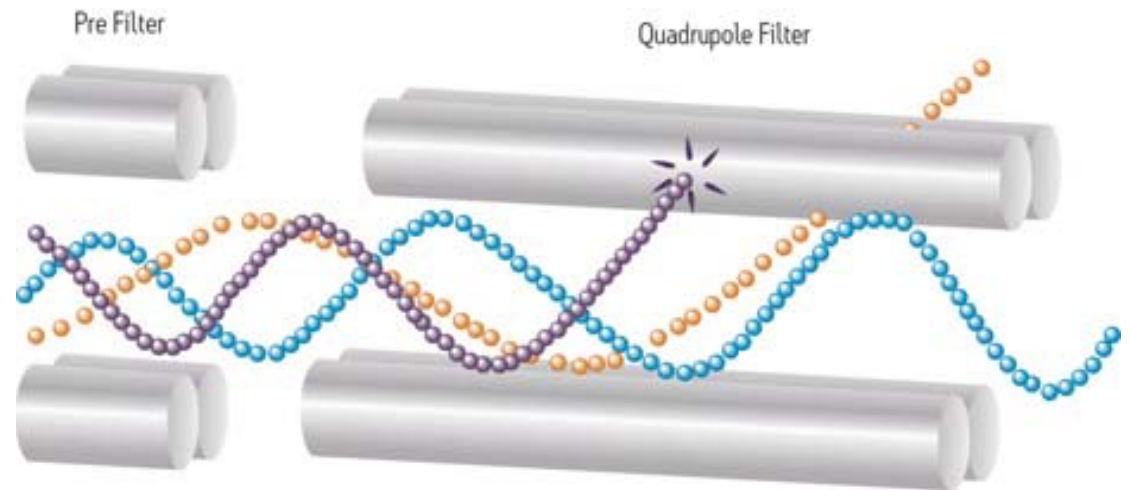
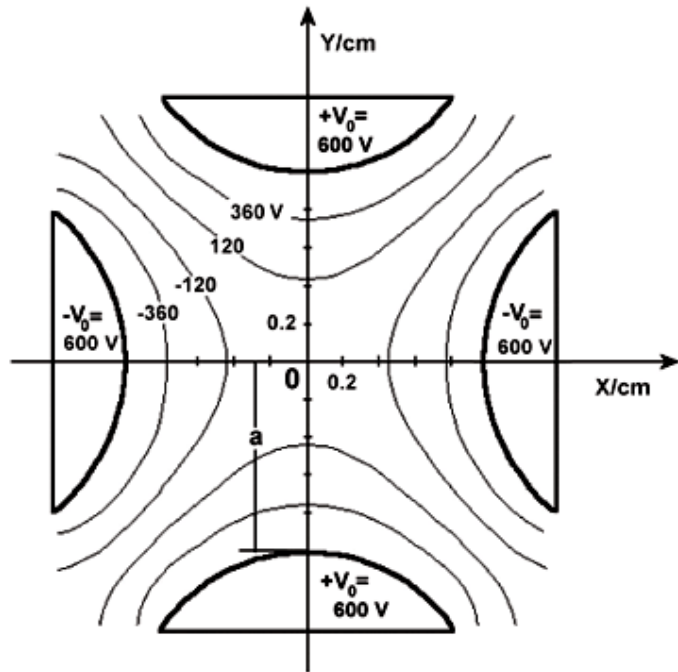
↓ **Fourier transformation**



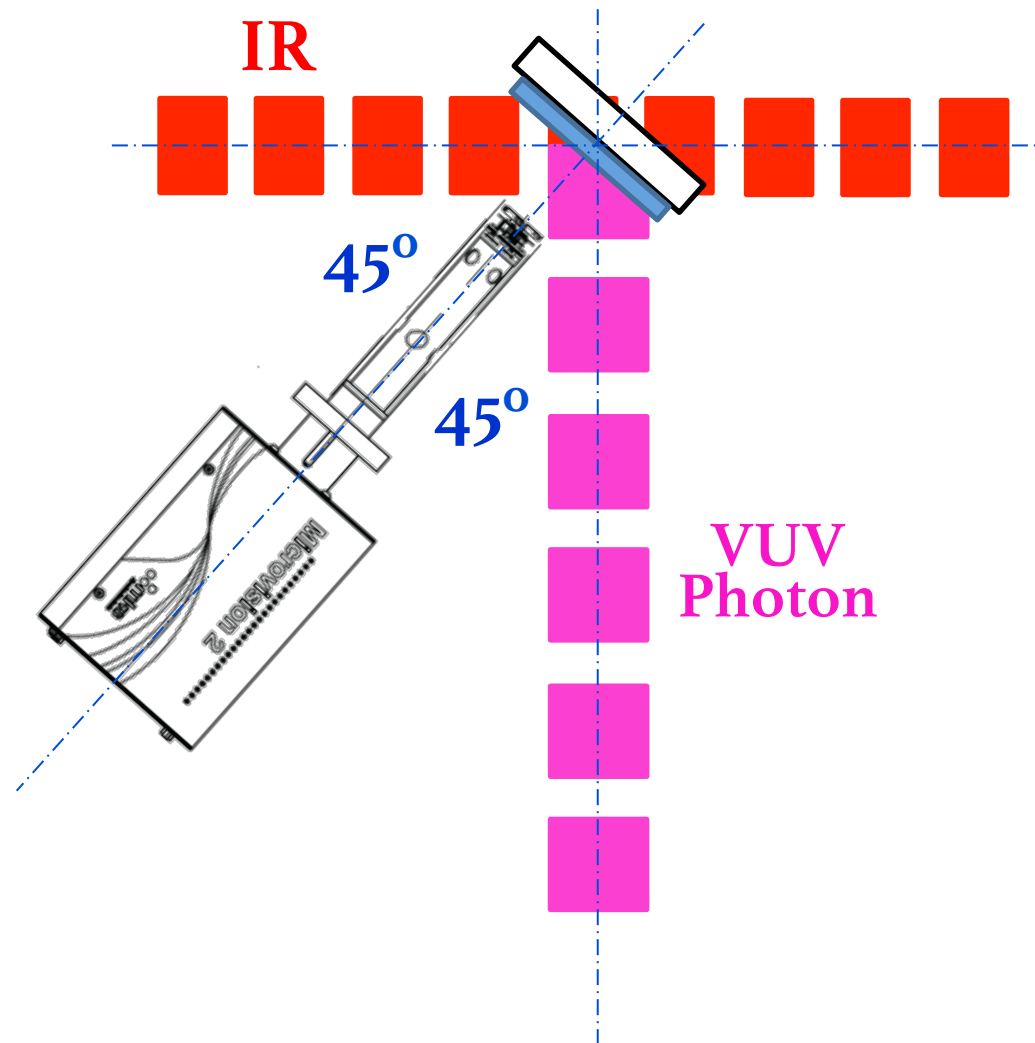
Quadrupole Mass Spectrometer



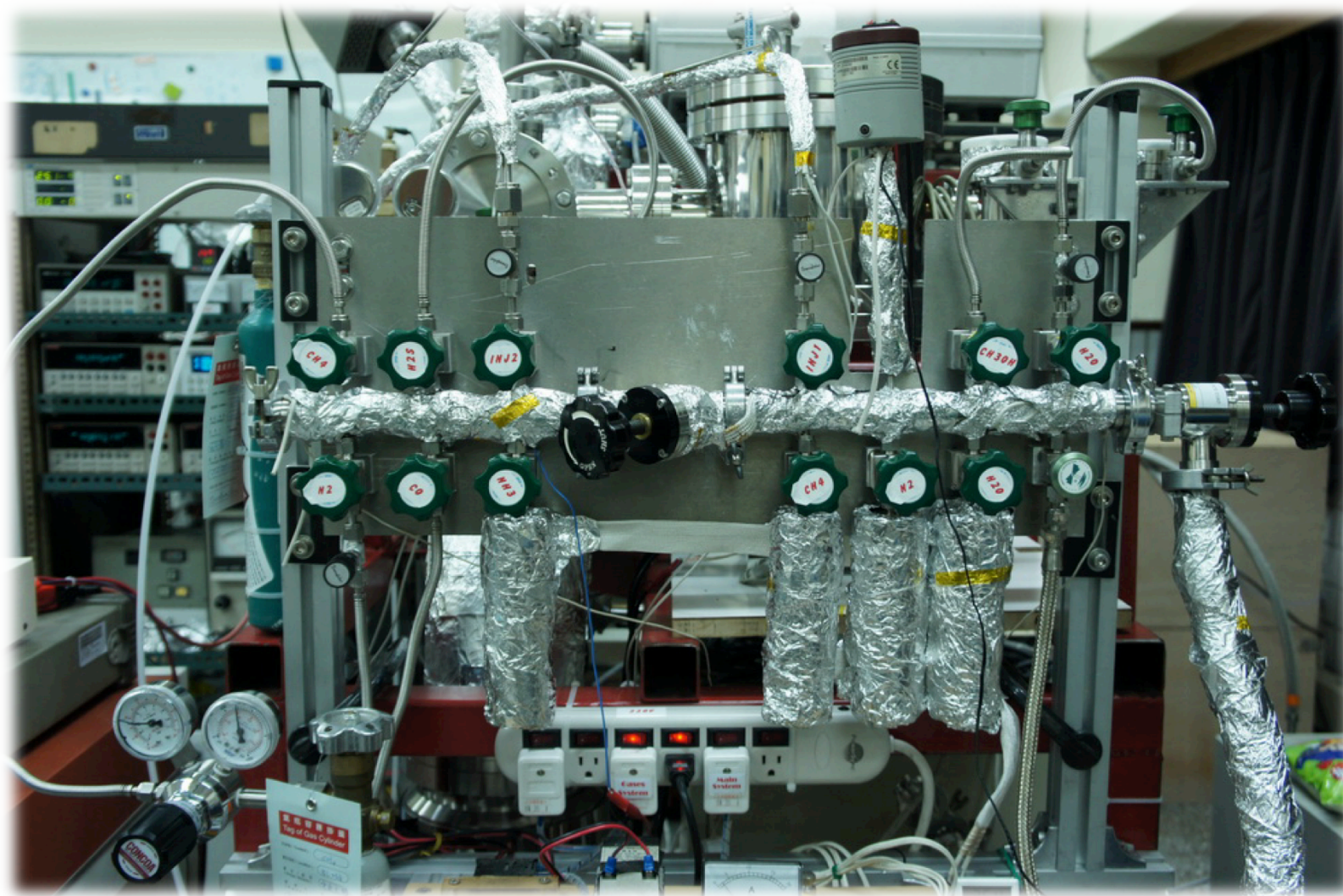
Quadrupole Mass Spectrometer

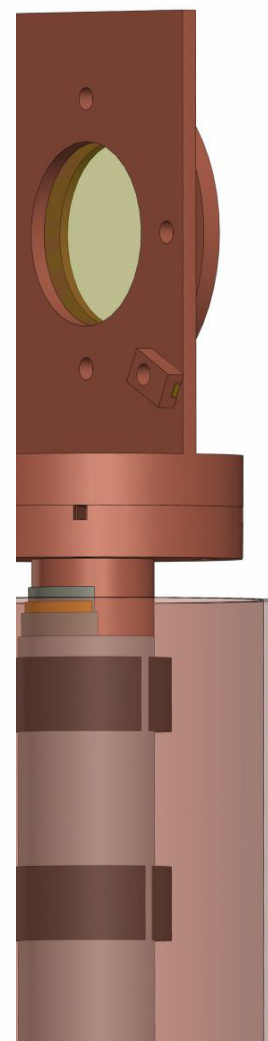
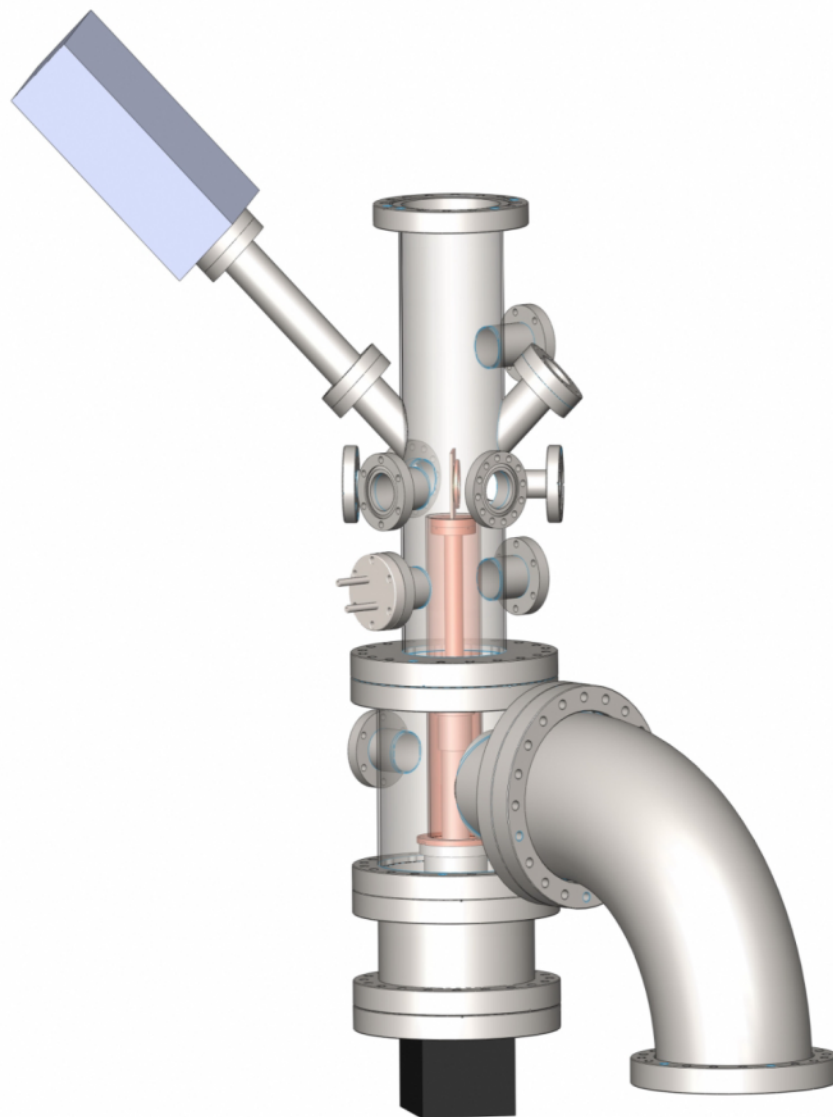


