A database of VUV photo-absorption cross sections in the gas and solid phase using synchrotron radiation

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The Open University

Kasteel Oud Poelgeest, Leiden, February 3 (4) -5, 2014

VUV spectroscopy in astronomy and planetary science

- **(V)UV region (90) 110 – 320 nm**
- Spectroscopic diagnostics of the plasmas found in a wide variety of astronomical objects.

(1) Wind and mass-loss properties of hot, massive stars;

(2) Chromospheric activity and mass loss in cool stars

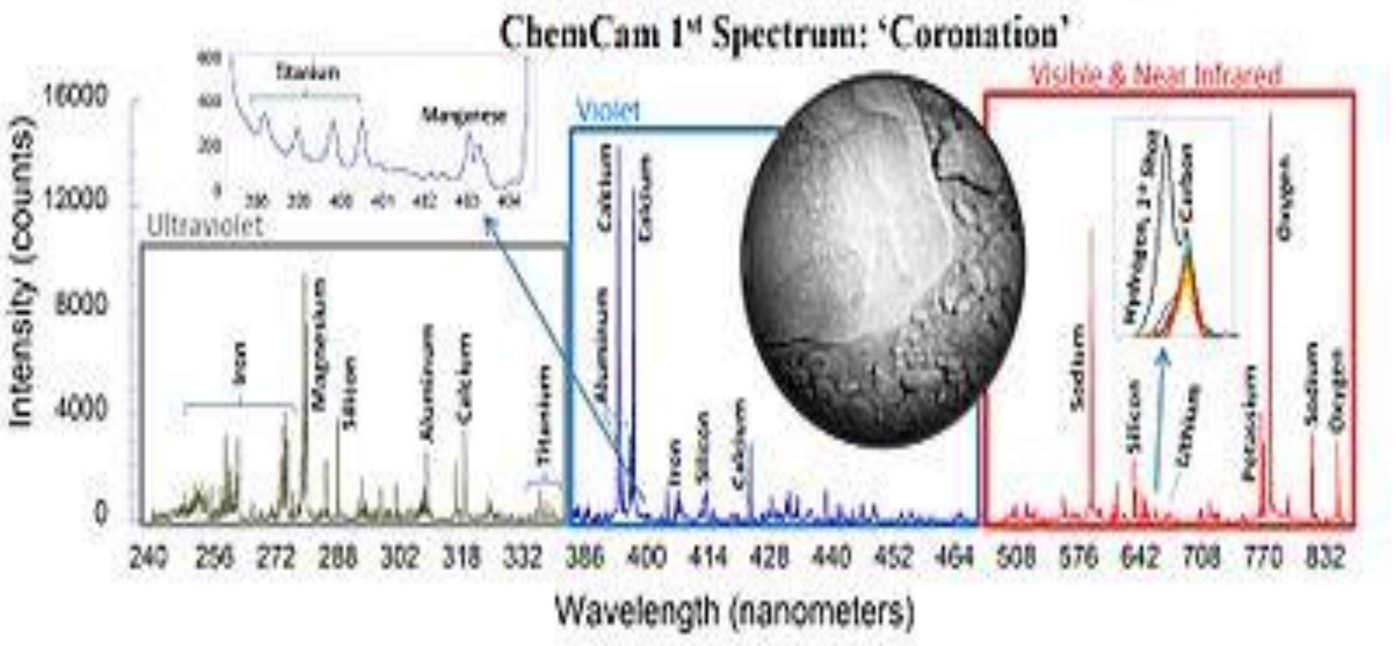
(3) Precise determination of stellar masses in binaries;

(4) The evolution of starburst galaxies

(5) The variability of active galactic nuclei.

VUV spectroscopy in astronomy and planetary science

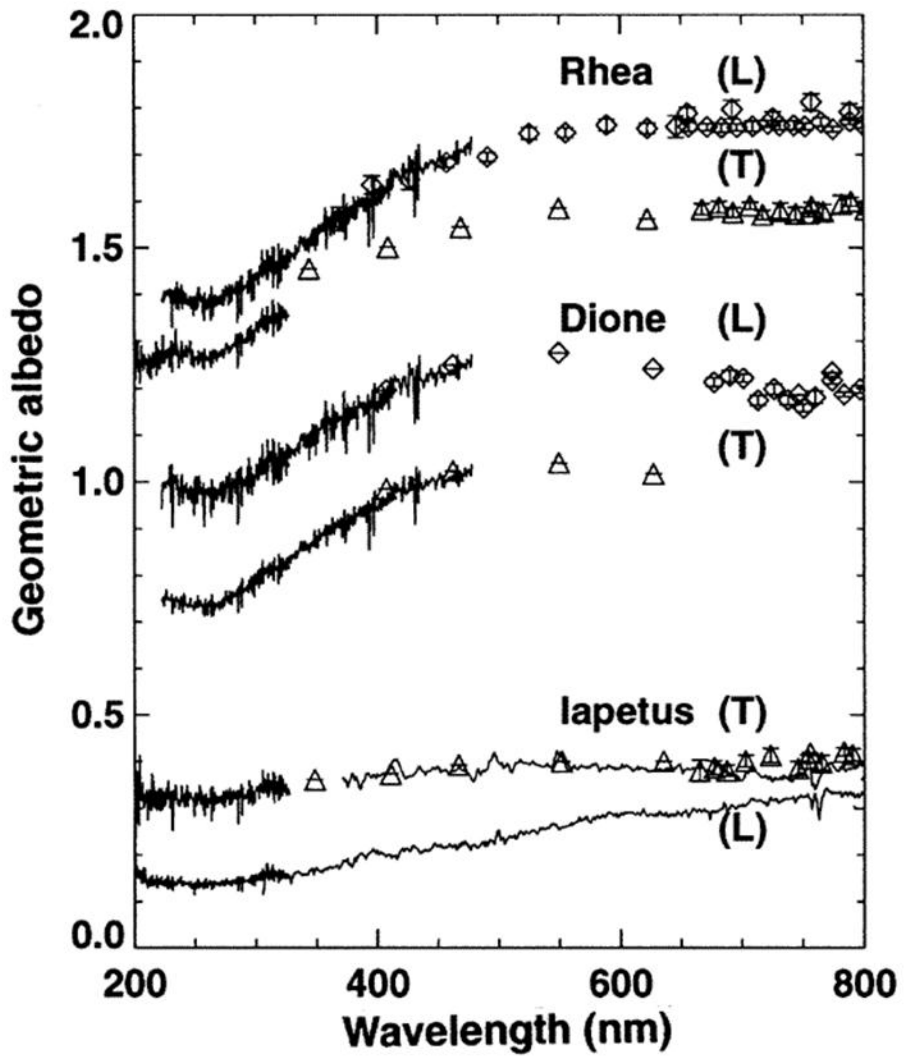
- **Planetary Science;**
- This is the first laser spectrum from the Chemistry and Camera (ChemCam) instrument on NASA's Curiosity rover, sent back from Mars on August 19, 2012.
- Credit: NASA/JPLCaltech/LANL/CNES/IRAP.



VUV spectroscopy in astronomy and planetary science

- Planetary ices;

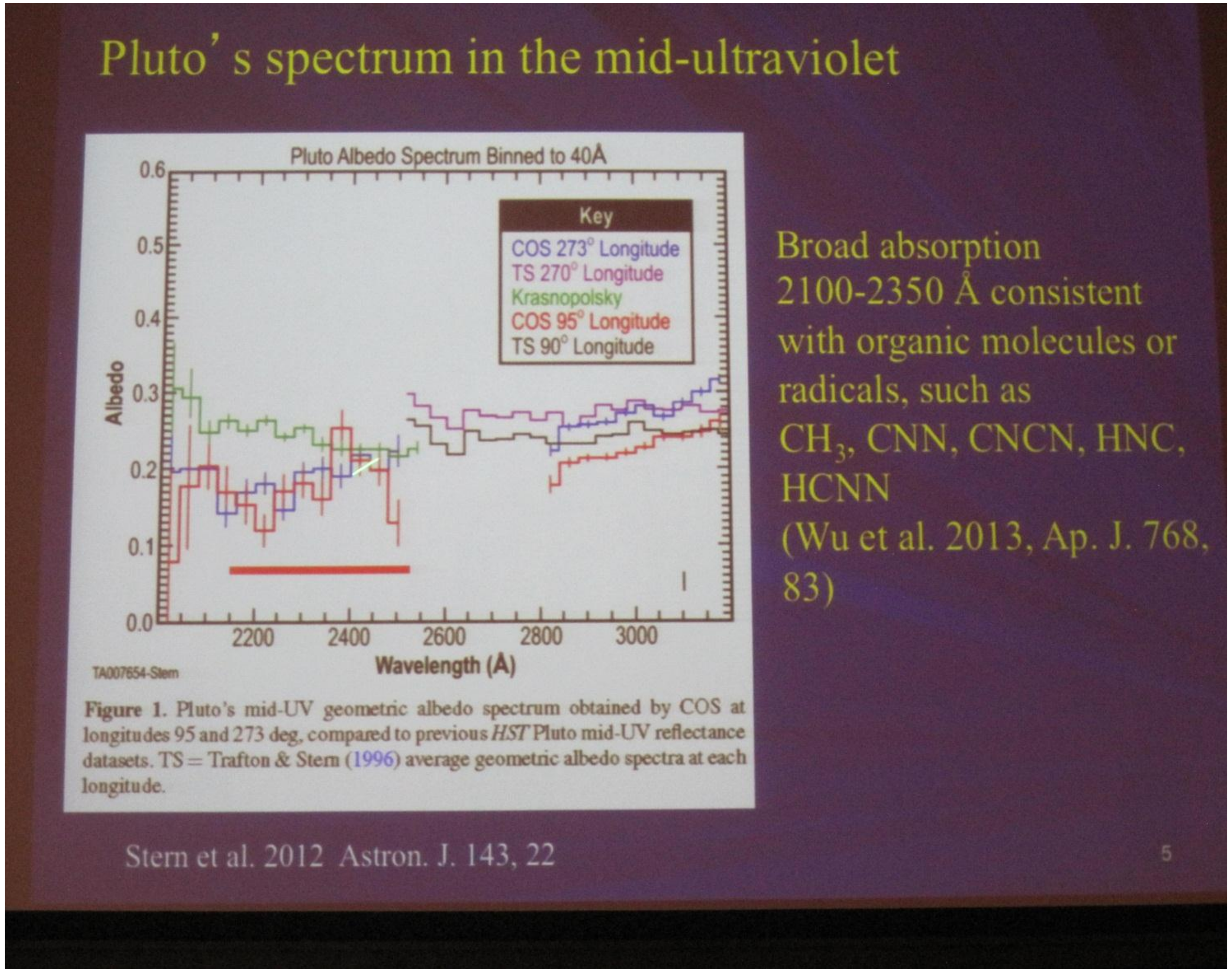
- Absorption in the (VUV) of ices on Saturn's moons



VUV spectroscopy in astronomy and planetary science

- Planetary ices;

Pluto UV spectrum from HST



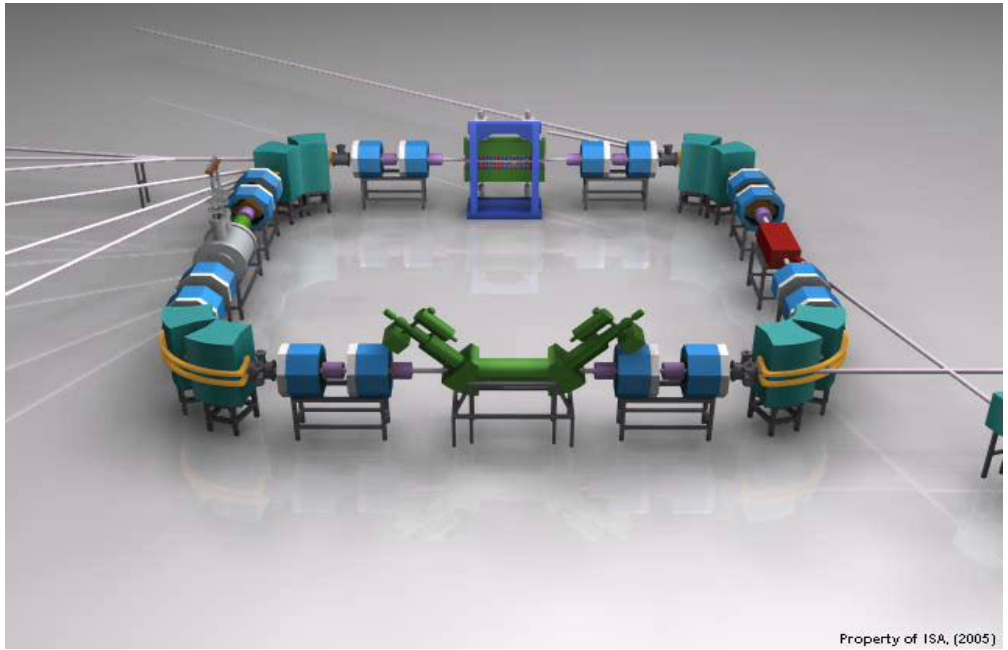
VUV spectroscopy

- Limited (whole range) gas studies since 1980's (classic text Robin)
- Almost no solid state studies
- Need (V)UV source – Synchrotron

Experiments at Synchrotron Facilities

Mimicing star light

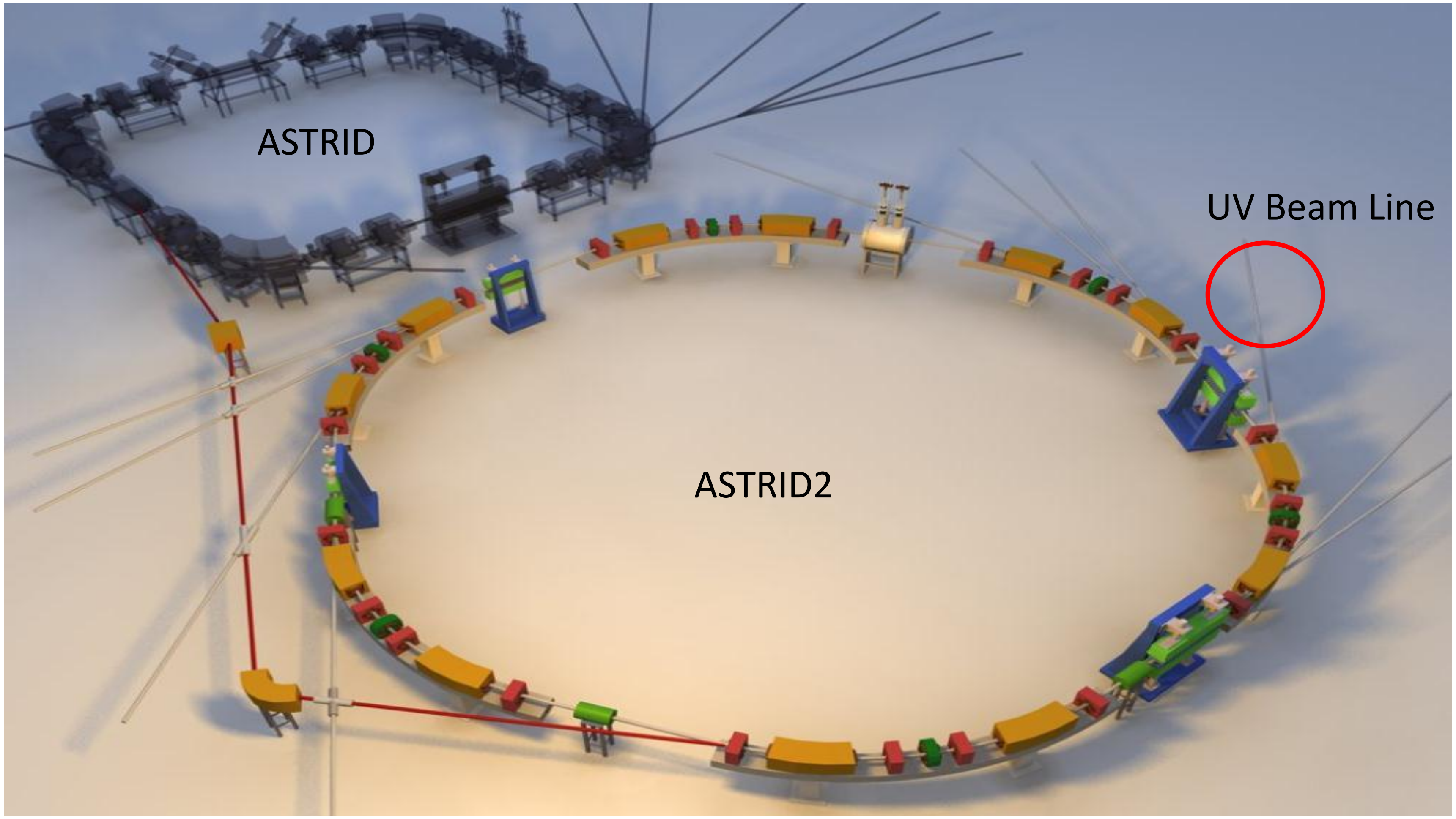
~~**UK Daresbury**~~ ~~**Aarhus Denmark**~~



ASTRID2

“The Ultimate Synchrotron Radiation Source” ‘D Field’ (FOR UV)

ISA- Institute for Storage Ring Facilities,
Department of Physics and Astronomy, University of Aarhus



Energy = 580 MeV
Circumference = 45.7 m
Lifetime = Infinite (top-up)

Measuring photo-absorption cross sections

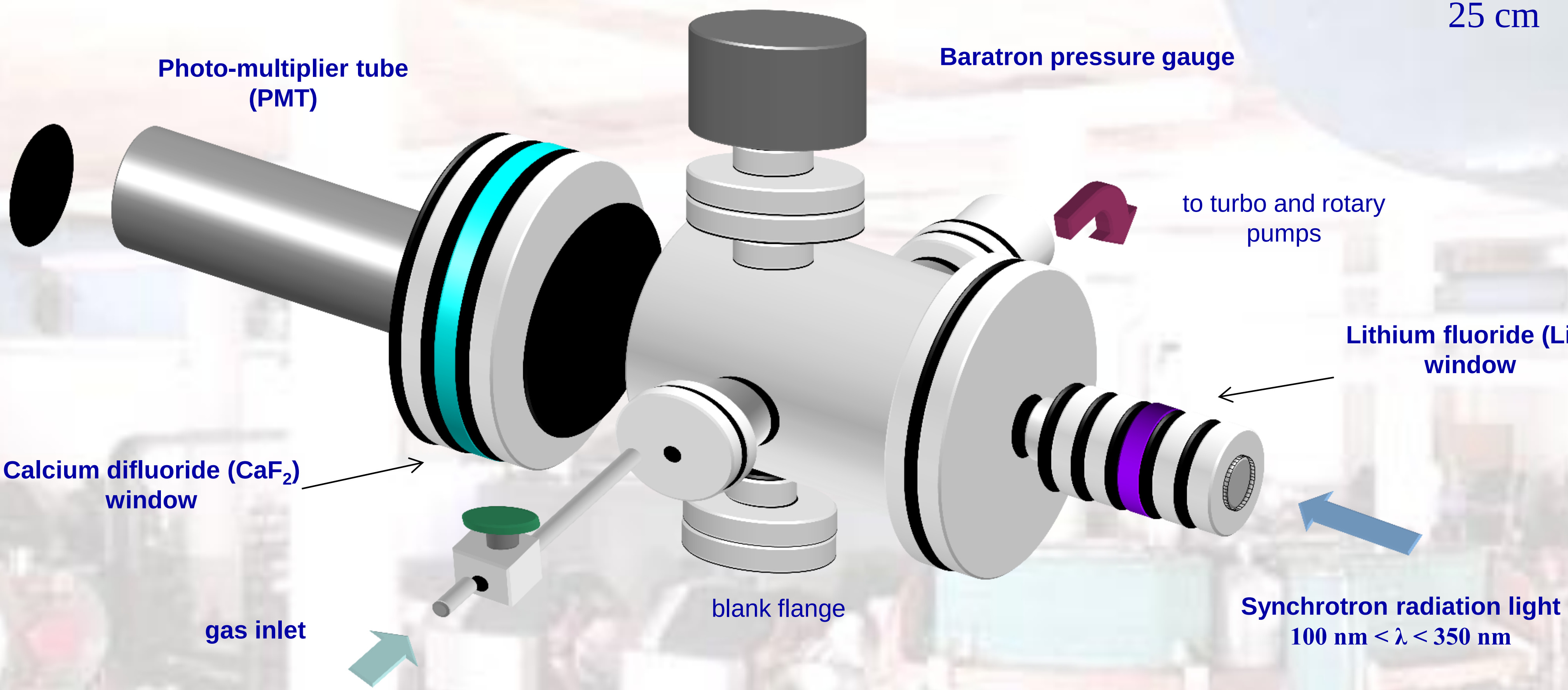
Absolute photo-absorption cross sections using the

Beer-Lambert law:

$$I_t = I_o \exp(-n\sigma x)$$

where I_t is the radiation intensity transmitted through the gas sample, I_o is that through the evacuated cell, n the molecular number density of the sample gas, σ the absolute photo-absorption cross section, and x the absorption path length (25 cm).

absorption path length
25 cm



grating mirror
2000 lines / mm

gas cell pressure
0.3 mbar – 1.0 mbar

Now add the people !

Gas phase VUV spectroscopy

- Experiments since 1996
- Over 100 molecules studied
- Electronic spectroscopy explored
- Rydberg/Valence states characterised
- Comparison with Theory

- Comparison and update of ‘bible’
  Robin -- 2017

Lets make ice..