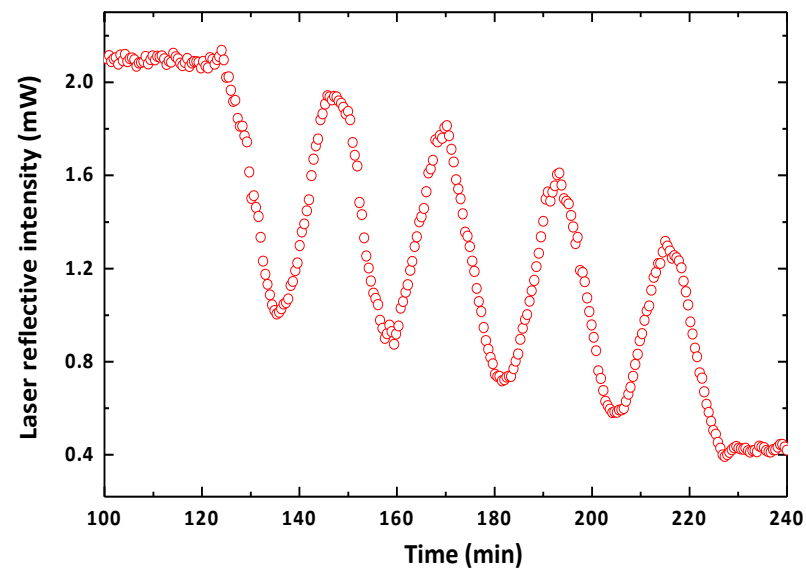
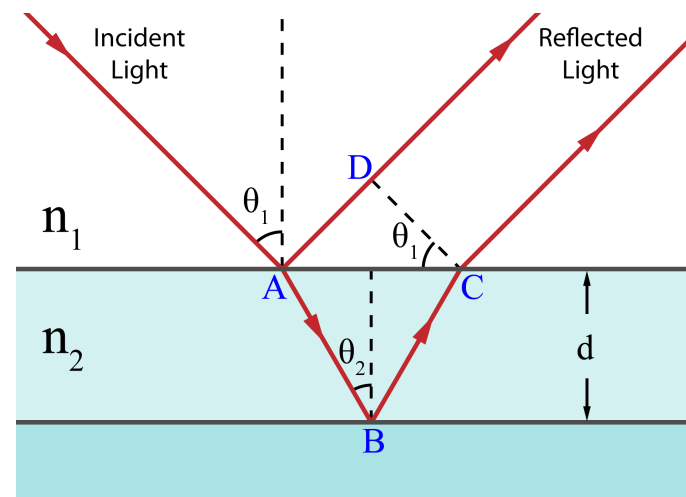
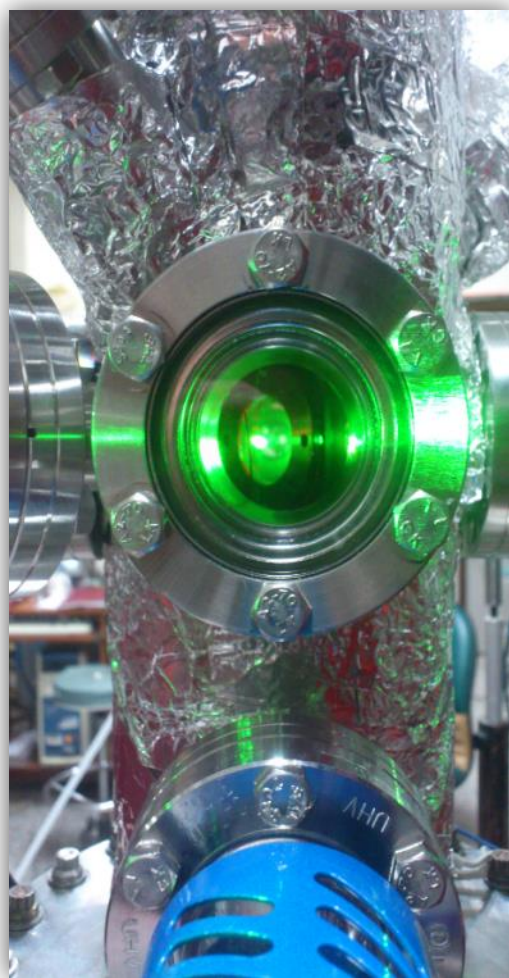
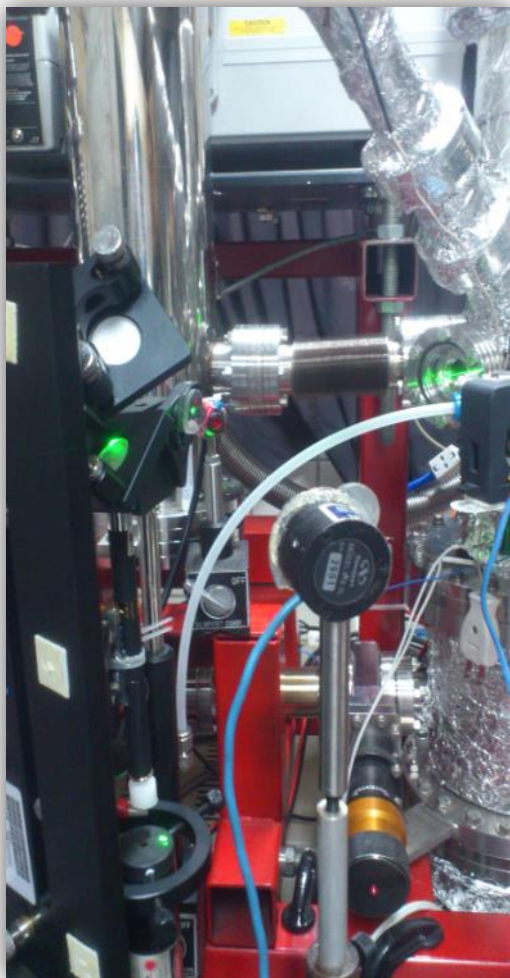
Transmission-FTIR + Quadrupole Mass Spectrometer



Premixing Gas-line System





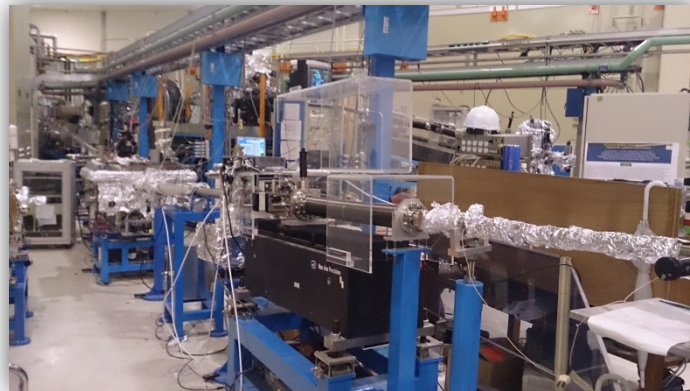
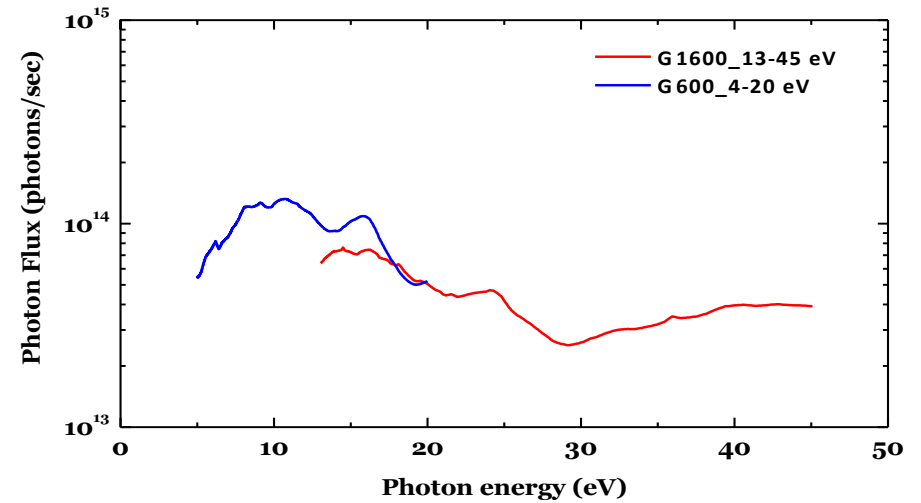


Light sources

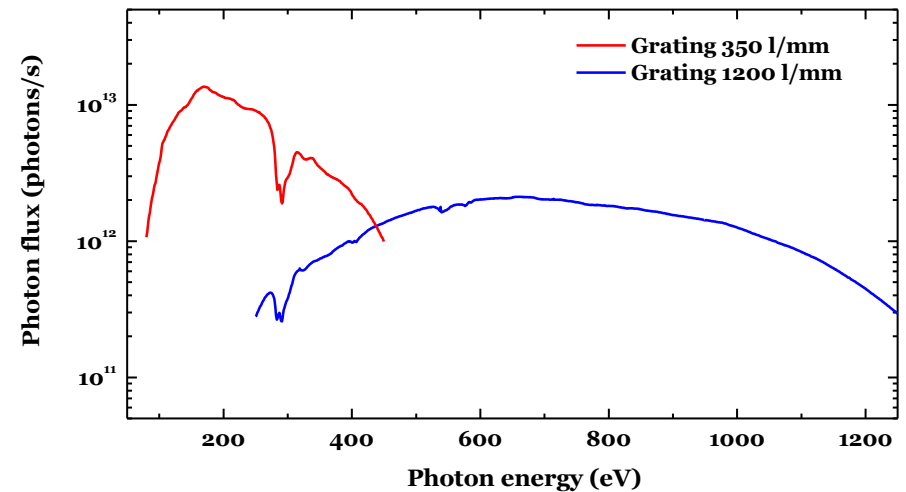
National Synchrotron Radiation Research Center, Taiwan



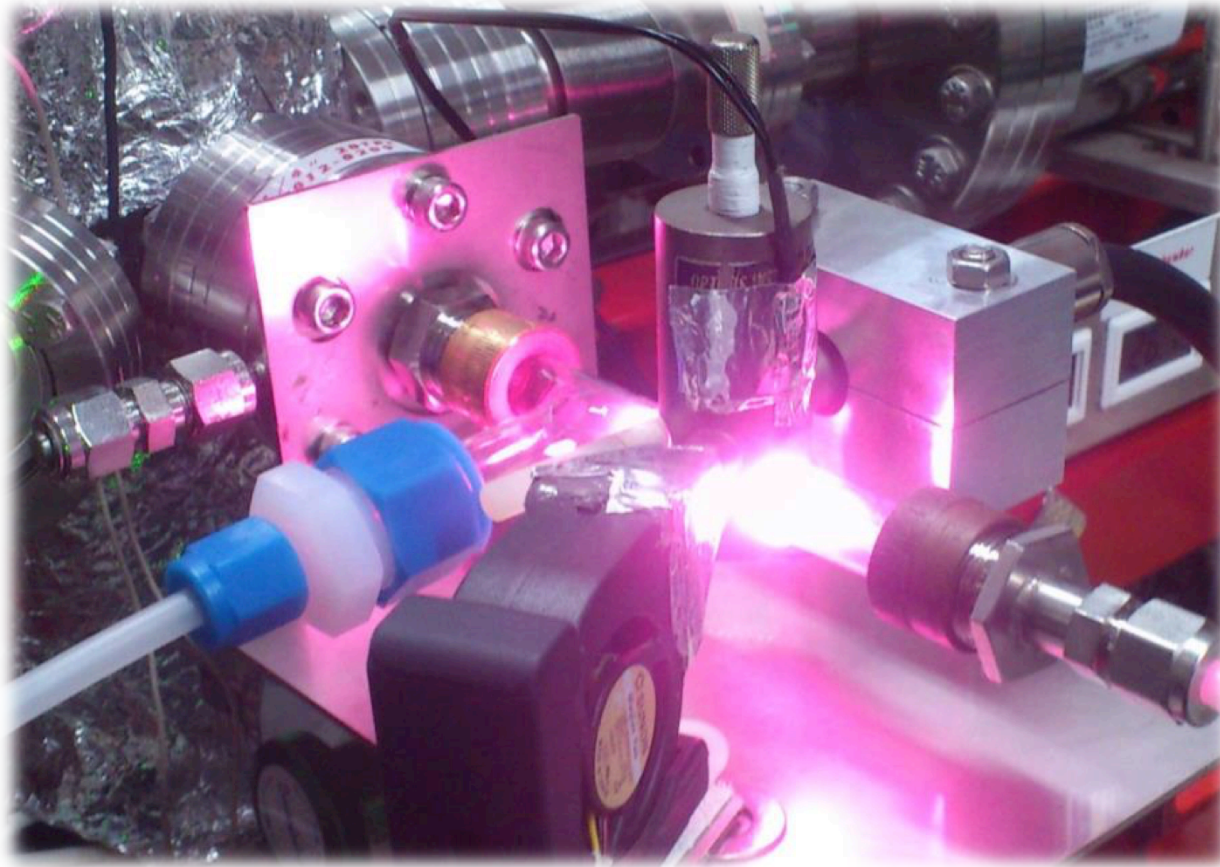
BL03A (4–45 eV)



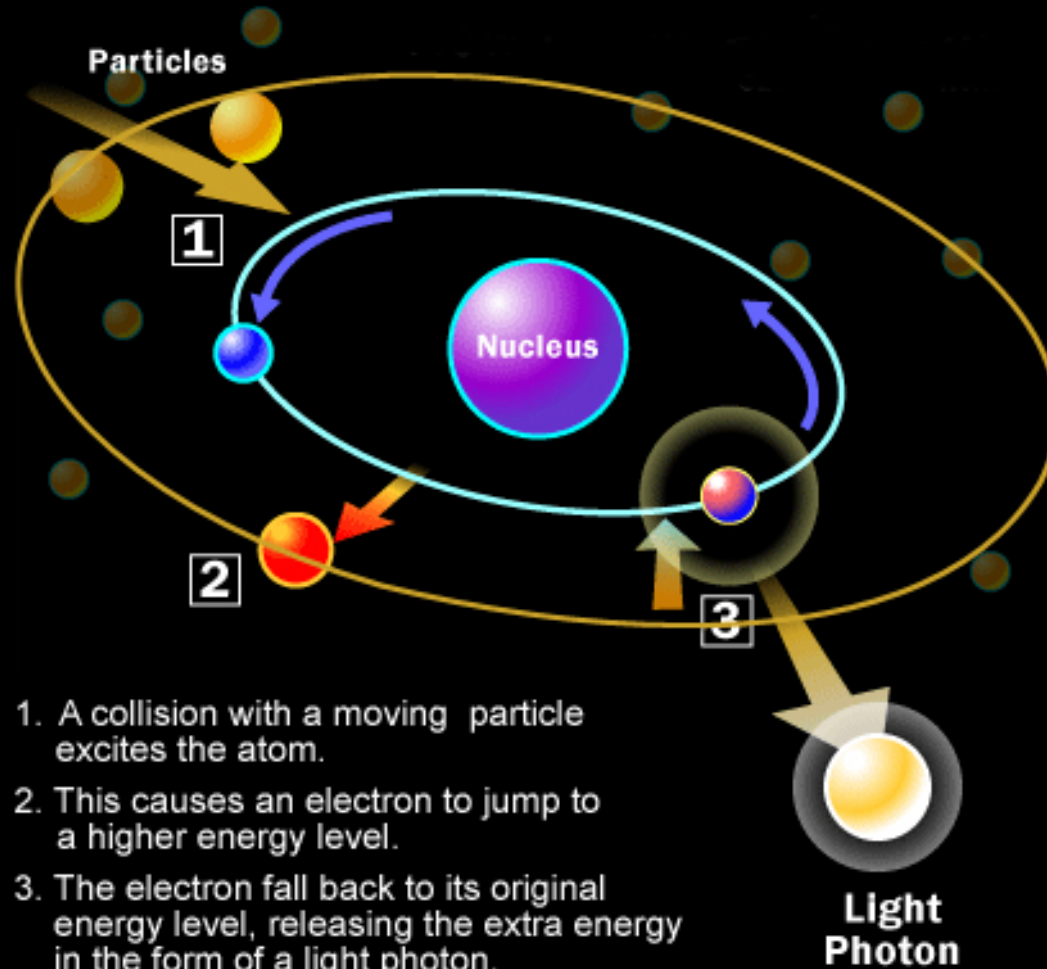
BL08B (80–1200 eV)