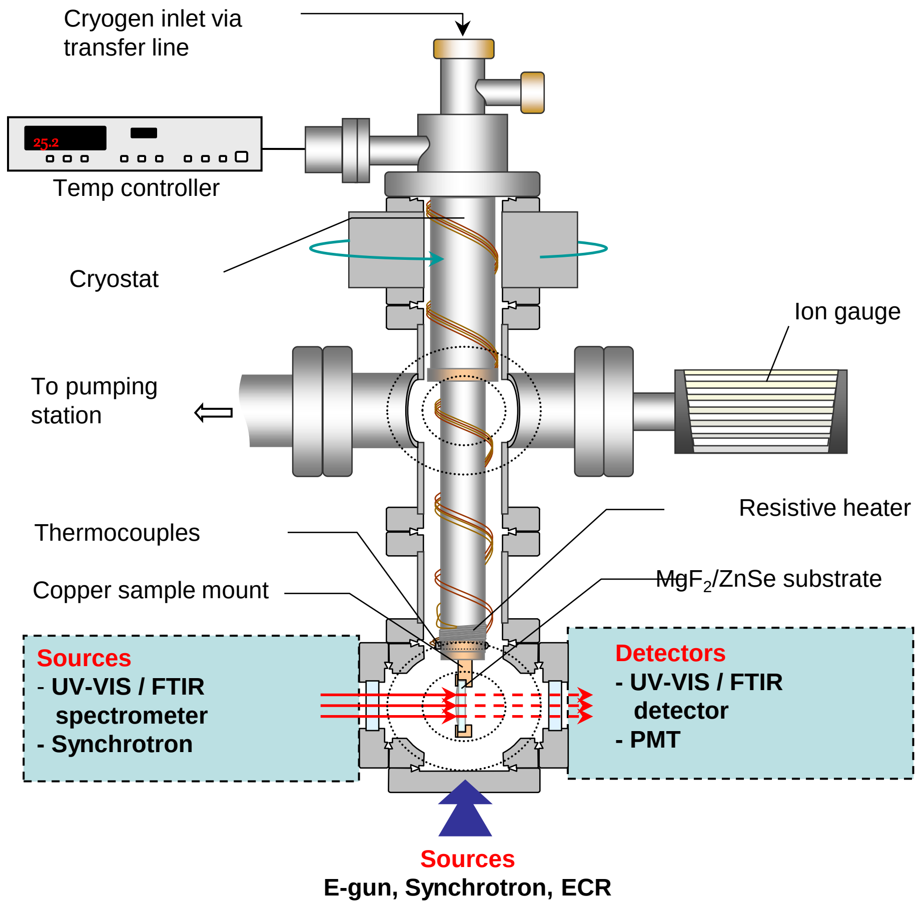
Experimental Programme at the OU

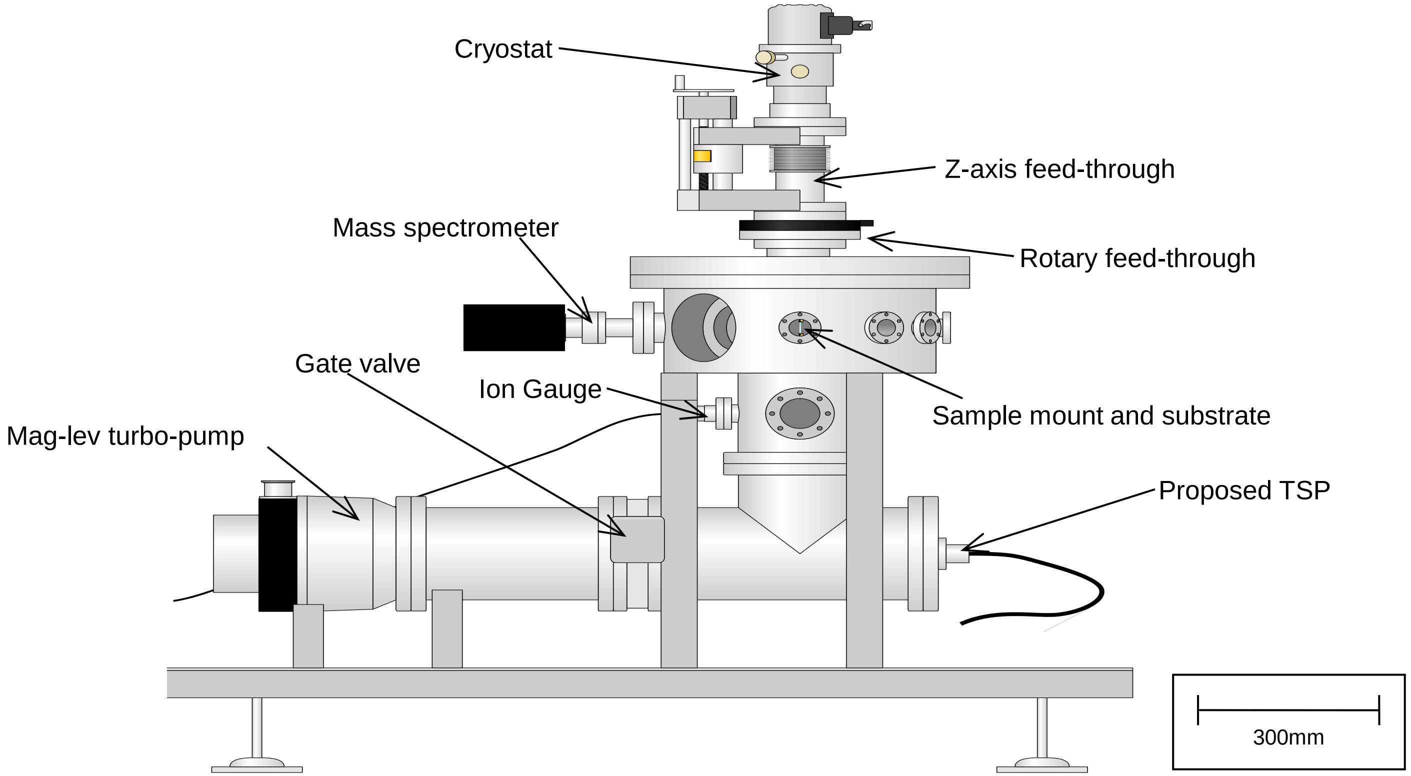
OU Portable System:

- Transmission UV & FTIR Spectroscopy and Processing
- Designed to be transported to central facilities → Synchrotrons, RAL, QUB

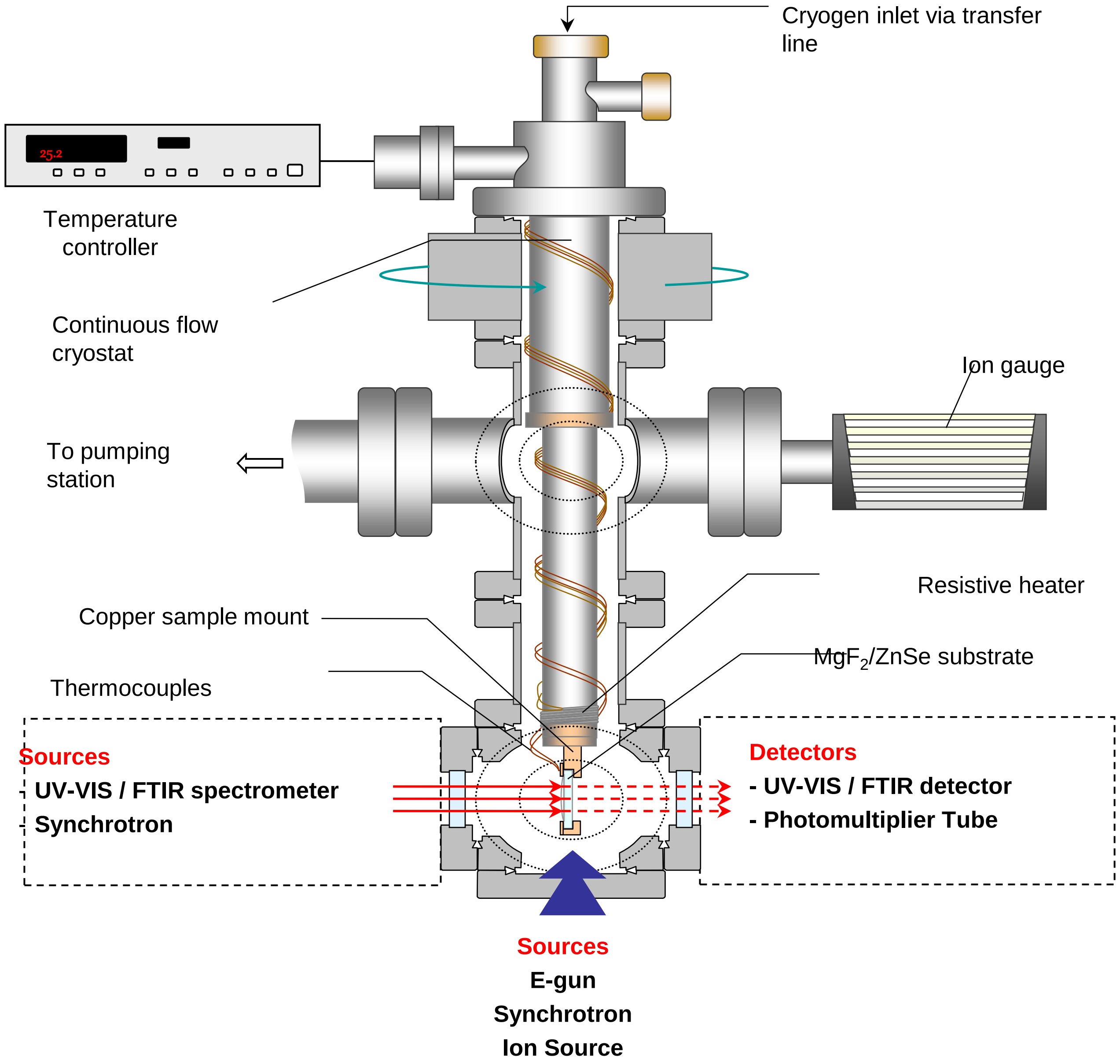
OU Static System:

- TPD, RAIRS and Processing
- Molecular synthesis with electrons and photons → E-gun, UV lamp





- **HV (UHV) chamber - Portable:**
  - **$P \sim 10^{-8}9 - 10^{-10}$ mbar**
- **Temperature**
  - **Continuous flow LHe/LN2 cryostat**
    - **12 K < T < 450 K**
- **Substrate**
  - **CaF_2 / MgF_2 (VUV) or ZnSe (IR) window**
    - ***transmission* spectroscopy of bulk ices**
- **Samples**
  - **deposited *in situ* by vapour deposition**
  - **0.1 – 1 μm**
  - **Ignore the effects of the substrate**
  - **Looking at bulk ice reactions**