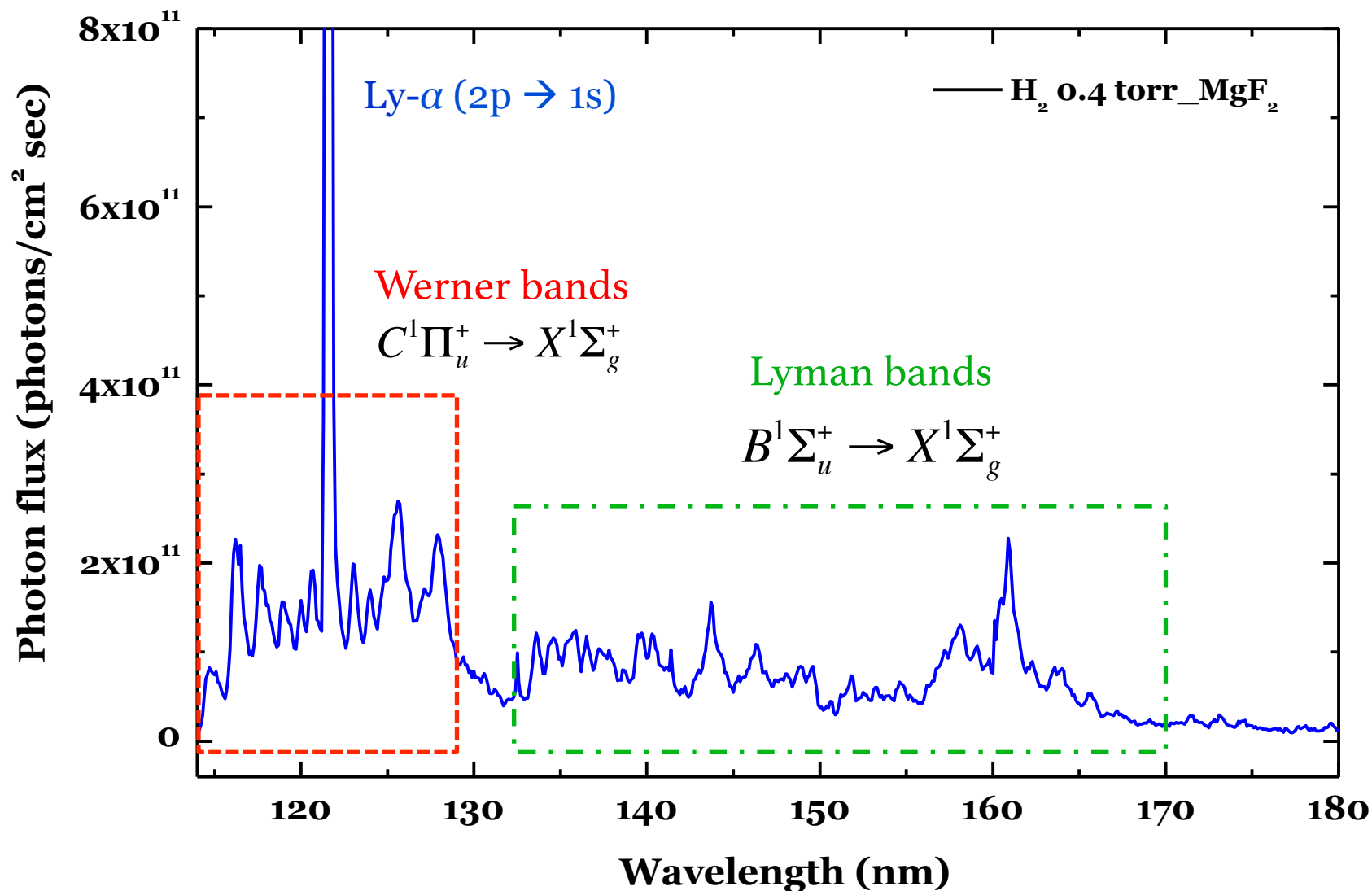
Microwave-Discharge Gas-flow Lamp



HOW ATOMS EMIT LIGHT



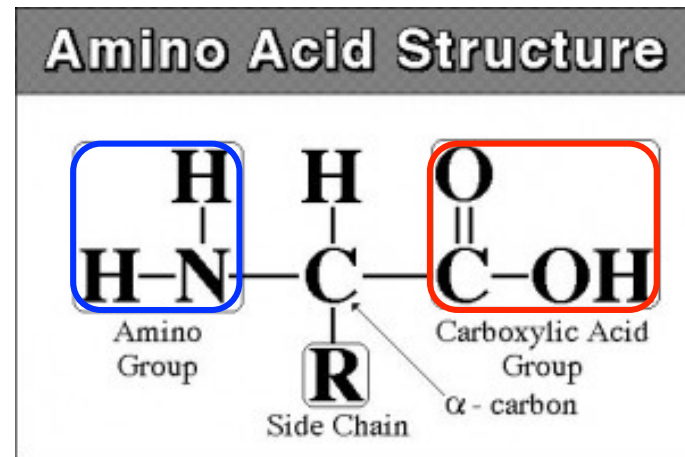
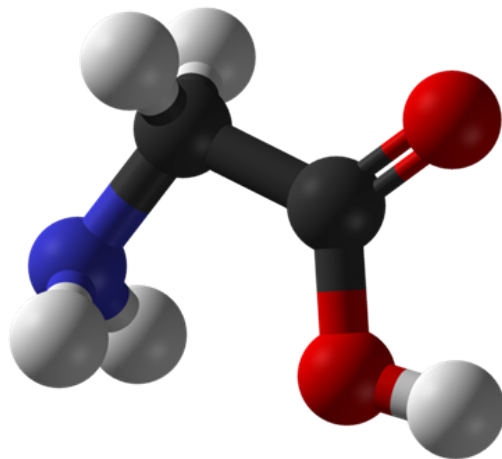
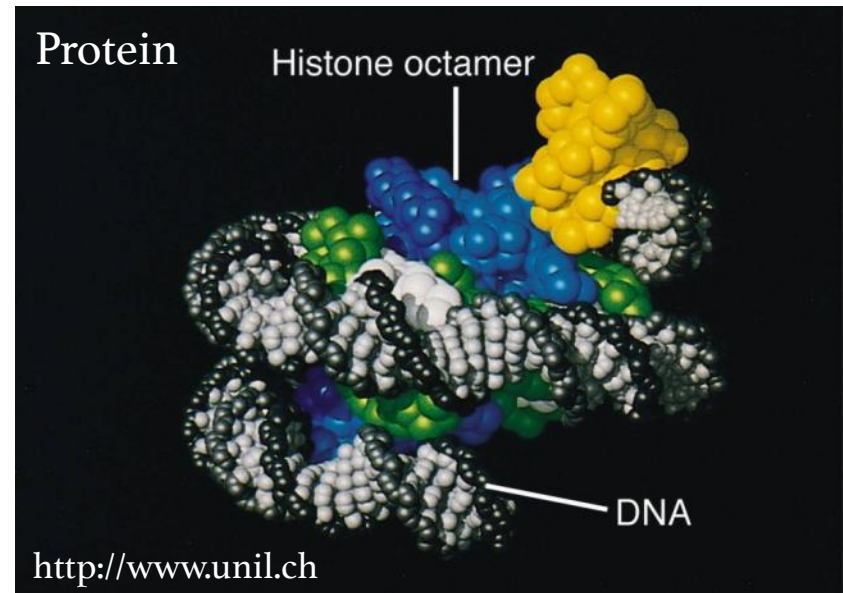
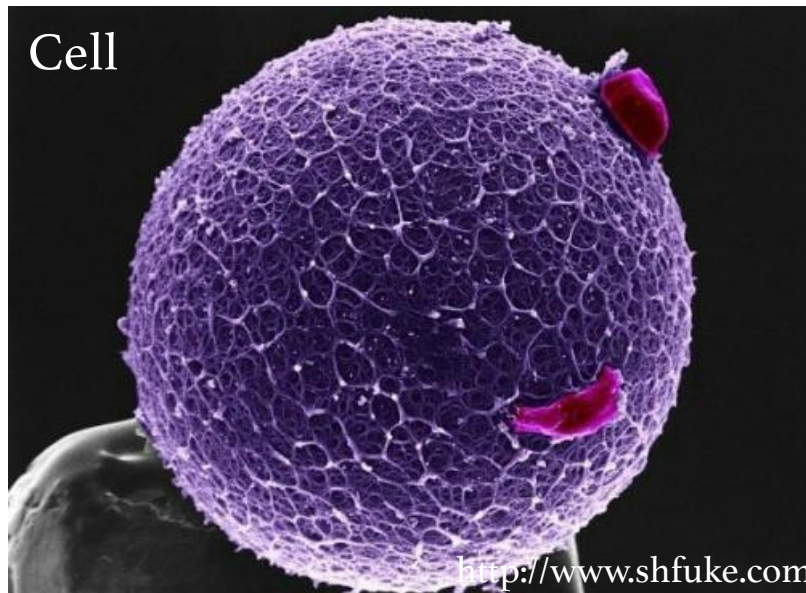
VUV Spectrum of Microwave-Discharge H₂-flow Lamp



Grain Surface

Photo-induced Chemistry

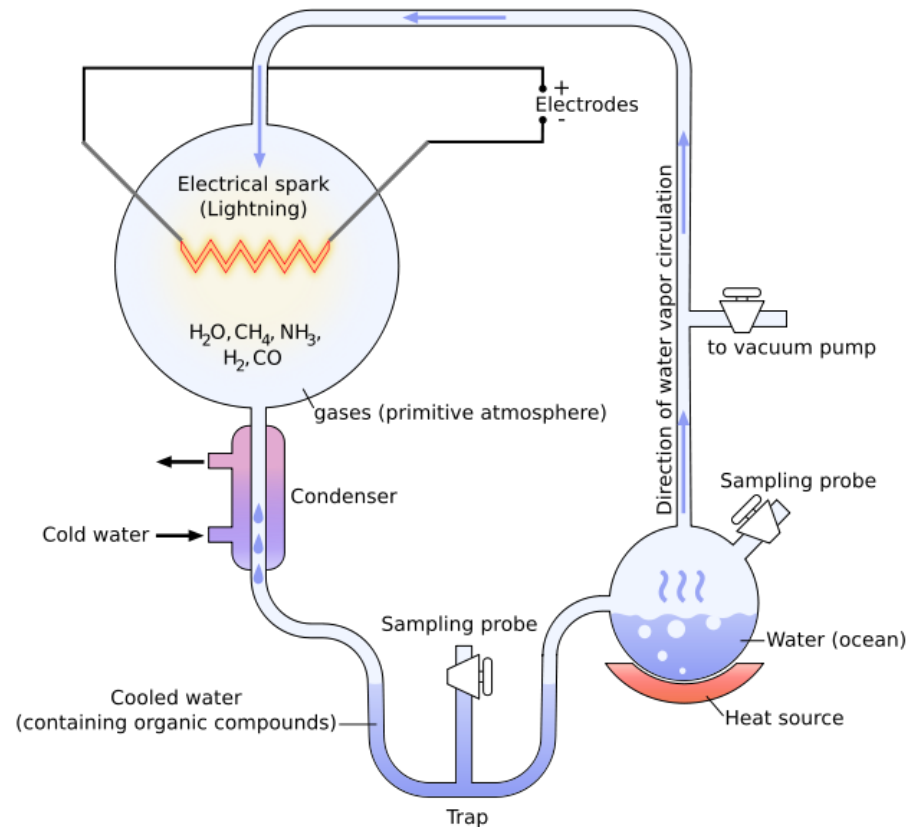
The Origin of Prebiotic Molecules on Primitive Earth



The Origin of Life on Earth



2 % C → amino acids



Argument

There is an absence of **oxygen** and **nitrogen** which are the main elemental constituents of our present environment

Production **CN-bearing molecules** is difficult in an oxidating atmosphere

The oxidation state of Hadean magmas and implications for early Earth's atmosphere

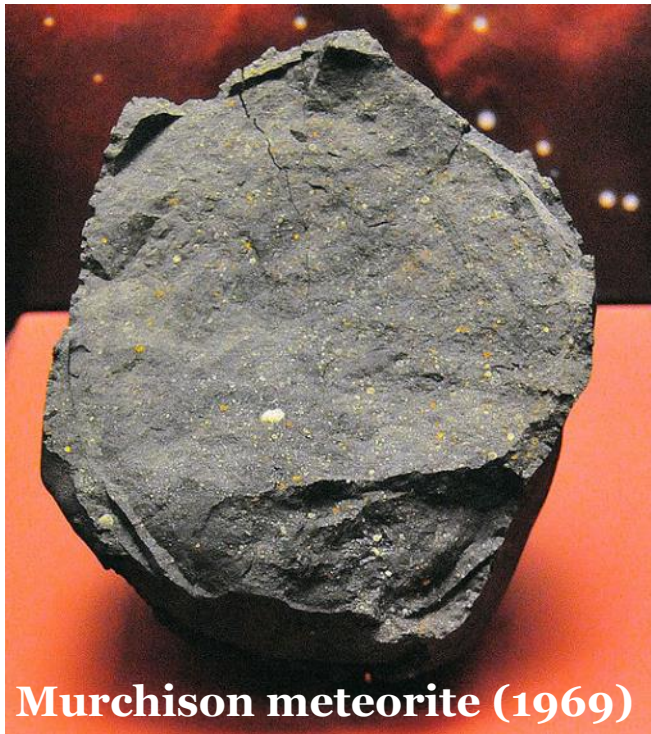
Dustin Trail^{1,2}, E. Bruce Watson^{1,2} & Nicholas D. Tailby^{1,2}

Magmatic outgassing of volatiles from Earth's interior probably played a critical part in determining the composition of the earliest atmosphere, more than 4,000 million years (Myr) ago¹. Given an elemental inventory of hydrogen, carbon, nitrogen, oxygen and sulphur, the identity of molecular species in gaseous volcanic emanations depends critically on the pressure (fugacity) of oxygen. Reduced melts having oxygen fugacities close to that defined by the iron-wüstite buffer would yield volatile species such as CH₄, H₂, H₂S, NH₃ and CO, whereas melts close to the fayalite-magnetite-quartz buffer would be similar to present-day conditions and would be dominated by H₂O, CO₂, SO₂ and N₂ (refs 1–4). Direct constraints on the oxidation state of terrestrial magmas before 3,850 Myr before present (that is, the Hadean eon) are tenuous because the rock record is sparse or absent. Samples from this earliest period of Earth's history are limited to igneous detrital zircons that pre-date the known rock record, with ages approaching ~4,400 Myr (refs 5–8). Here we report a redox-sensitive calibration to determine the oxidation state of Hadean magmatic melts that is based on the incorporation of cerium into zircon crystals. We find that the melts have average oxygen fugacities that are consistent with an oxidation state defined by the fayalite-magnetite-quartz buffer, similar to present-day conditions. Moreover, selected Hadean zircons (having chemical characteristics consistent with crystallization specifically from mantle-derived melts) suggest oxygen fugacities similar to those of Archaean and present-day mantle-derived lavas^{2–4,9,10} as early as ~4,350 Myr before present. These results suggest that outgassing of Earth's interior later than ~200 Myr into the history of Solar System formation would not have resulted in a reducing atmosphere.

Here we report a calibration to determine the oxidation state of a magmatic melt based on the incorporation of cerium (Ce) into zircon. Cerium is unique among elements that partition into zircon (and among the rare-earth elements, REEs) in that it can exist in melts as either Ce⁴⁺ or Ce³⁺. The magnitude of Ce enrichment in zircon depends on the Ce⁴⁺/Ce³⁺ ratio of the medium from which it crystallizes. Because Ce⁴⁺ is vastly more compatible than Ce³⁺ in zircon, more-oxidized melts will yield higher Ce contents in the mineral. To explore the details of Ce uptake, zircons were grown in a piston cylinder apparatus at a pressure of 1 GPa and at temperatures of 900–1,300 °C from hydrous silicate melts (~72 wt% SiO₂) doped with lanthanum (La), Ce and praseodymium (Pr) (with and without phosphorus). Lanthanum and Pr were included as 'bracketing' elements because these exist only as 3+ ions, and partition coefficients for zircon trivalent REEs are known to monotonically increase from La to lutetium (Lu) (ref. 13); by convention, partition coefficients are expressed as the crystal/melt concentration ratio, $D_{\text{REE}}^{\text{zrc/melt}}$ (here zrc indicates zircon, the crystal concerned). This systematic behaviour provides a convenient reference for natural zircon to characterize the relative enrichment of Ce in zircon, relative to other REEs, with changes in f_{O_2} . This is expressed as a 'Ce anomaly', $(\text{Ce}/\text{Ce}^*)_D$, and is calculated in the following manner:

$$\left(\frac{\text{Ce}}{\text{Ce}^*}\right)_D = \frac{D_{\text{Ce}}^{\text{zrc/melt}}}{\sqrt{D_{\text{La}}^{\text{zrc/melt}} \times D_{\text{Pr}}^{\text{zrc/melt}}}} \quad (1)$$

where $D_{\text{Ce}}^{\text{zrc/melt}}$ is the combined partition coefficient of Ce⁴⁺ and Ce³⁺ in zircon, and $D_{\text{La}}^{\text{zrc/melt}}$ and $D_{\text{Pr}}^{\text{zrc/melt}}$ are respectively the partition coefficients for trivalent La and Pr. The denominator on the right hand



Murchison meteorite (1969)

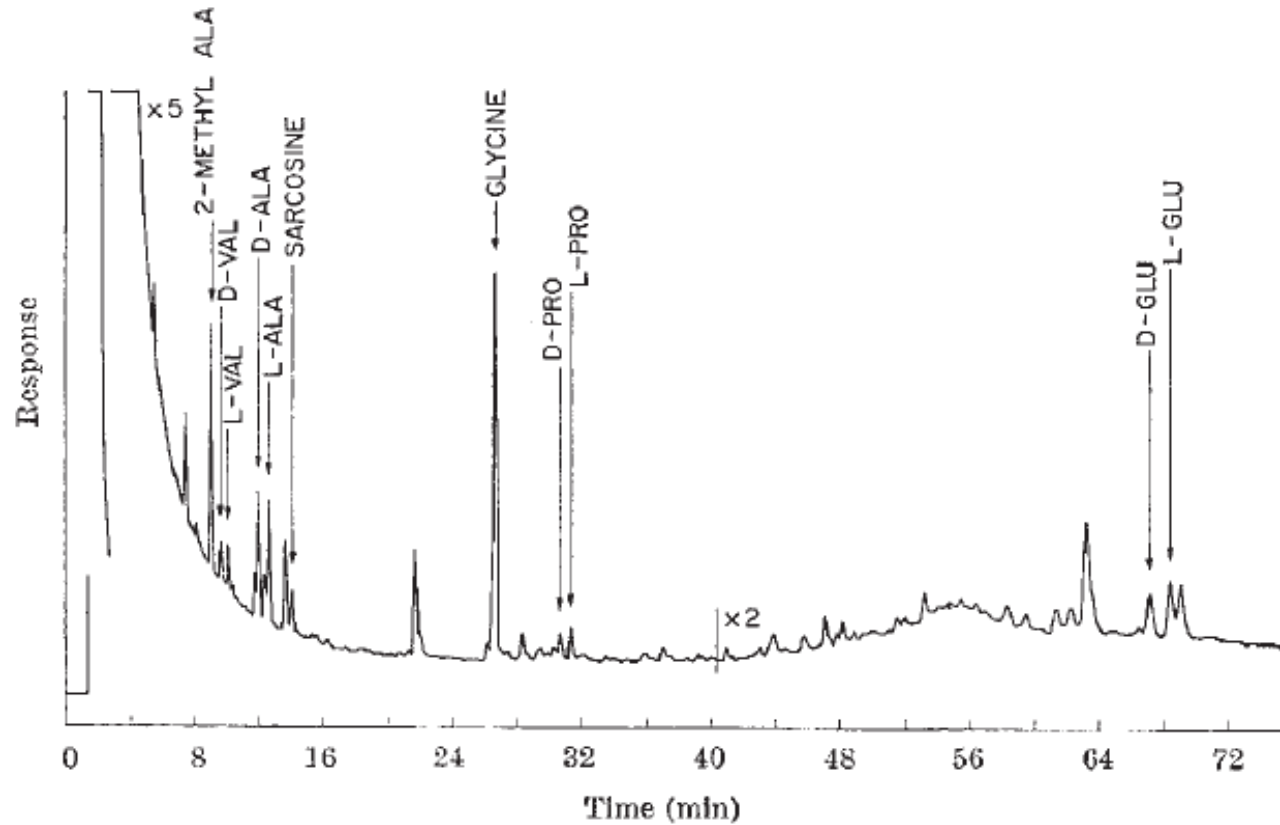


**High-performance
liquid chromatography**



**Gas chromatography–
mass spectrometry**

Over **15** amino acids have been identified



Kvenvolden *et al.* 1970, *Nature*, **228**, 923

Contamination ?

Isotope Fractionation

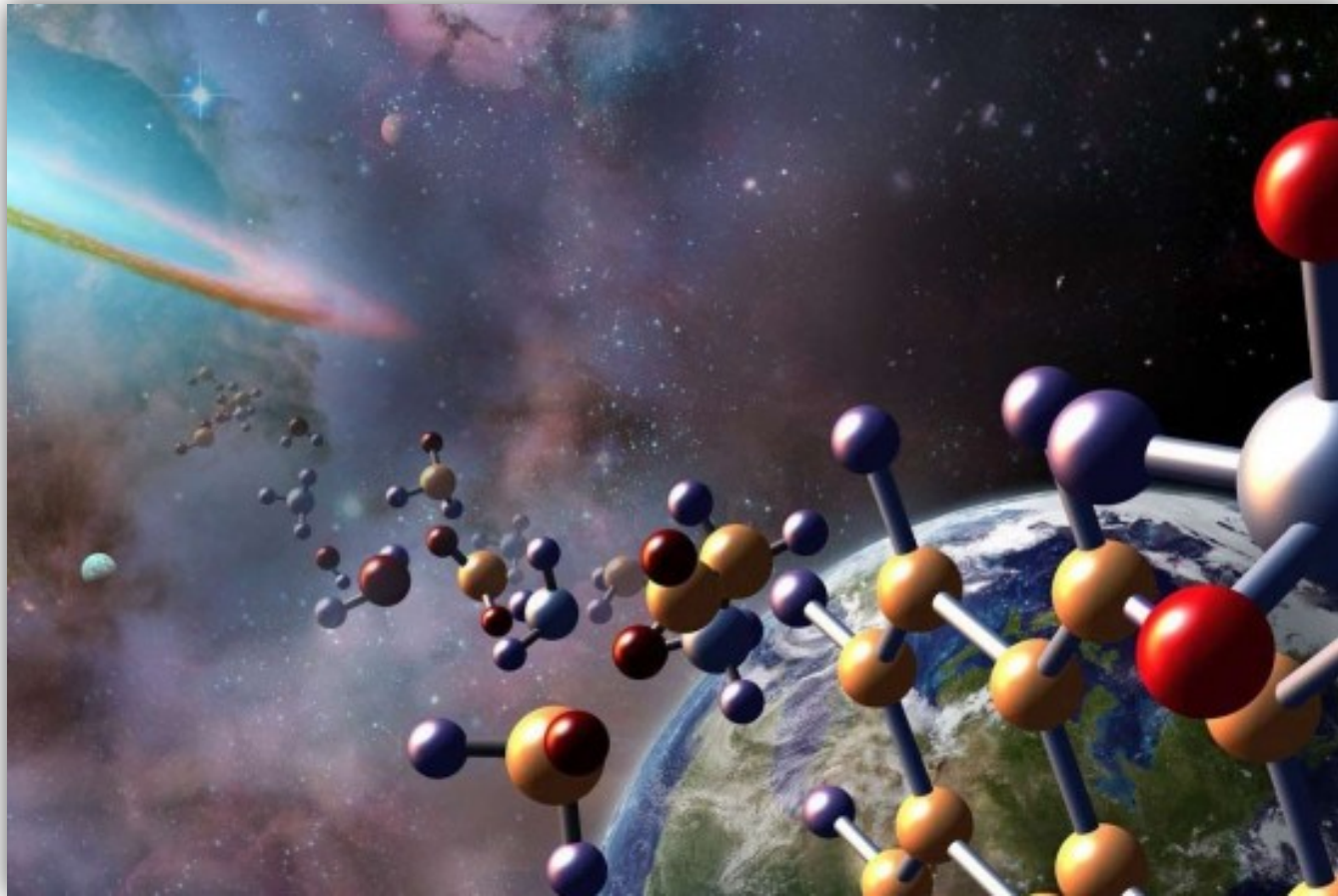
Table 1 Amino-acid abundances and $\delta^{15}\text{N}$ values

Amino acid	Concentration (nmol g ⁻¹)	$\delta^{15}\text{N}$ (‰)*
α -Aminoisobutyric acid	20.1	+184
Sarcosine	ND†	+129
Isovaline	8.0‡	+66
Glycine	24.5	+37
β -Alanine	12.8	+61
D-Alanine	–§	+60
L-Alanine	10.4‡	+57
L-Leucine	2.5§	+60
D,L-Proline	ND†	+50
D,L-Aspartic acid	4.7§	+61
D-Glutamic acid	–§	+60
L-Glutamic acid	10.8§	+58

$$\delta^{15}\text{N}(\text{‰}) = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right] \times 10^3$$

Engel *et al.* 1997, Nature **389**, 265

A possible scenario of the origin of life



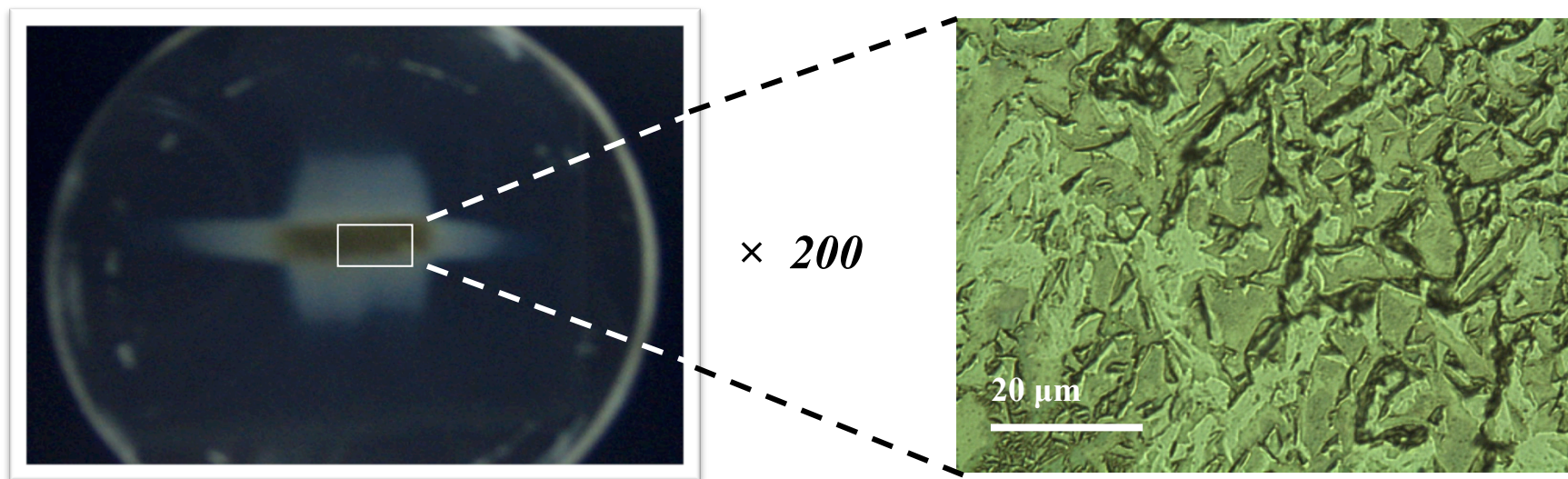
What can we do for the hypothesis
Origin of Life Came From Outer Space?