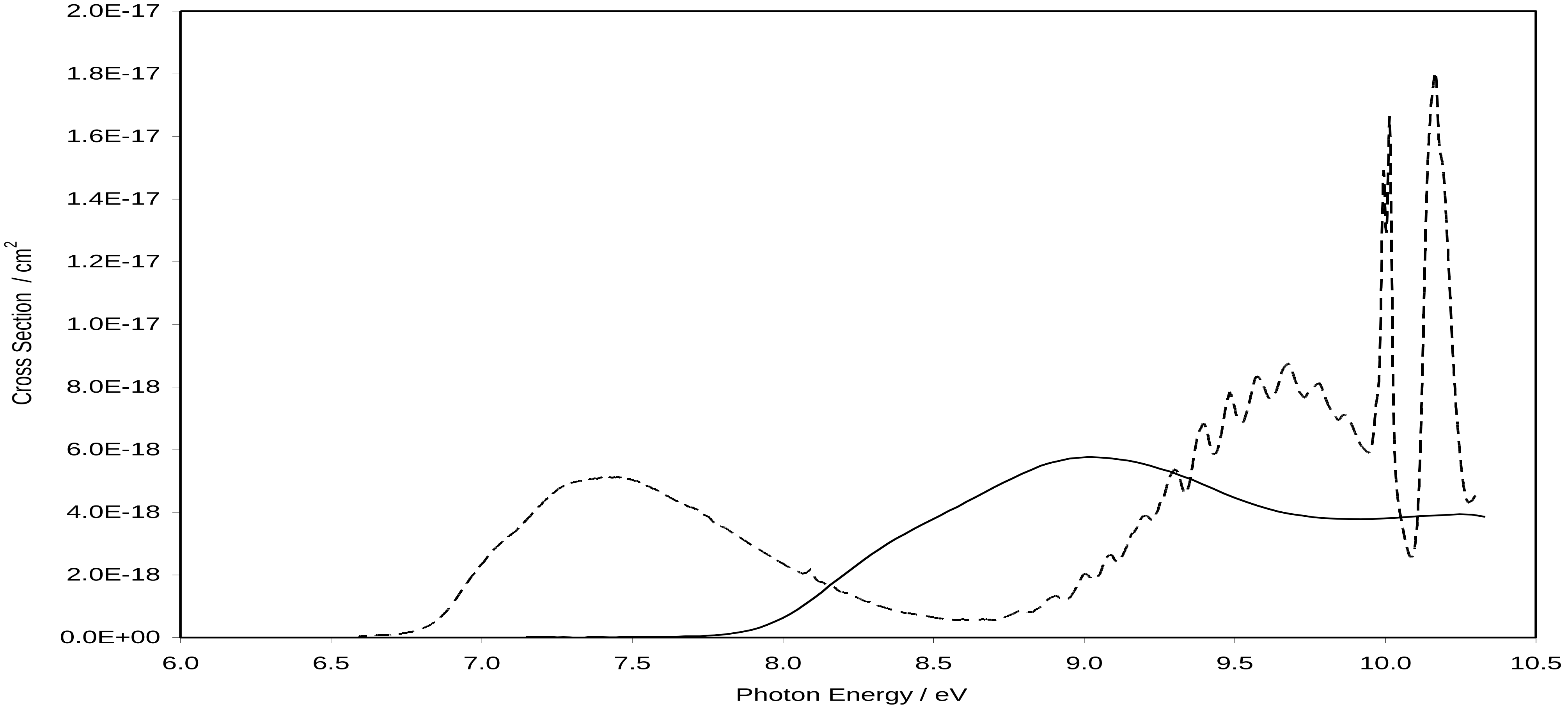


Some results…

- A selected set of results …

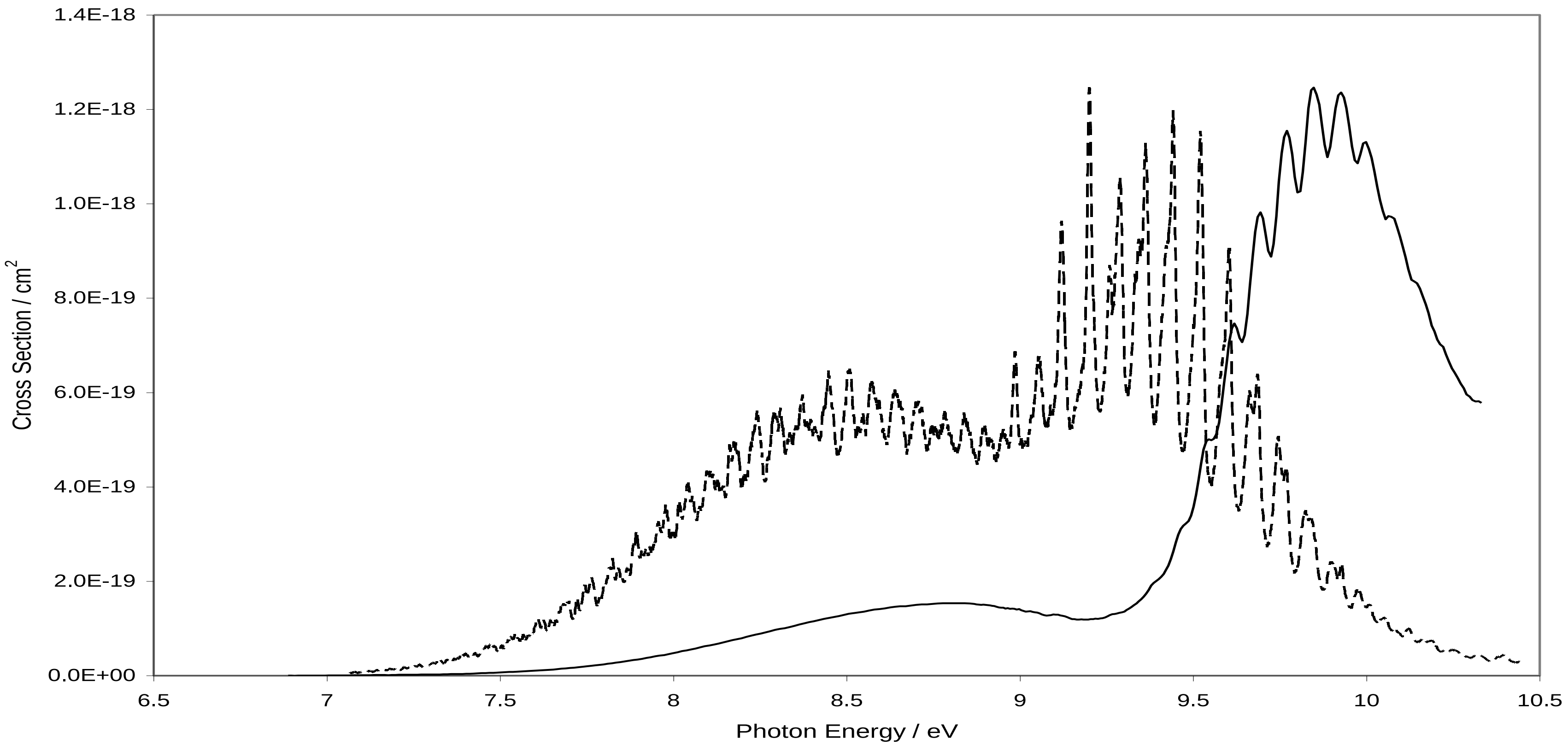
VUV Spectrum of water ice <90K (for Ewine !)