Species	Comet Hale-Bopp ^a	NGC 7538 IRS 9 ^b	W33A ^b
H ₂ O	100	100	100
CO	20	16	9
CO ₂	6	22	14
NH ₃	0.6	13	15
CH ₃ OH	2	5	22
H ₂ CO	1	4	1.7-7
HCOOH	0.05	3	0.4-2
CH ₄	1	2	2
C ₂ H ₂	0.5
C ₂ H ₆	0.5
OCN ⁻	0.37	1	3
OCS,XCS	0.7	...	0.3
SO ₂	0.15

a. Crovisier et al. 1998, Faraday Discussion, 109, 437

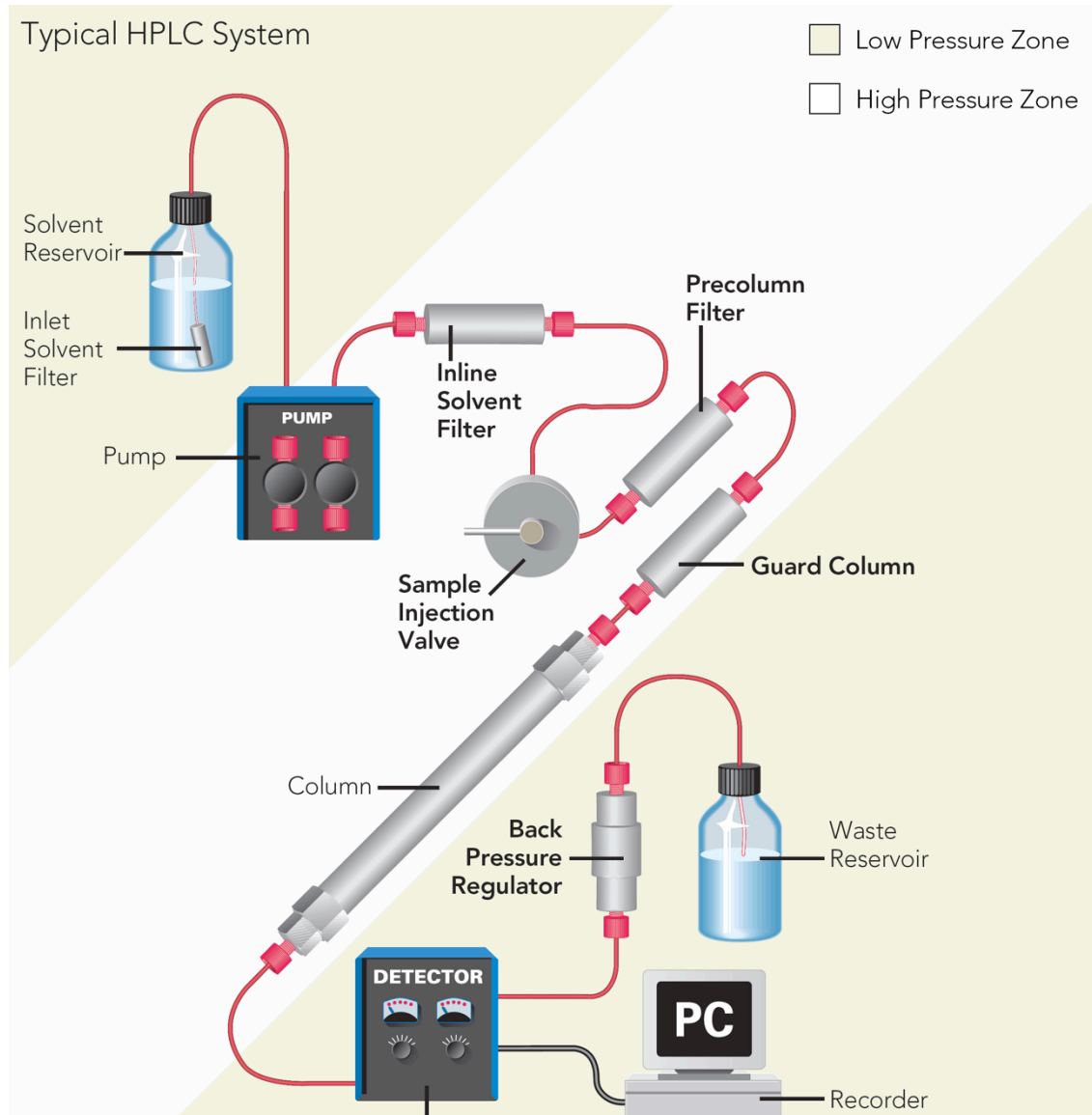
b. Gibb et al. 2000, ApJ, 536, 347

Residue of $H_2O+CO_2+NH_3$ ice mixture

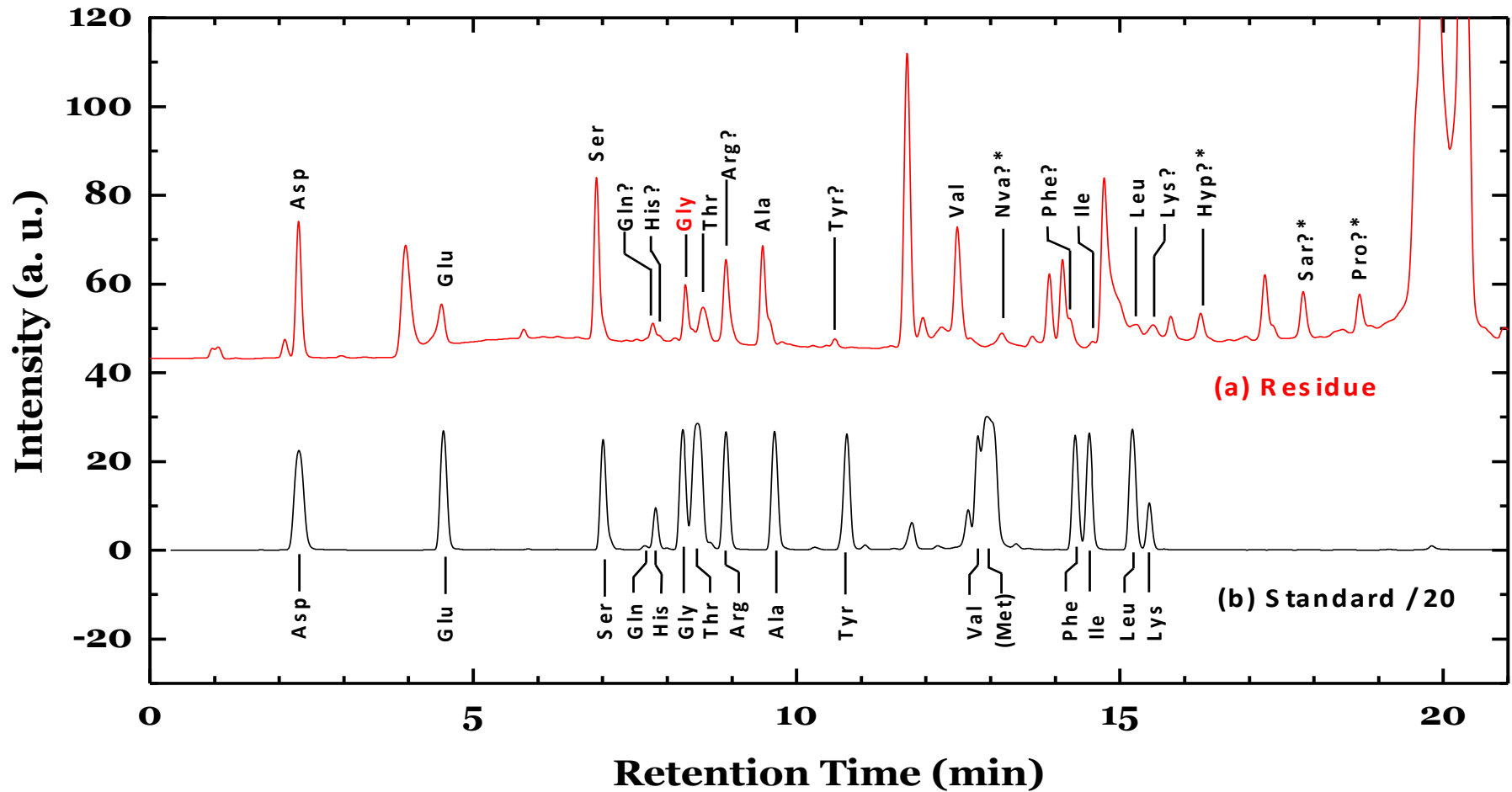


After broad band VUV/EUV irradiation (4-20 eV) and warmed up (15-300 K)

High-performance liquid chromatography



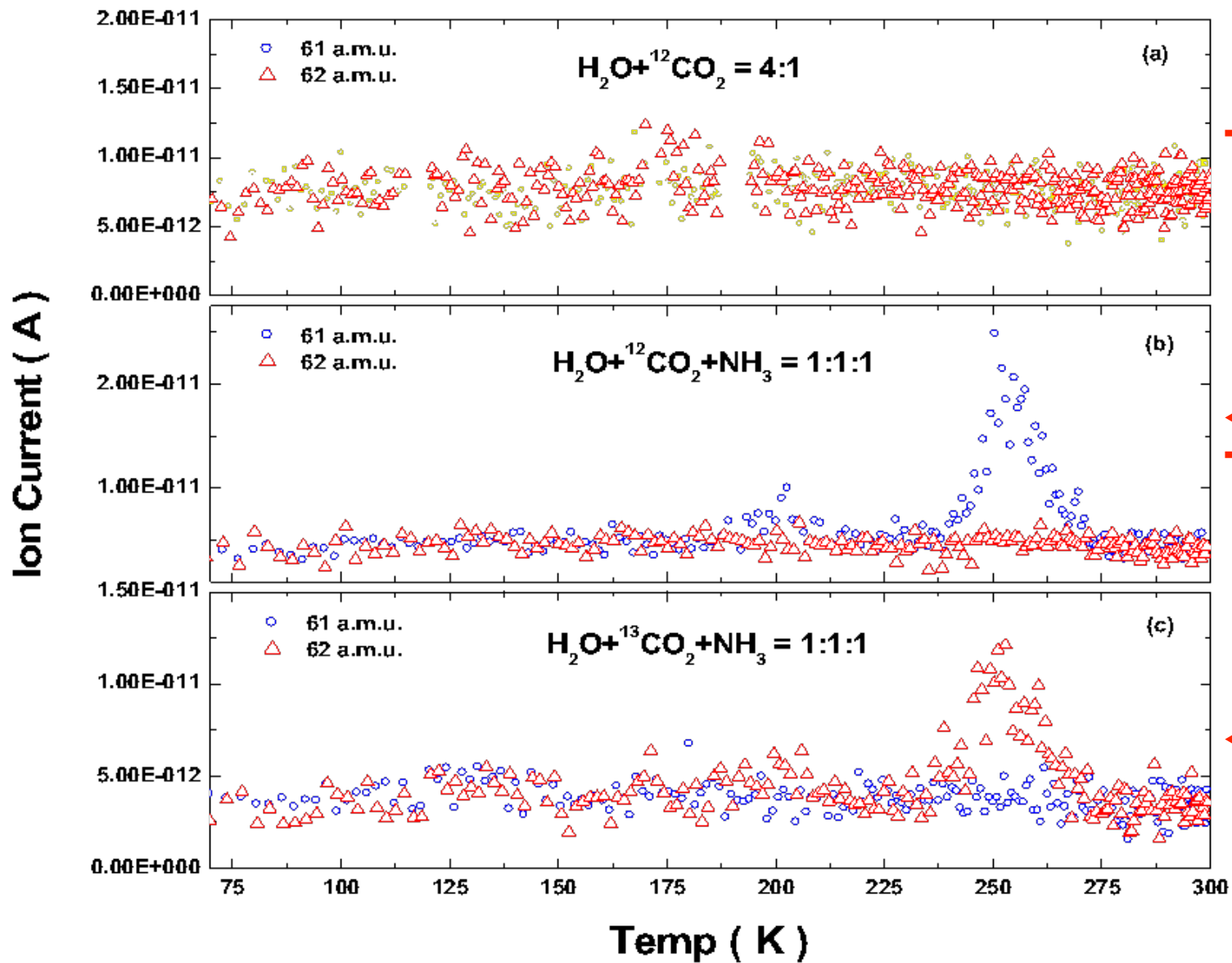
> 9 amino acids have been identified



Nuevo et al. 2007, Adv. Space Res., 40, 1628

It seems that amino acids are not
difficult to be produced !

But the problems is **How** amino acids
be produced ?