Note : Blue shift in the solid phase

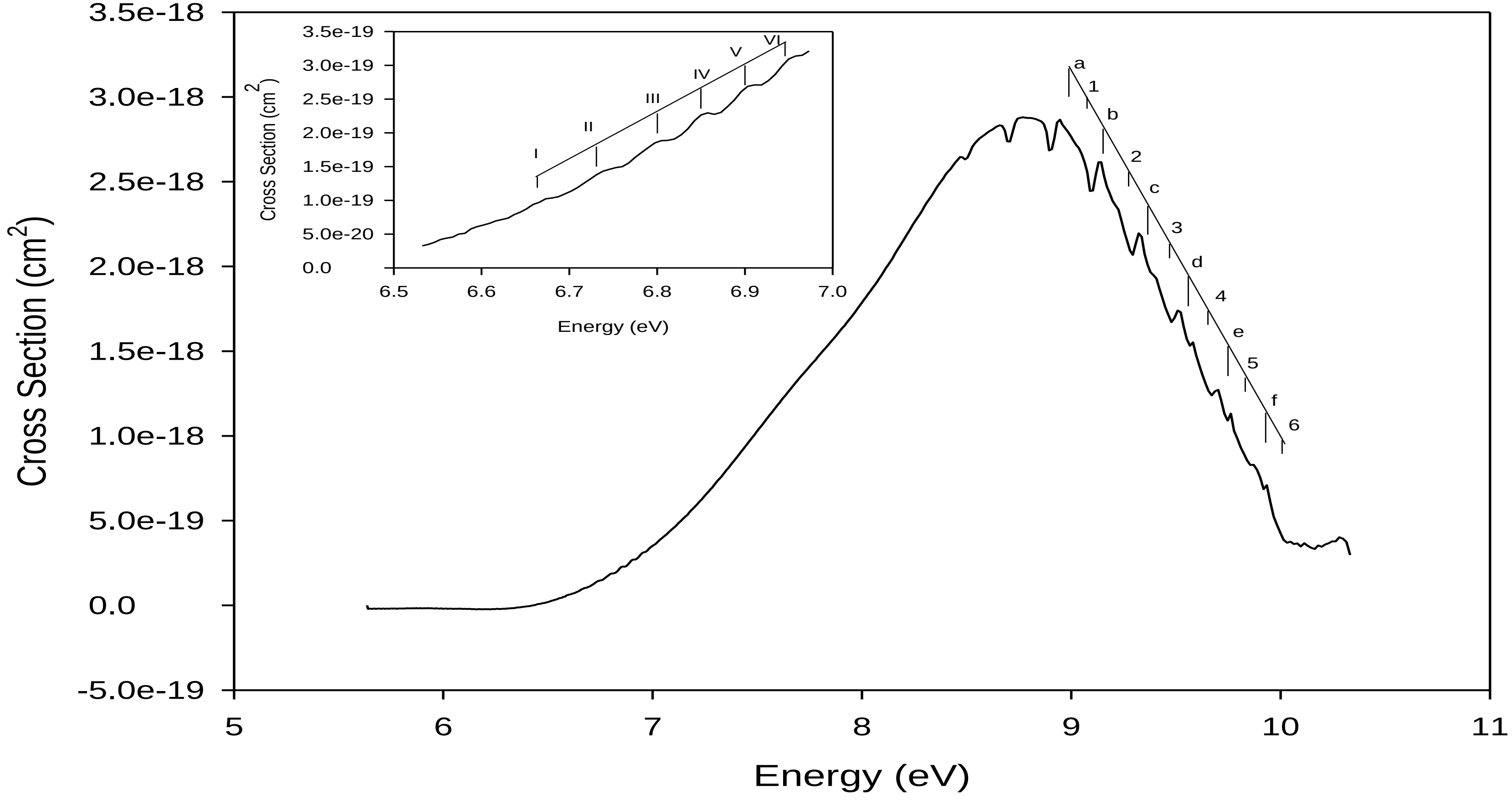


VUV Spectrum of carbon dioxide ice <90K

Note : Blue shift in the solid phase

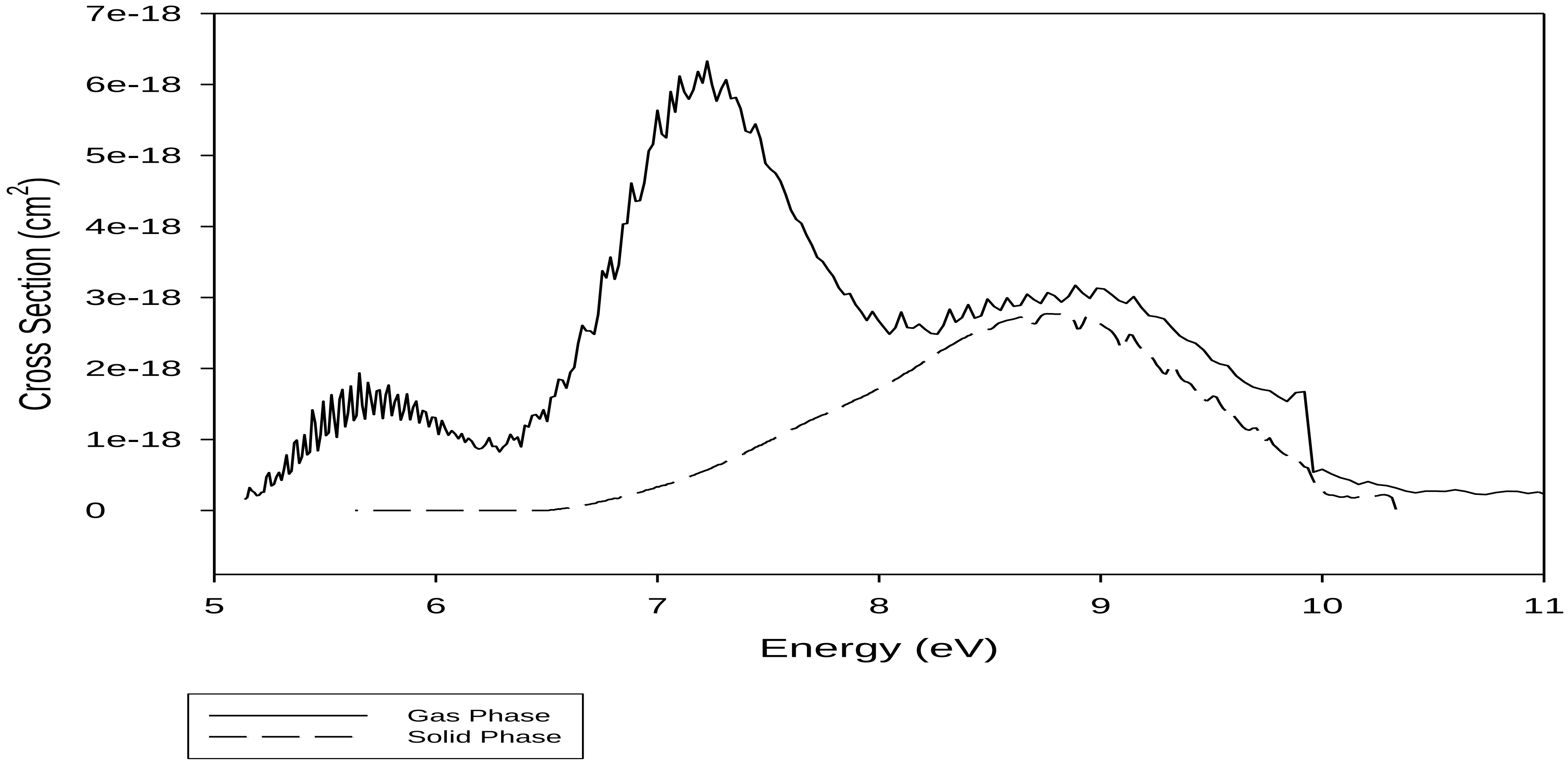


VUV Sepectrum of Methylamine ice CH_3NH_2

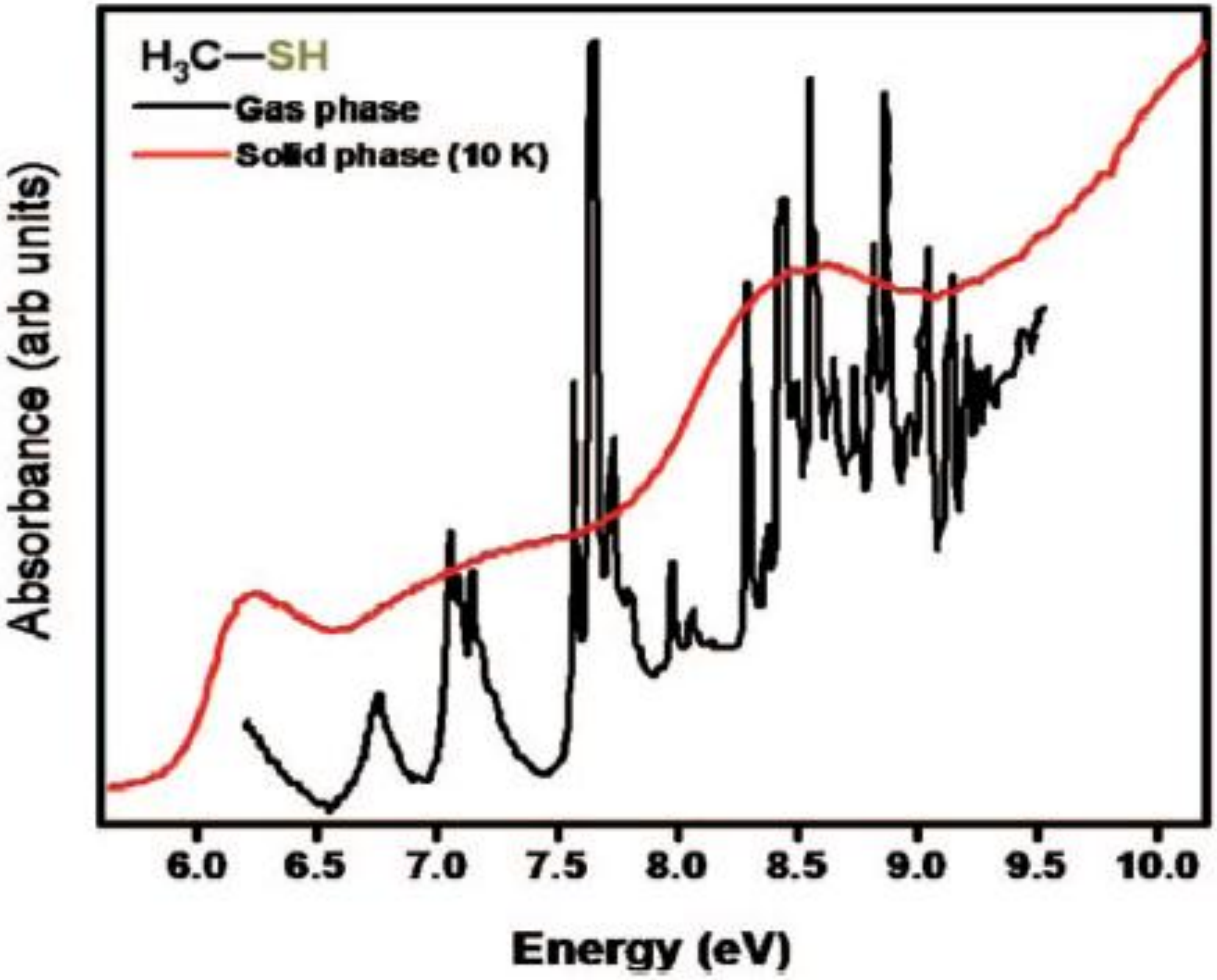


Comparison of gas and solid phase Methylamine

Note absence of low lying bands in solid phase



Methanethiol (CH_3SH)

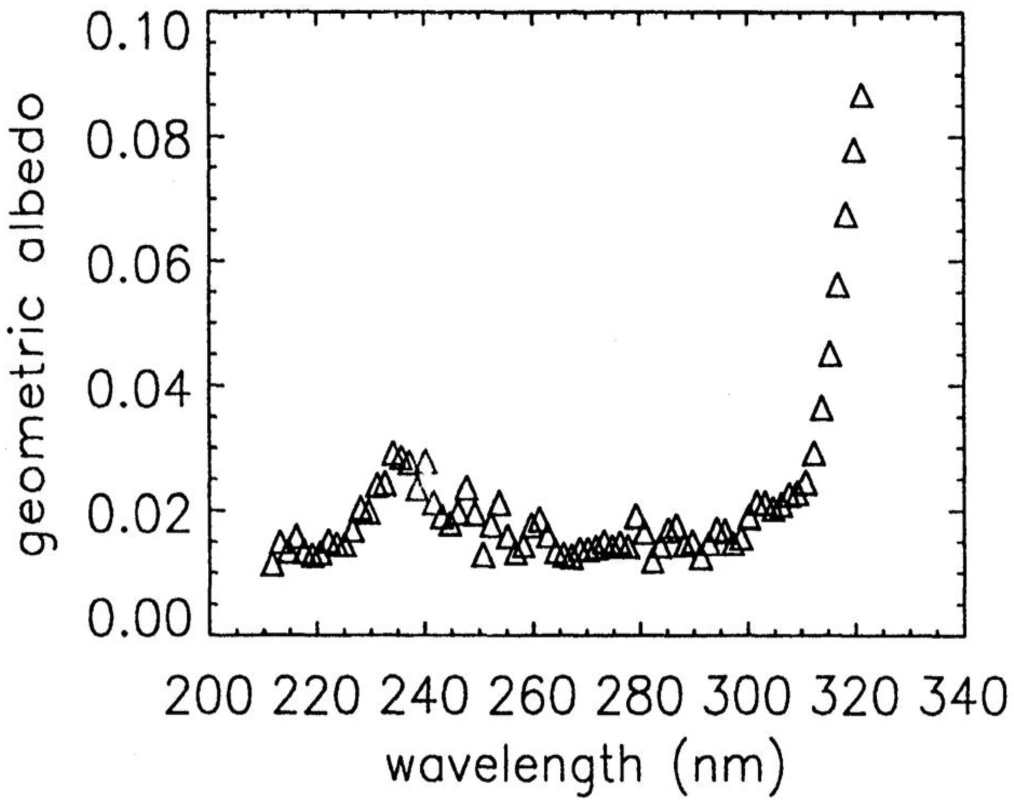


Some ‘first’ conclusions

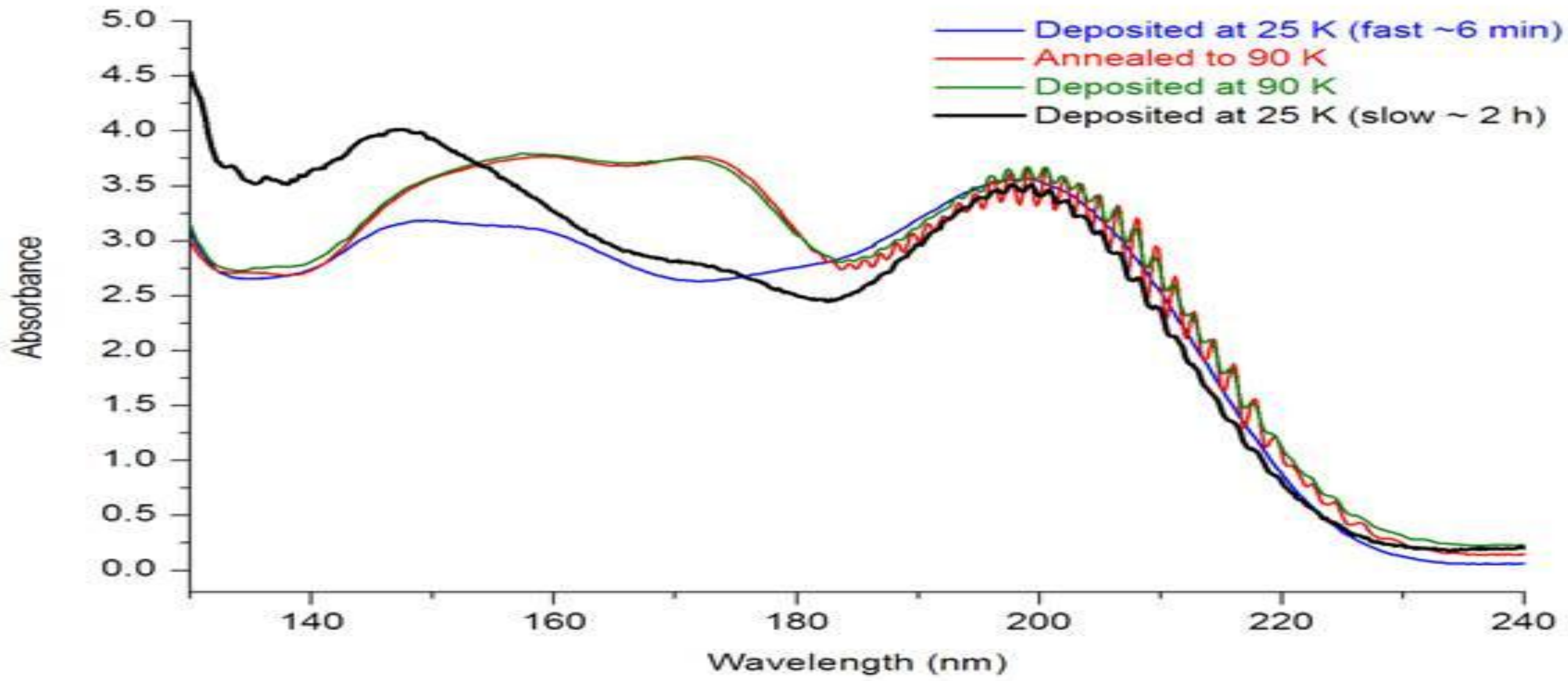
- Can not use gas phase data to predict position of electronic bands in the ice phase.
- Some electronic states are ‘missing’ in solid phase spectra.
- Cross sections (hence photodissociation rates) change from gas to solid.

SO_2 as observed on IO

Galileo UVS albedo spectrum of Io, showing the strong SO_2 frost absorption.