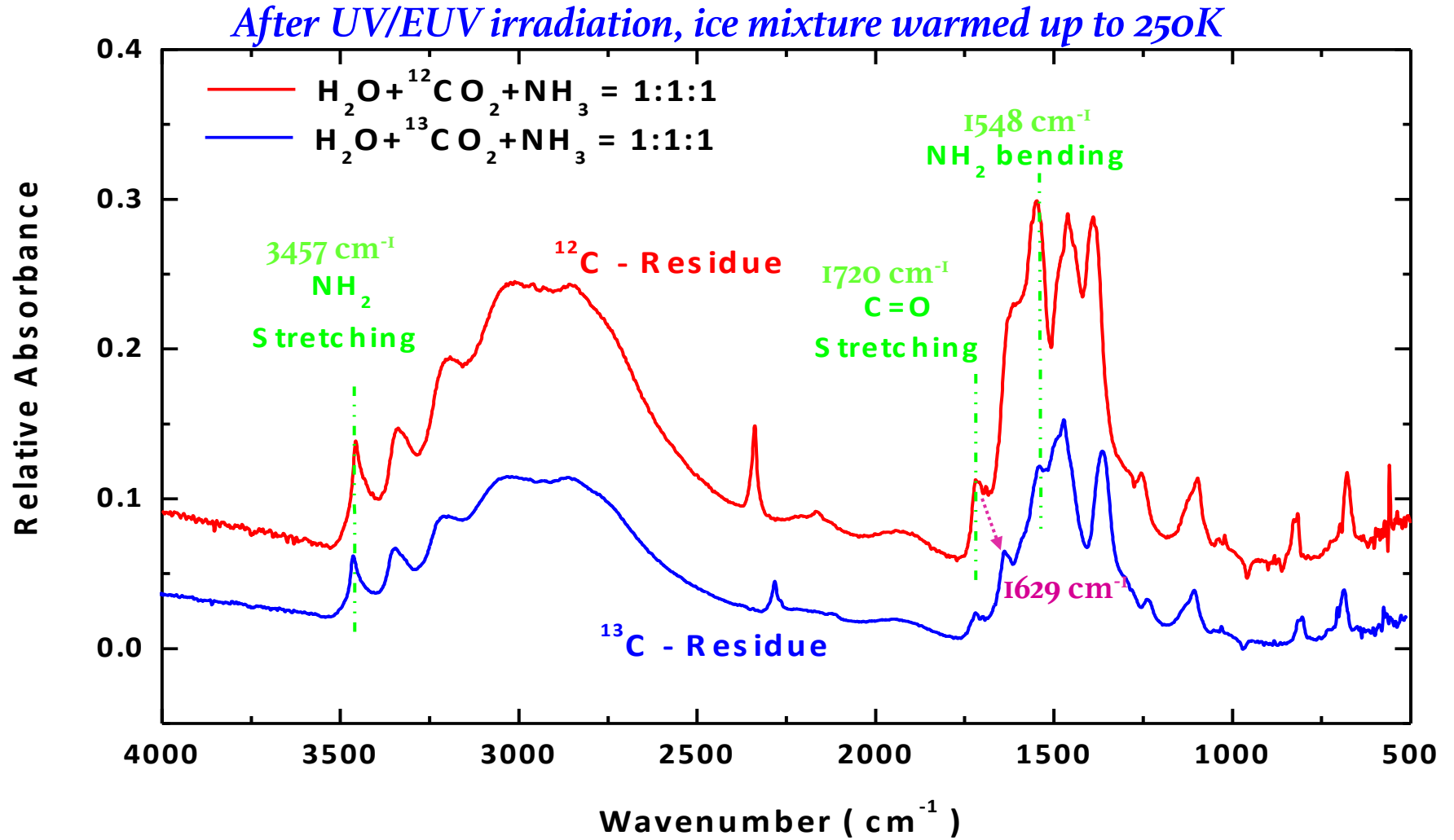


Contained

N

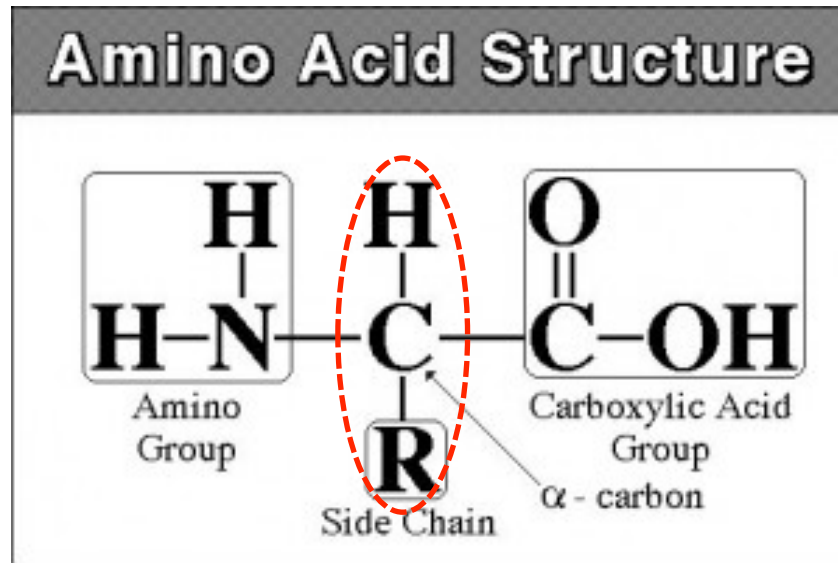
Contained only

One C

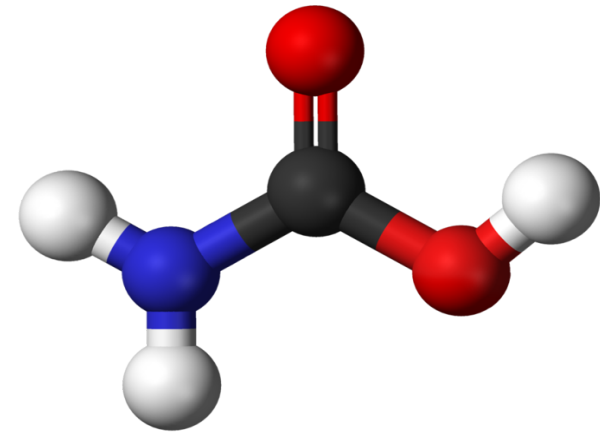


Chen *et al.* 2007, *A&A*, **464**, 253-257.

A Molecule called carbamic acid



$m/z = 61$

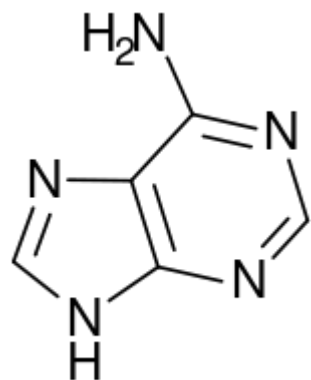


It is technically the simplest amino acid

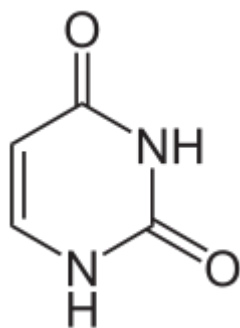
Besides amino acids, *Uracil* was also discovered in Murchison meteorite



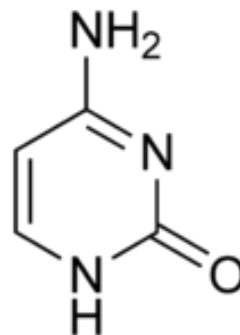
Ribonucleic acid (RNA) 核糖核酸



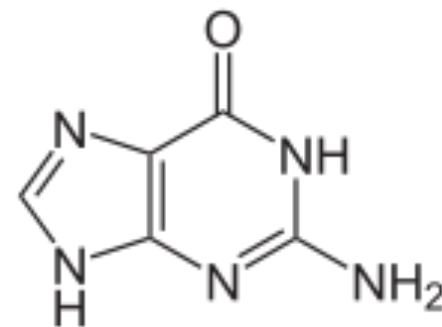
Adenine
腺嘌呤



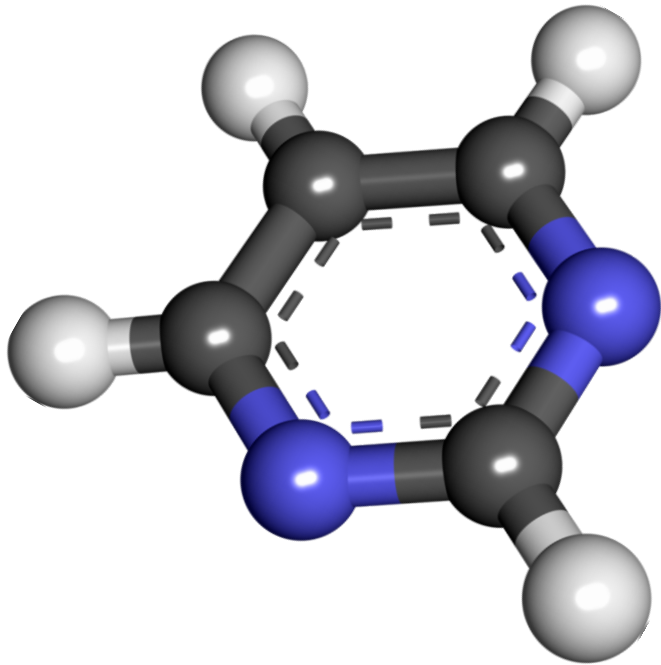
Uracil
尿嘧啶



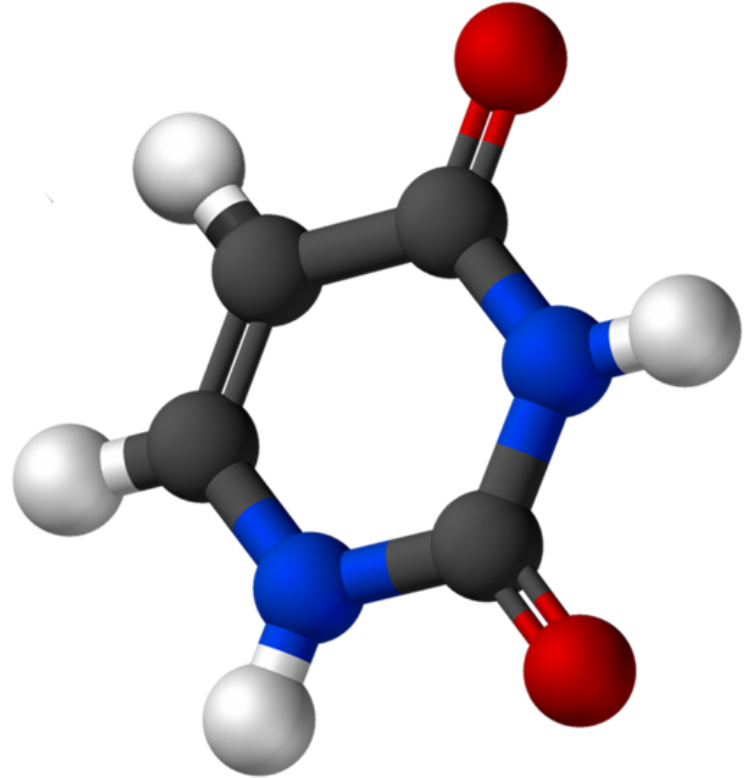
Cytosine
胞嘧啶



Guanine
鳥嘌呤



Pyrimidine
嘍啉

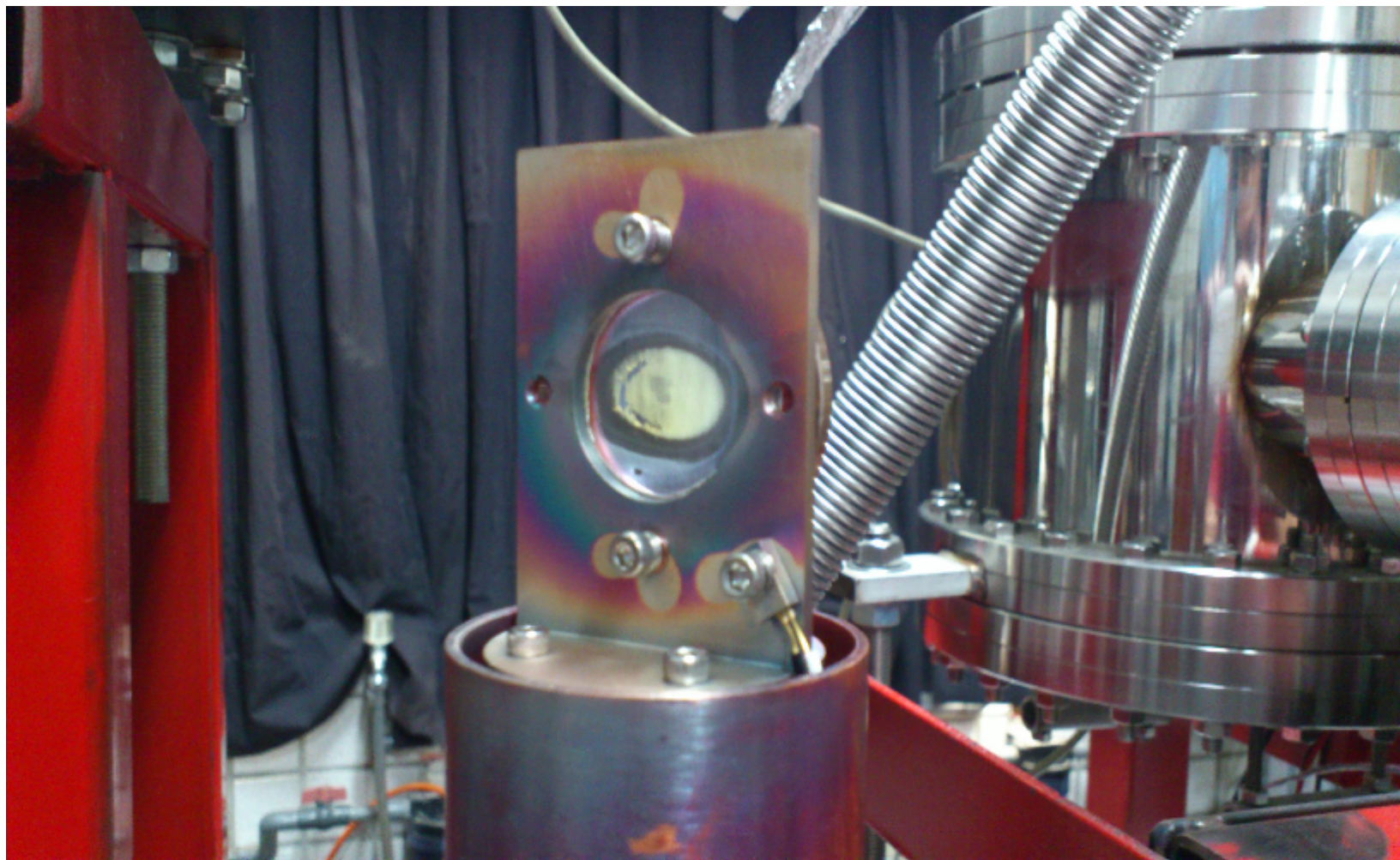


Uracil
尿嘍啉

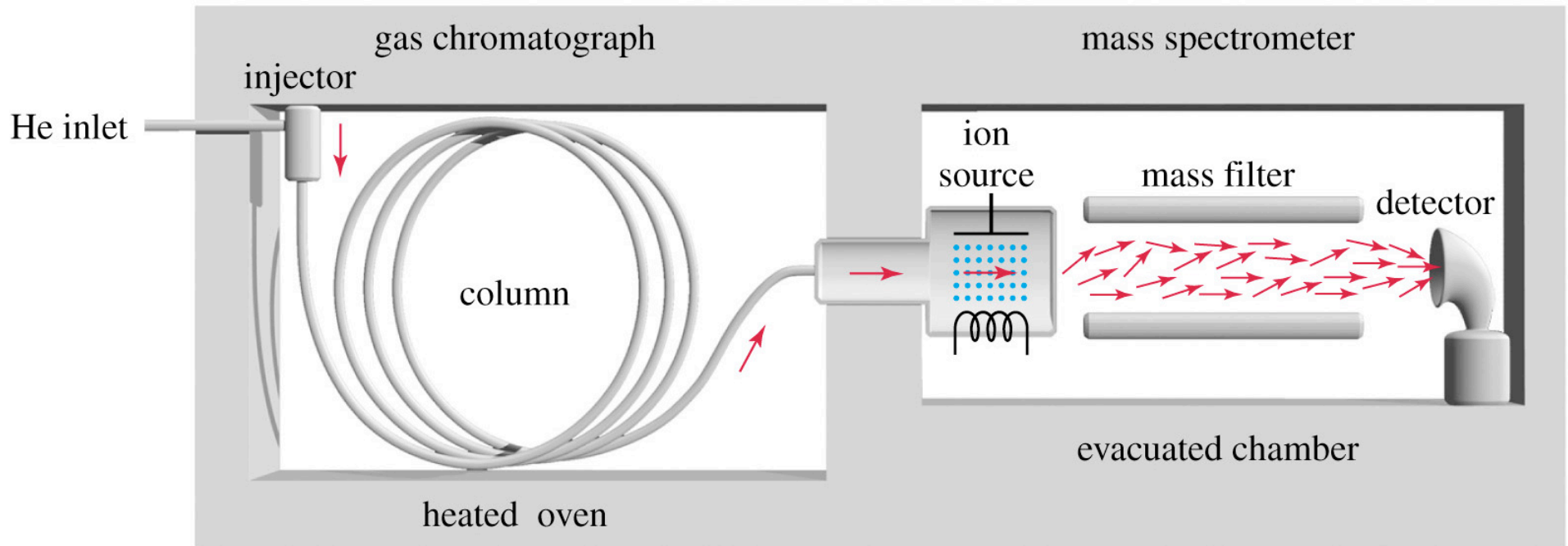


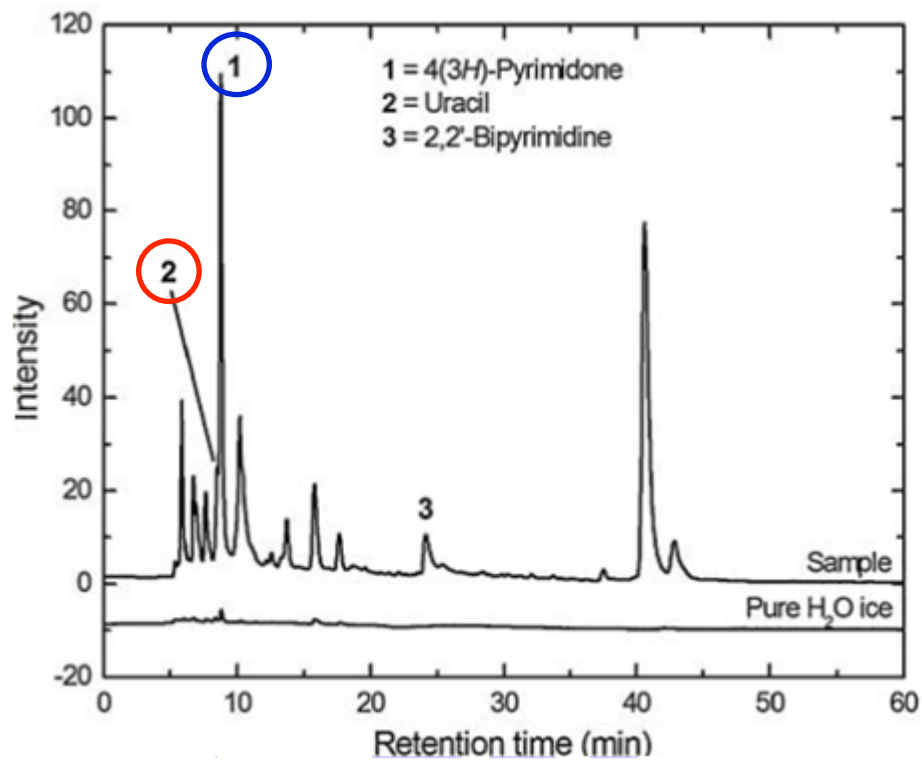
Irradiation and deposition simultaneously for 24 hr



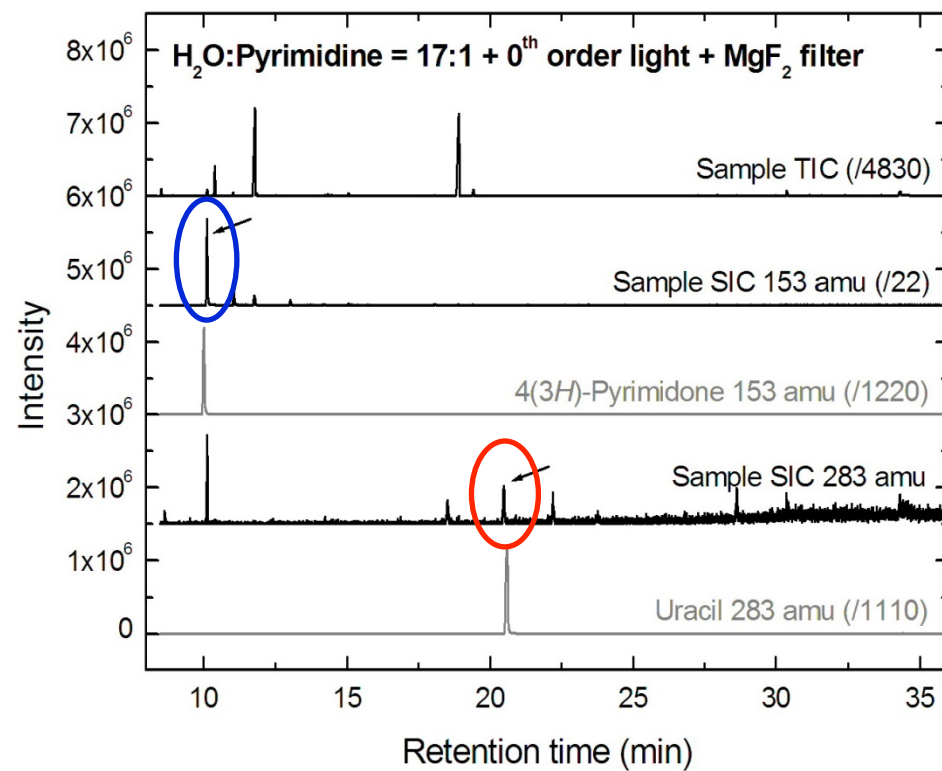


High-Performance Liquid Chromatography

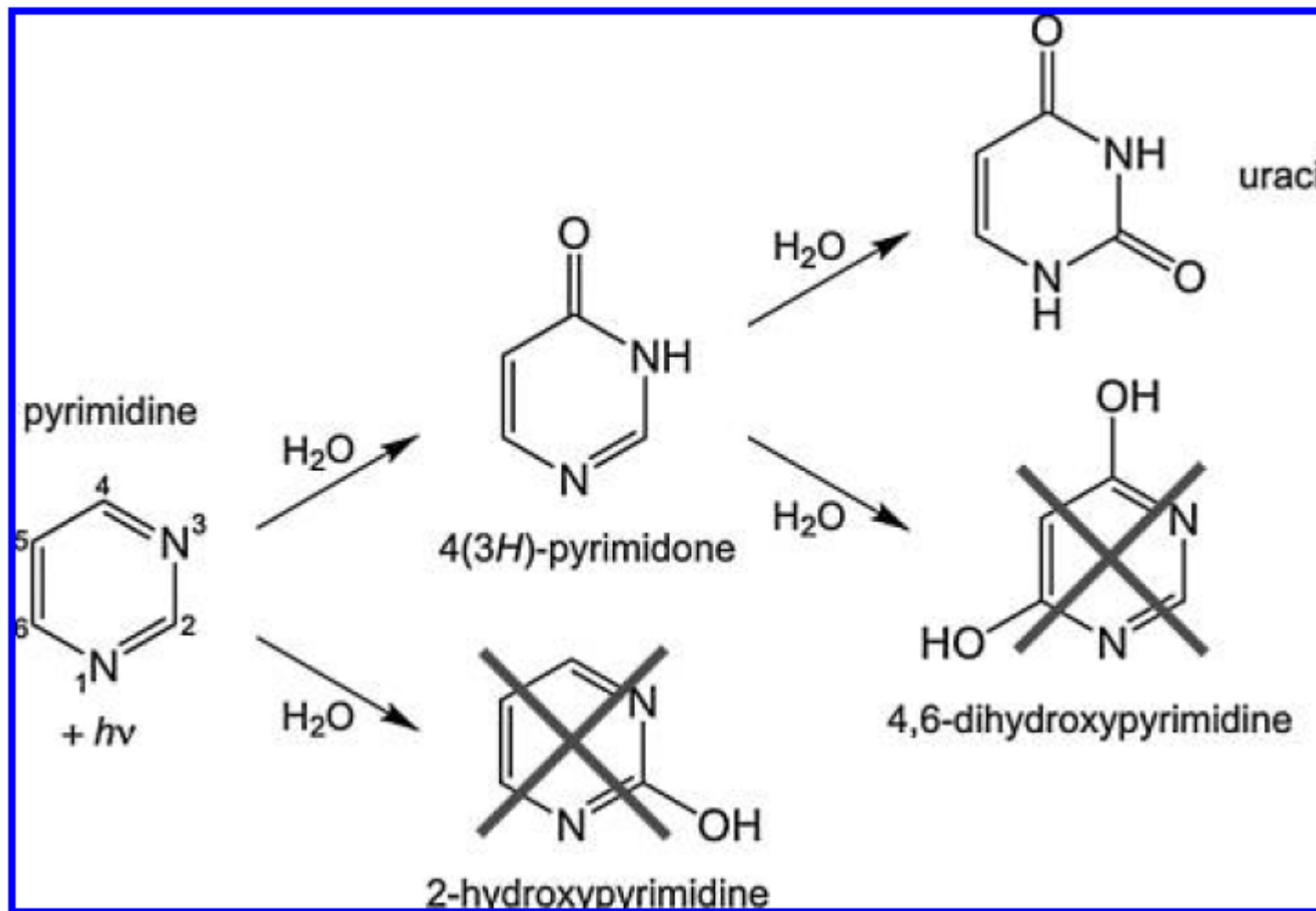




HPLC



GC-MS

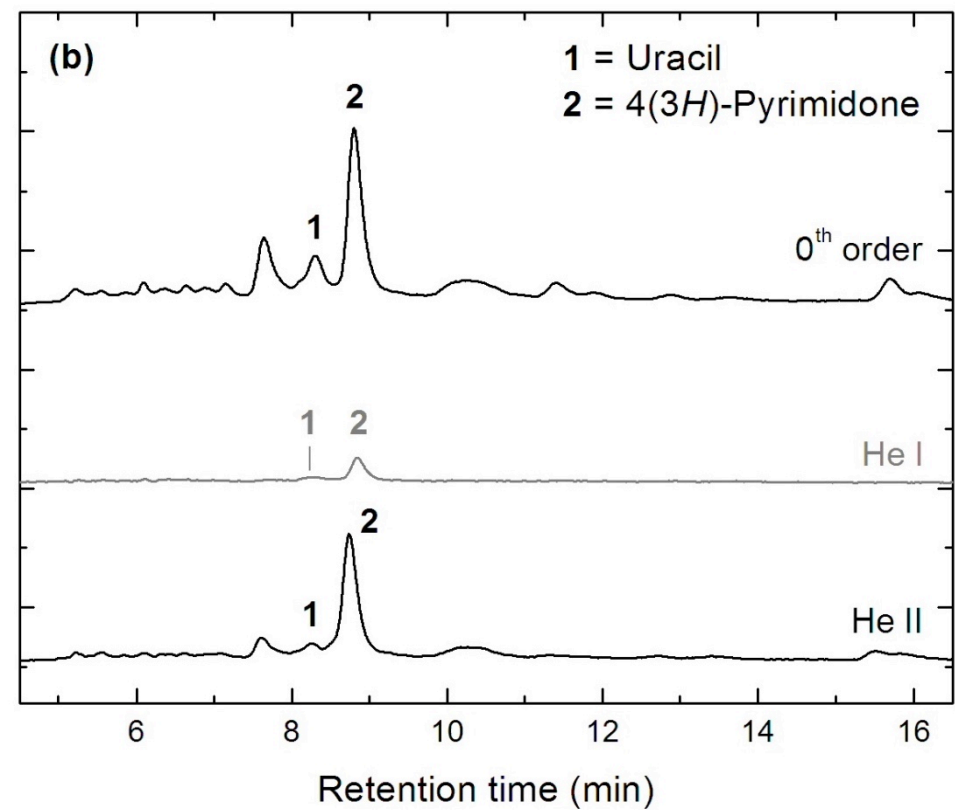
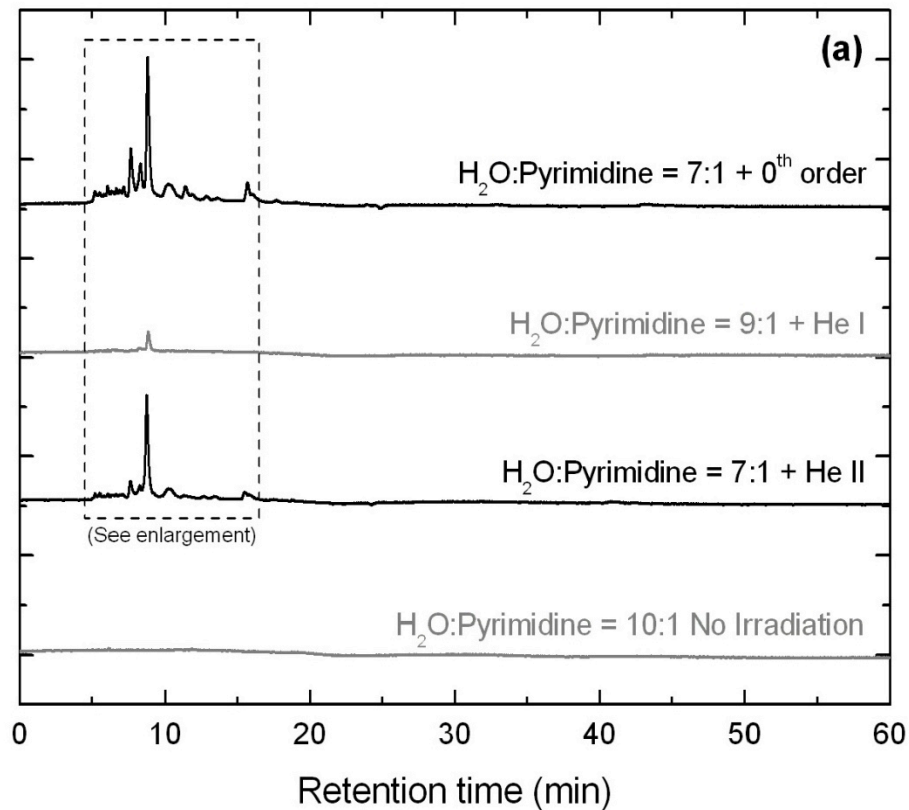


Nuevo *et al.* 2010, JCP, 133, 104303

Various astrophysical environments have various UV fields



Sample	4(3H)-Pyrimidone /Uracil
0 th Order Beam (4-45 eV)	4.4
He I Line (21.23 eV)	254
He II Line (40.78 eV)	36.5
H ₂ Lamp (7.3-10.9 eV)	13.9



Soft X-ray Irradiation

X-ray irradiation study (200 – 1200 eV)

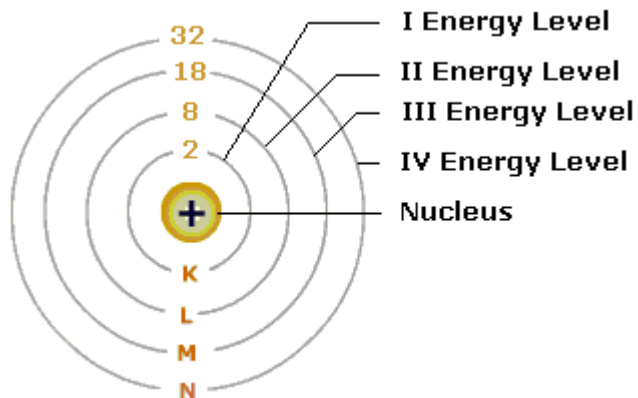
Young solar type stars emit X-rays at a level **3-4 orders** of magnitude higher than the present-day Sun.