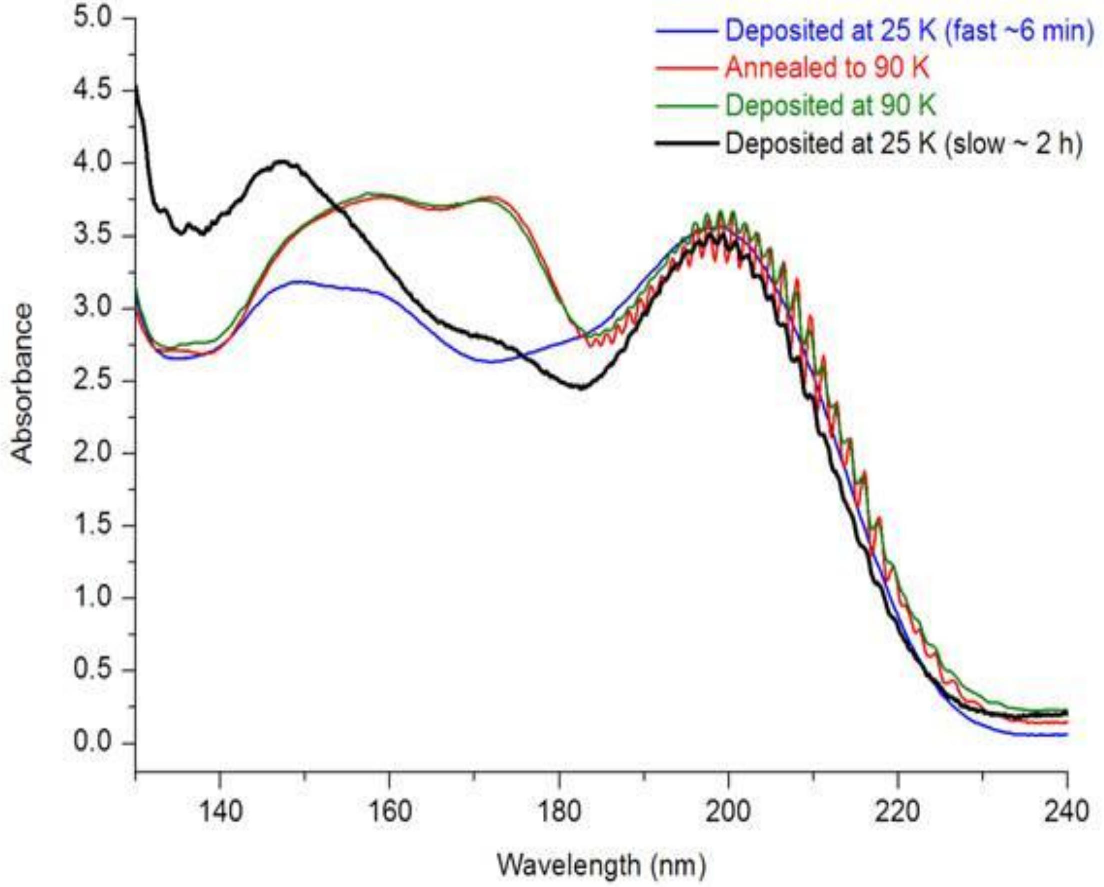


Case study of SO_2 – Morphology and temperature



SO_2 Morphology and temperature

- ‘Fast’ deposition at 25 K
  - No vibrational structure → Indicates amorphous ice
- Annealed to/deposited at 90 K
  - vibrational structure & evidence of Davydov splitting → Indicates crystalline ice
- Slow’ deposition at 25 K
  - Weak vibrational structure → evidence of some degree of crystallinity !



SO_2

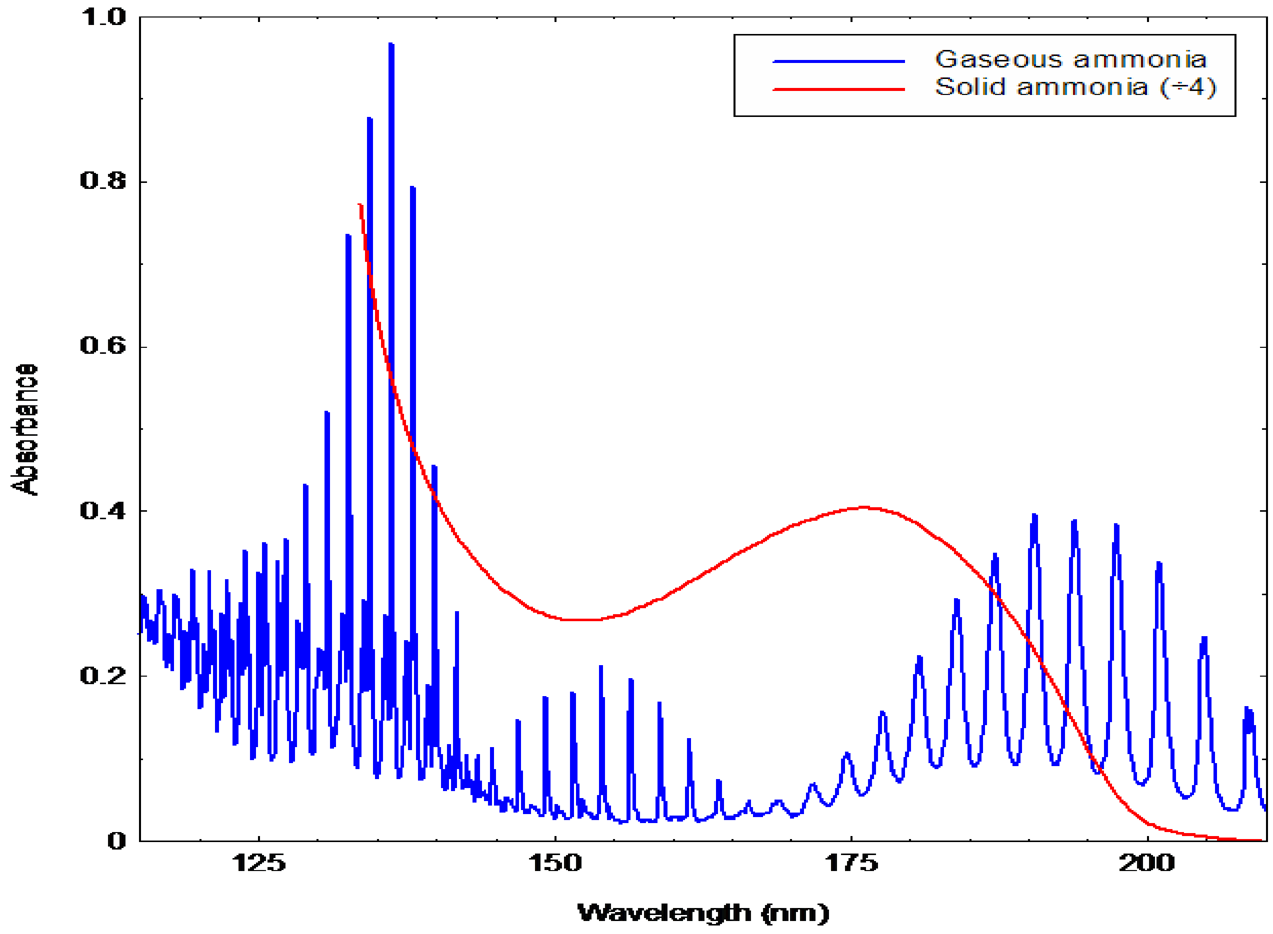
- Conclusions
- Rate of deposition is important in determining ice morphology.

- May form mixed amorphous/crystalline ice.

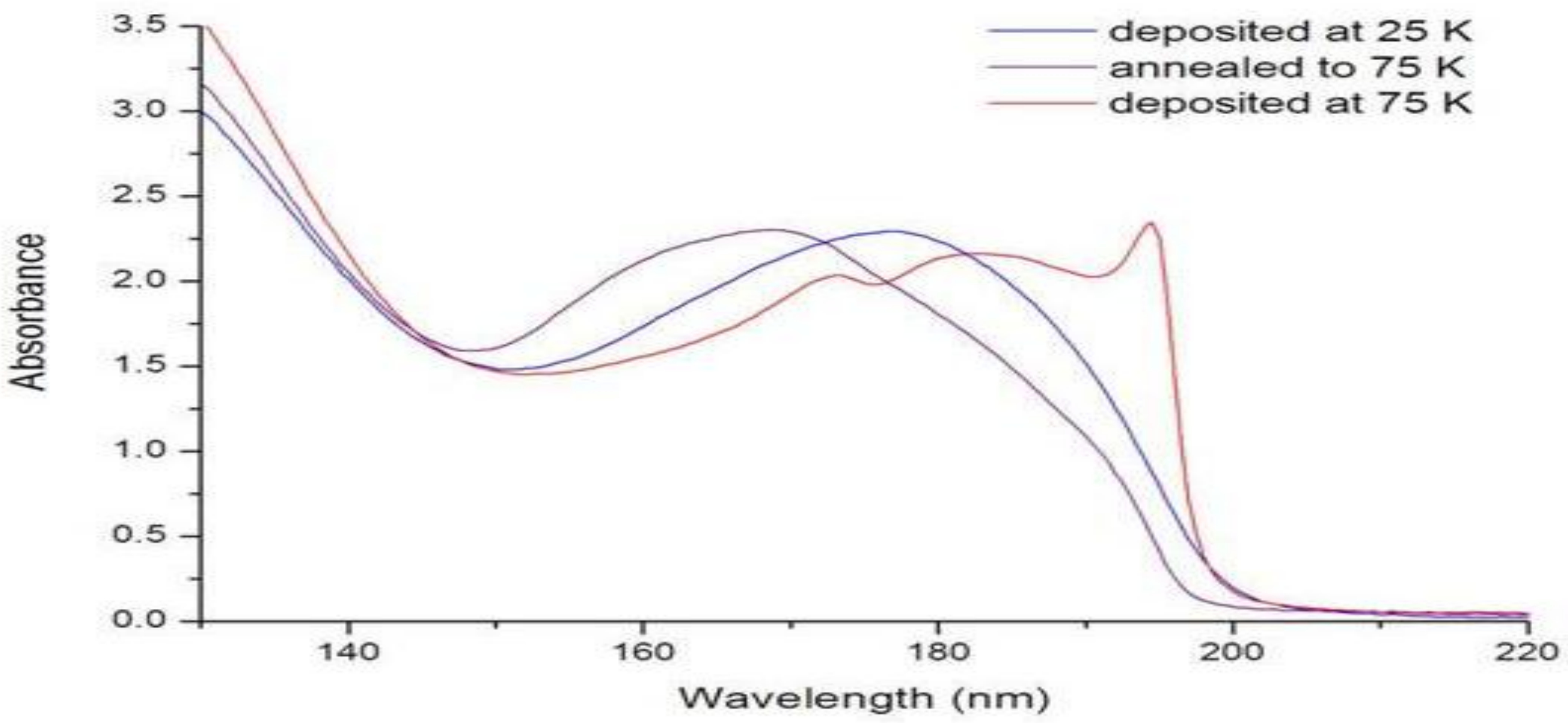
- Crystallinity is not always a signature of

temperature or thermal history !

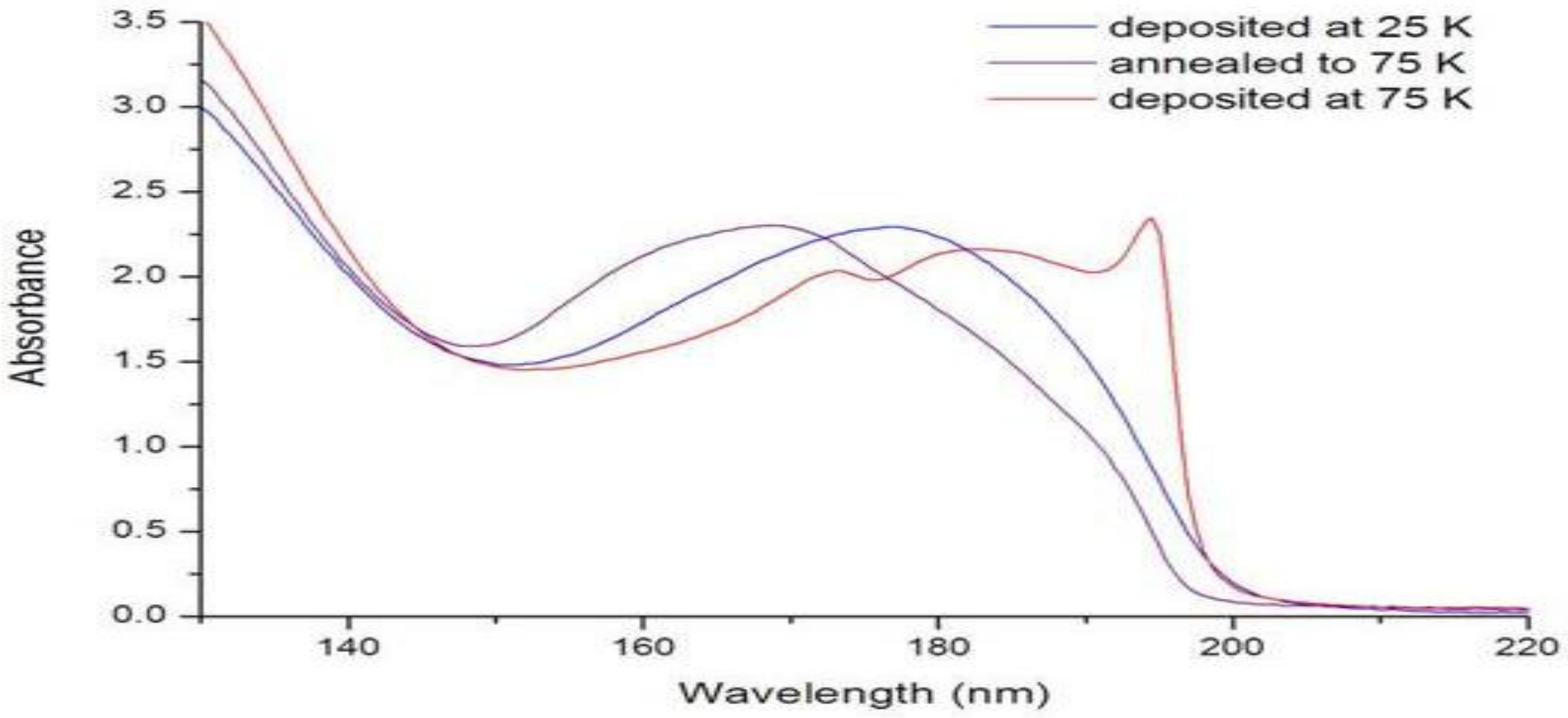
Ammonia gas vs solid (25K)



Ammonia Different T

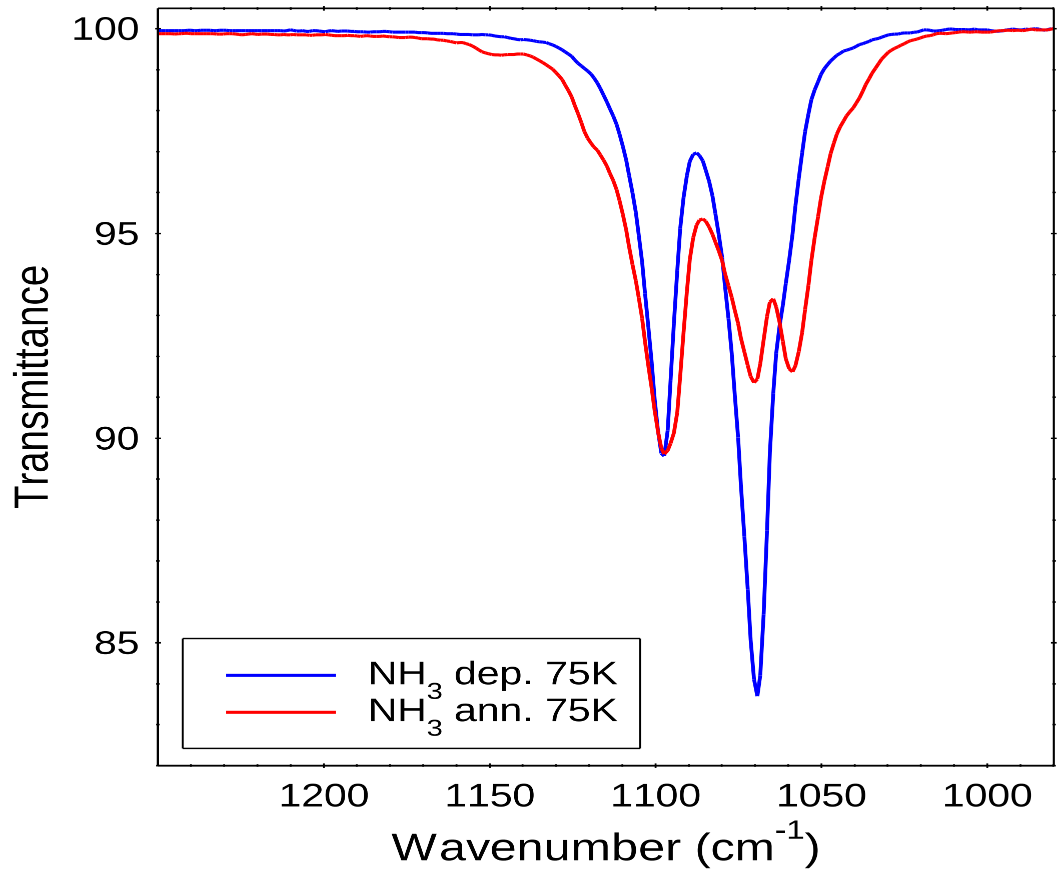


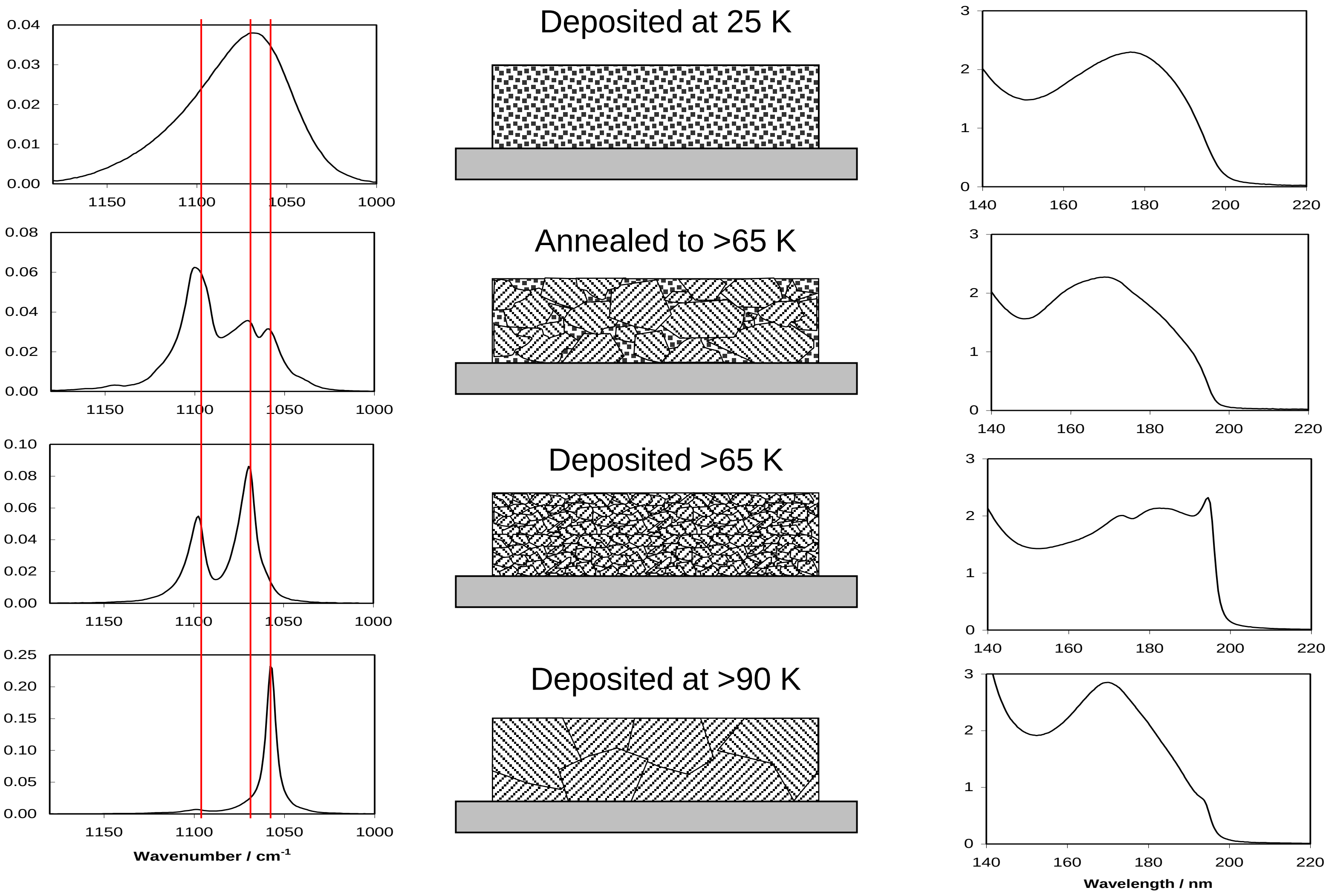
The band at 194 nm is indicative of ‘exciton’ formation



Ammonia ice in the IR

- 1060 cm^{-1} peak is evidence of crystalline structure.
- 1070 cm^{-1} peak is due to amorphous ice.
- The 1100 cm^{-1} peak indicative of **exciton measure of grain boudaries**





Amorphous: Disordered structure, thermodynamically unstable

Semi/polycrystalline: More ordered structure with crystallite & amorphous mix, thermodynamically stable

Polycrystalline: many **small crystallites**, large number of grain boundaries, thermodynamically stable

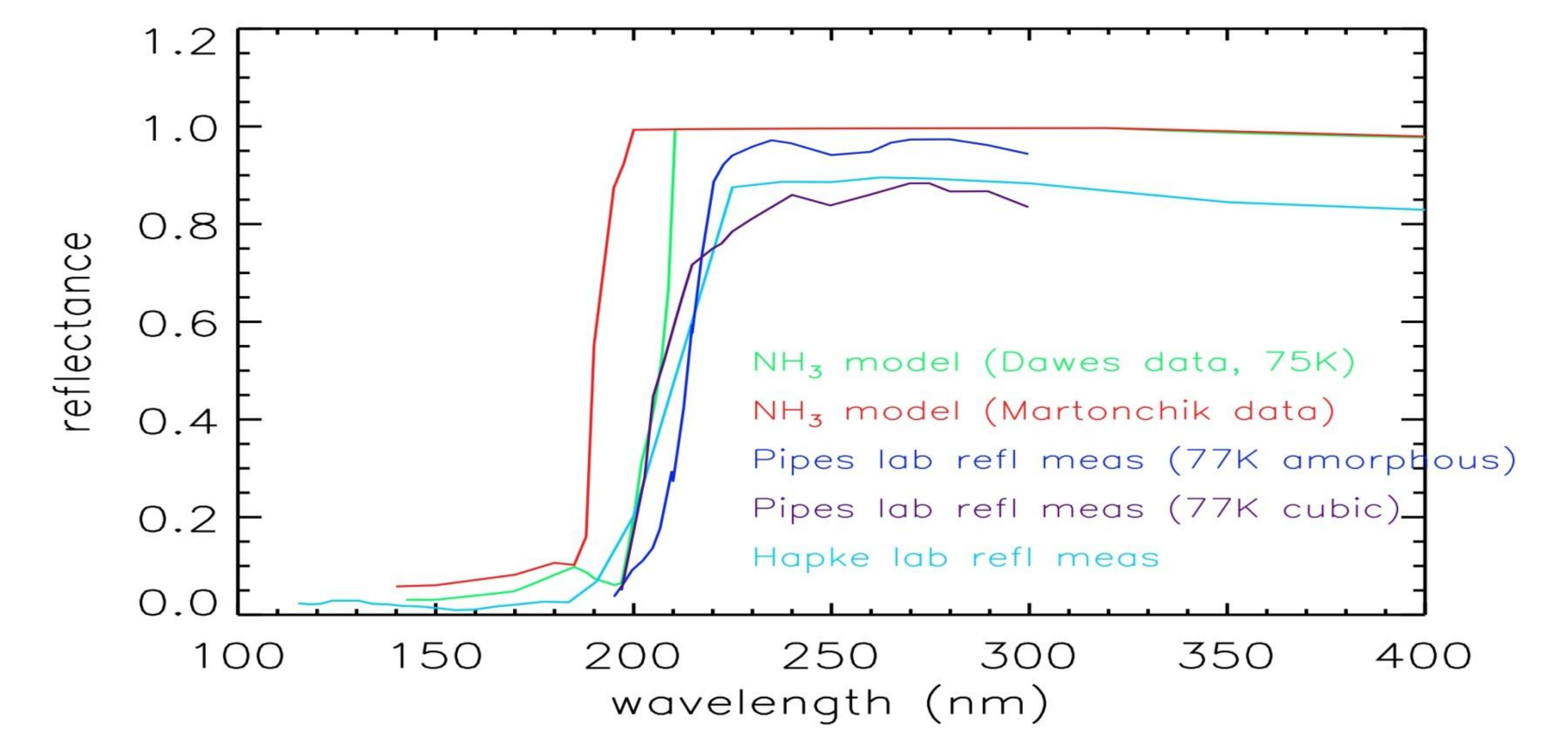
Crystalline: Large crystallites, few grain boundaries, thermodynamically stable