Feigelson et al. 2003, *ApJ*, **84**, 911
Favata et al. 2005, *ApJS*, **160**, 469

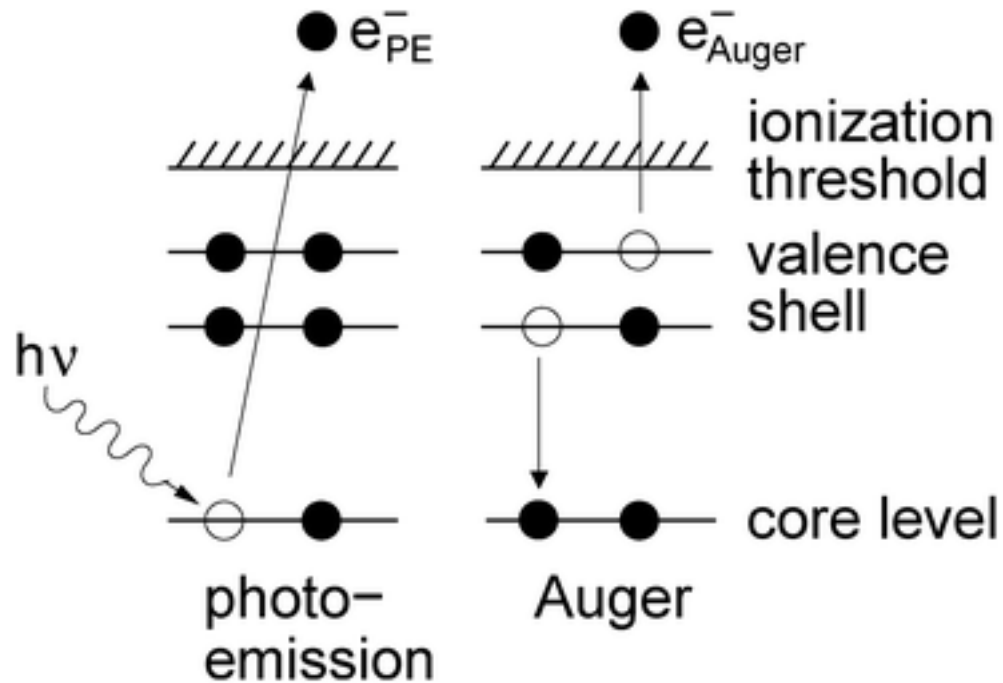


➤ Break bond

➤ Eject electron from inner shell



Photoelectron & Auger electron



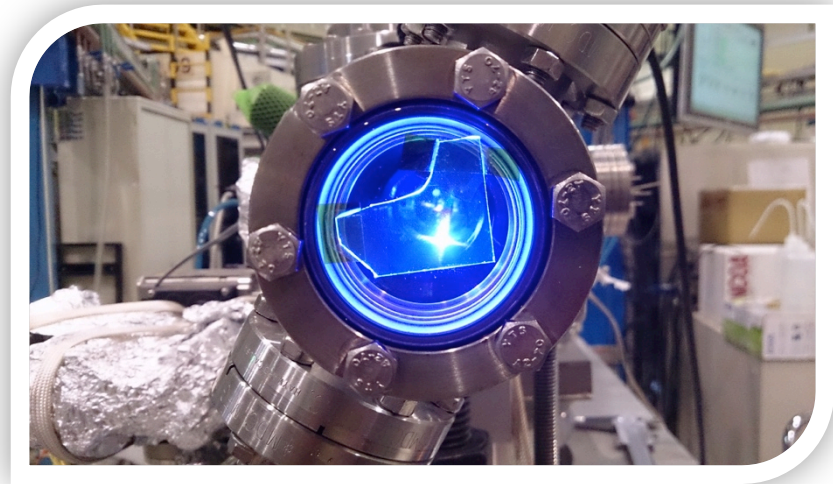
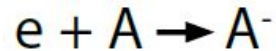
Eject electron from inner shell

High energy electrons

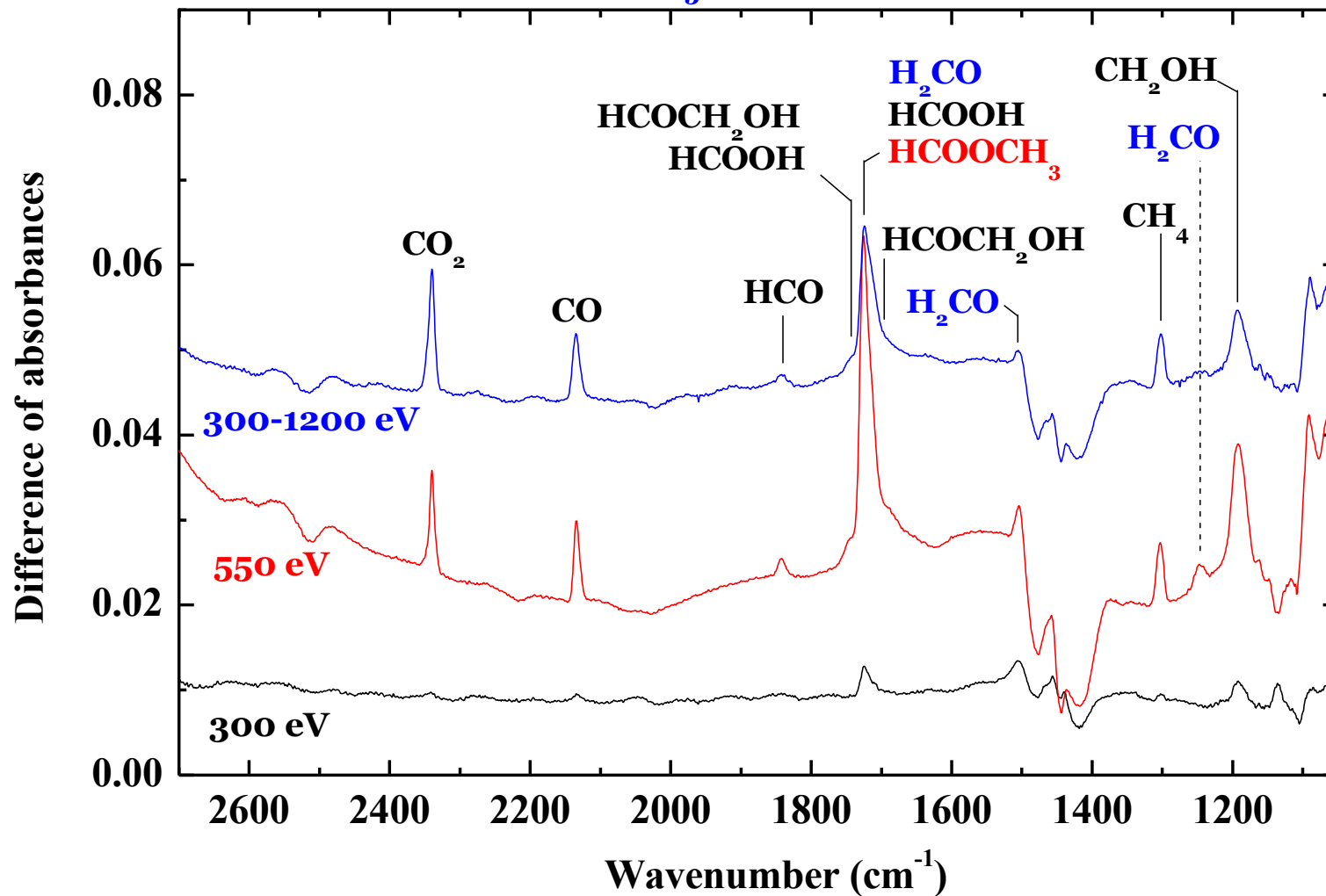
Degrade energies in multiple ionization events

Low energy electrons

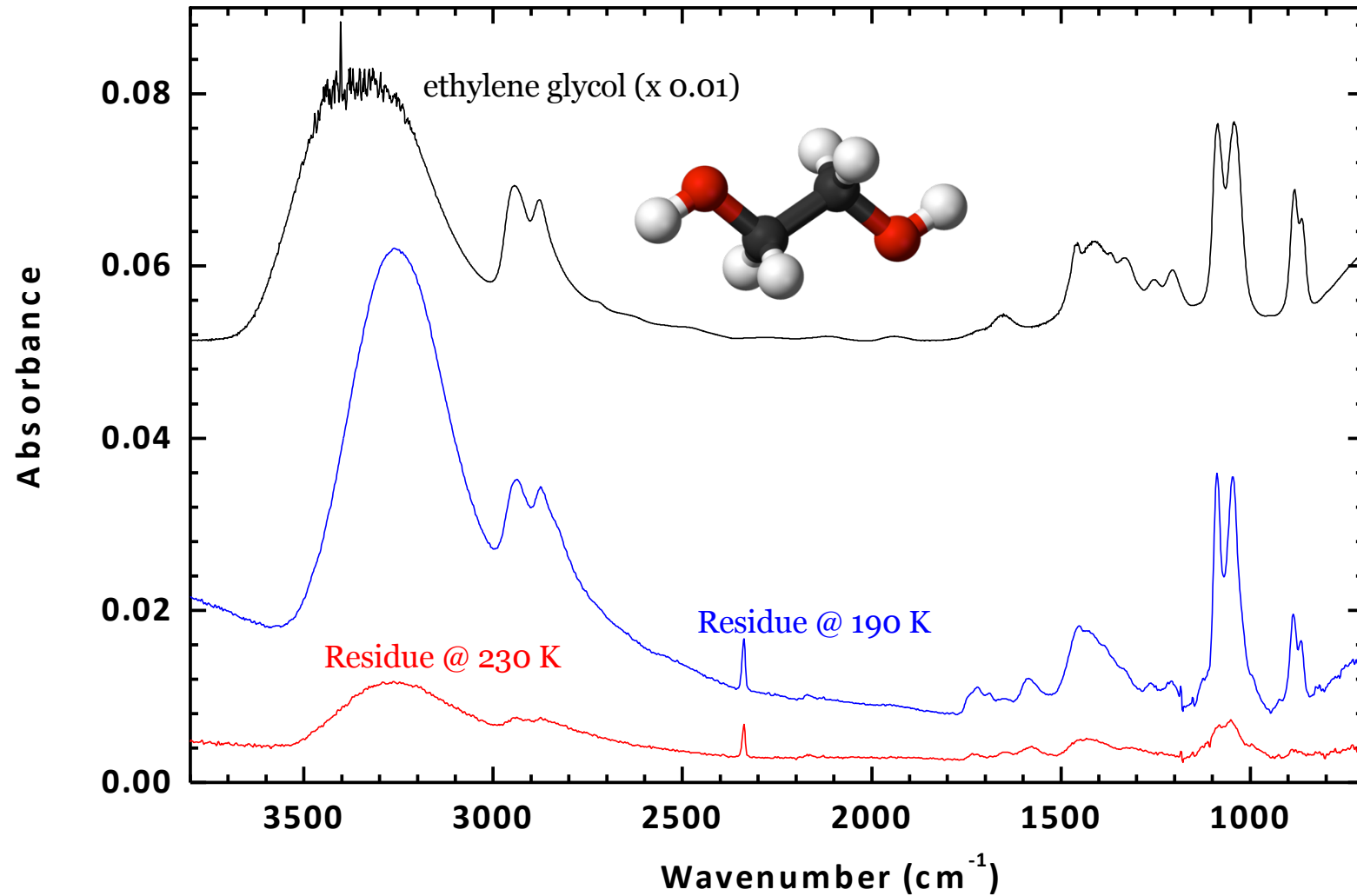
Dissociative electron attachment (DEA)



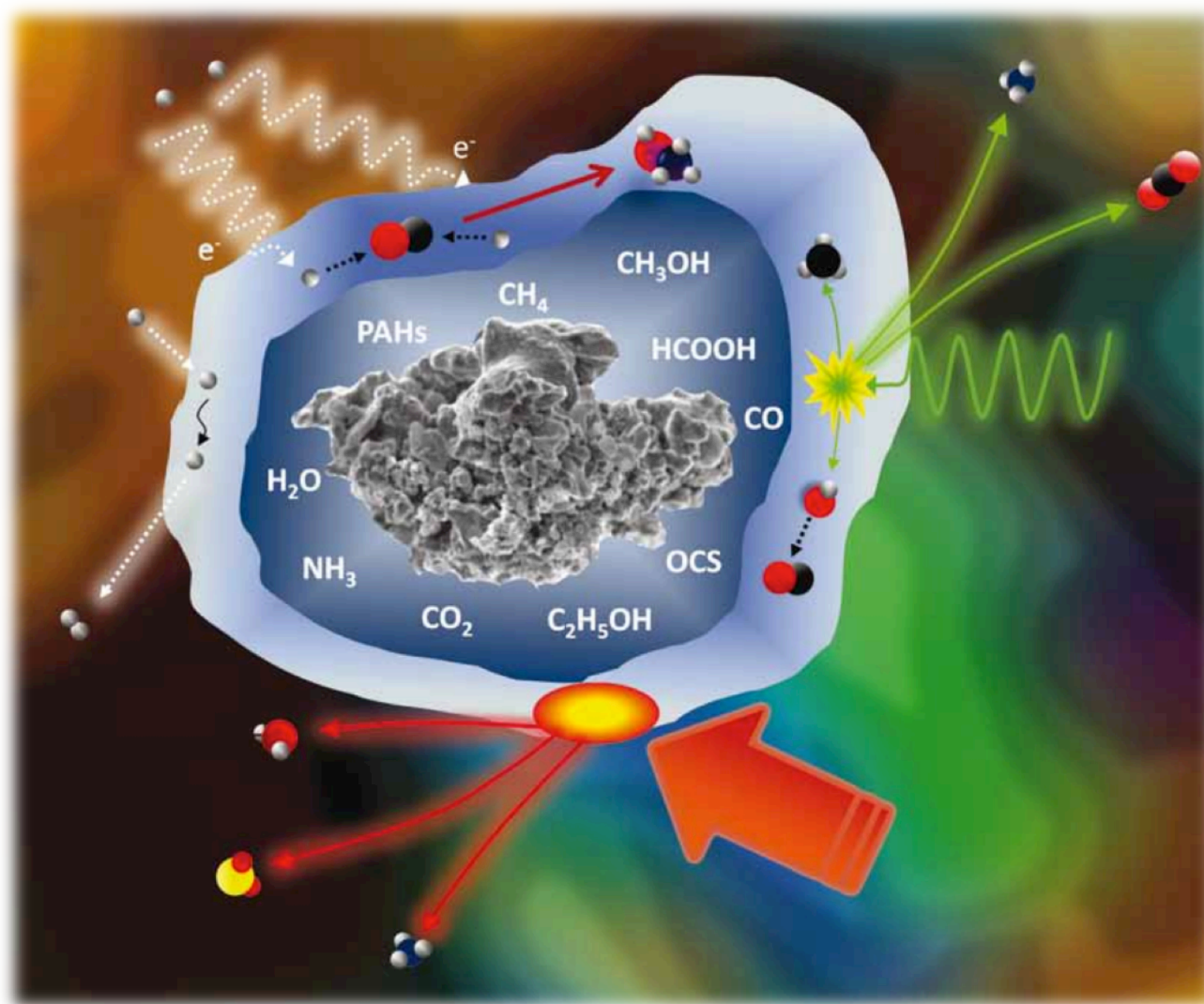
Pure CH₃OH ice @ 14 K



X-rays irradiation of pure CH₃OH ice



Summary



Cited: PCCP, 12, 5929 (2010)



Dr. A. Jimenez-Escobar



Dr. A. Ciaravella



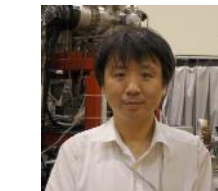
Prof. C. Cecchi-Pestellini



Prof. Wing-Huen Ip



Prof. Ching-Chi Chu



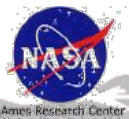
Dr. Hok-Sum Fung



Dr. G. M. Muñoz Caro



Dr. Michel Nuevo



Thank you for your attention