Ammonia

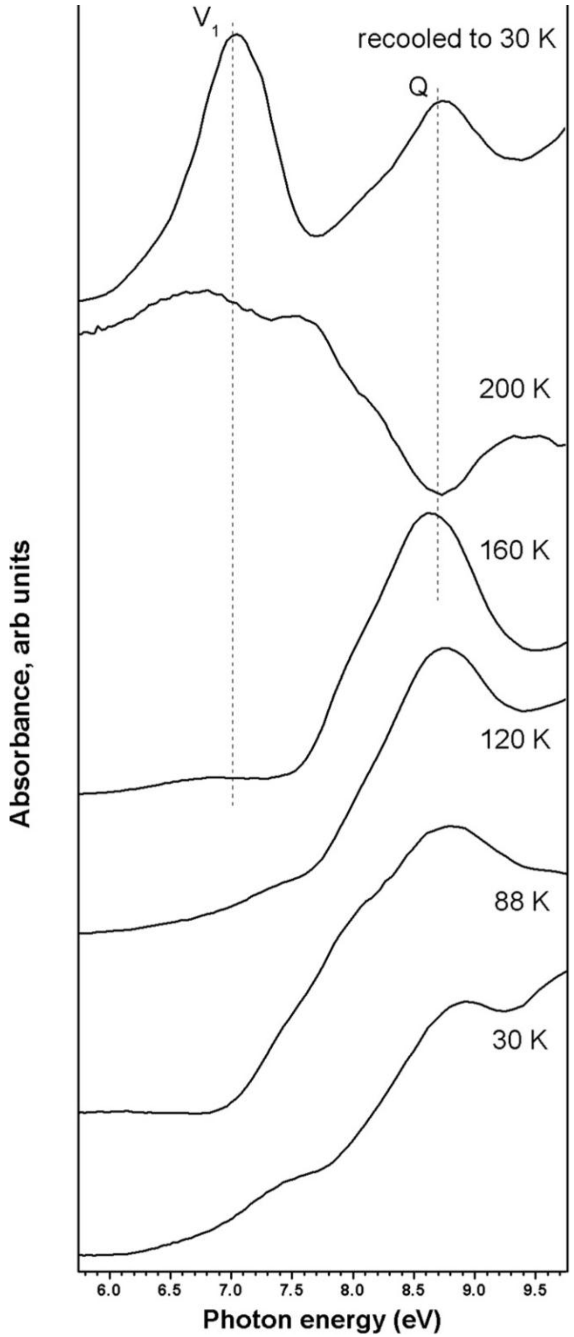
- Both UV and IR show features that are characteristic of exciton formation
- Complex ice morphology formation of regions of crystalline ice in an ‘amorphos sea’
- Crystallites
- Structure is random/statistical. Each sample is different ! Depends on deposition time.

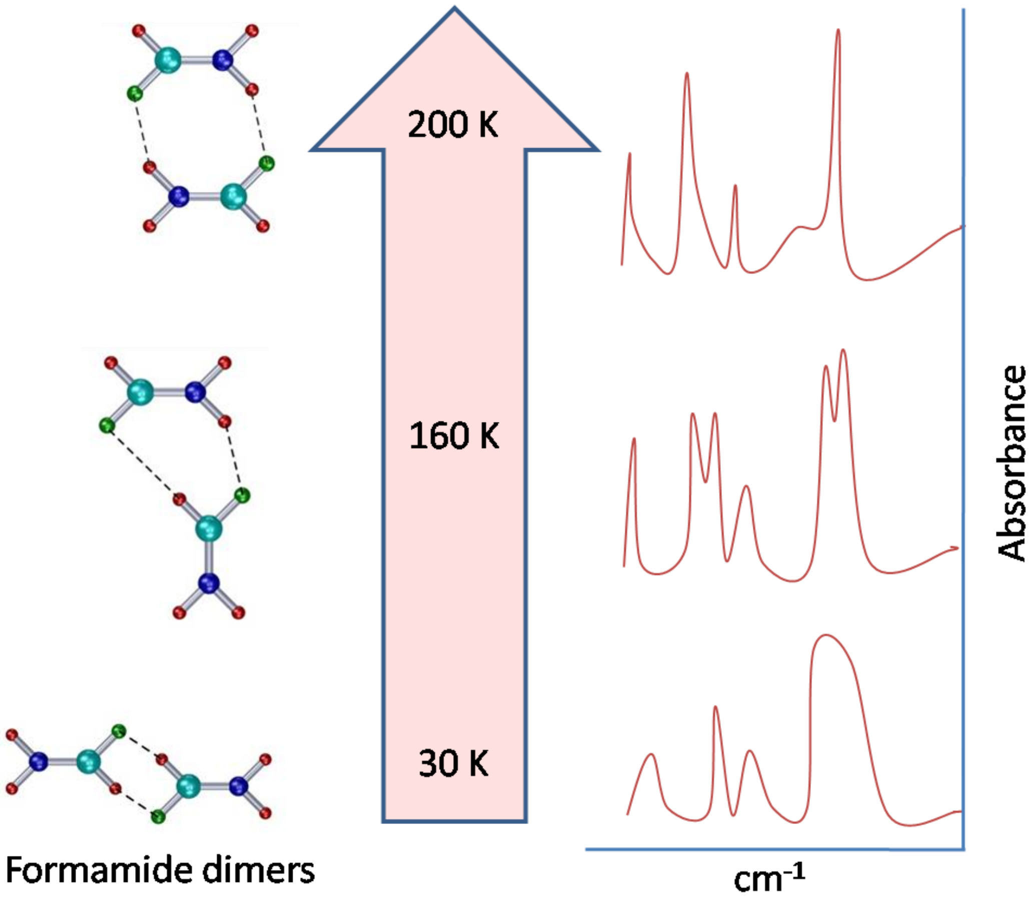
So how can this data be used ?

- Interpreting measured spectra eg deriving ammonia reflection spectra fior Quaoar.



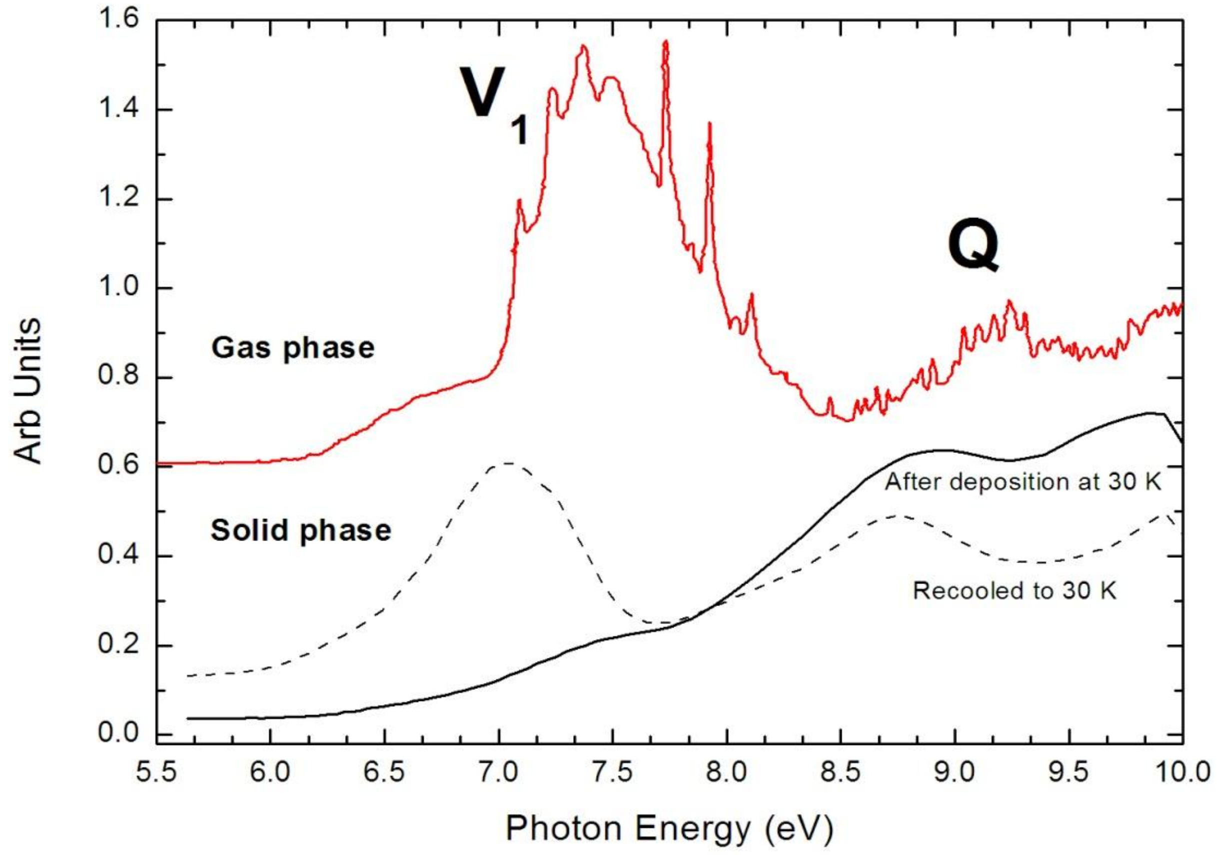
Formamide





Sivaraman et al, 2012.
Sivaraman et al, 2013.

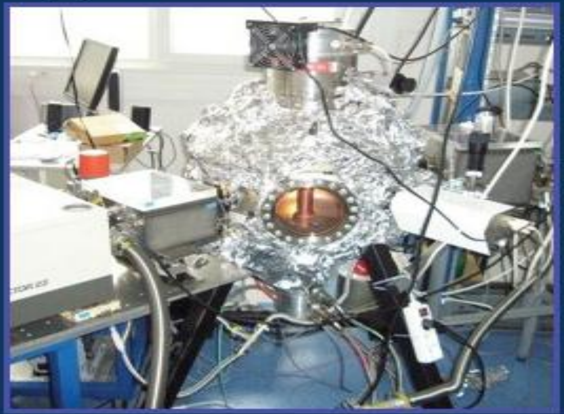
Formamide



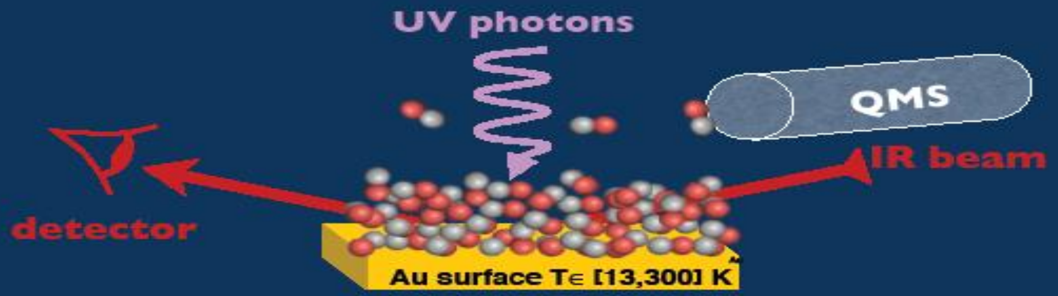
Sivaraman et al, 2012.

CO photodesorption

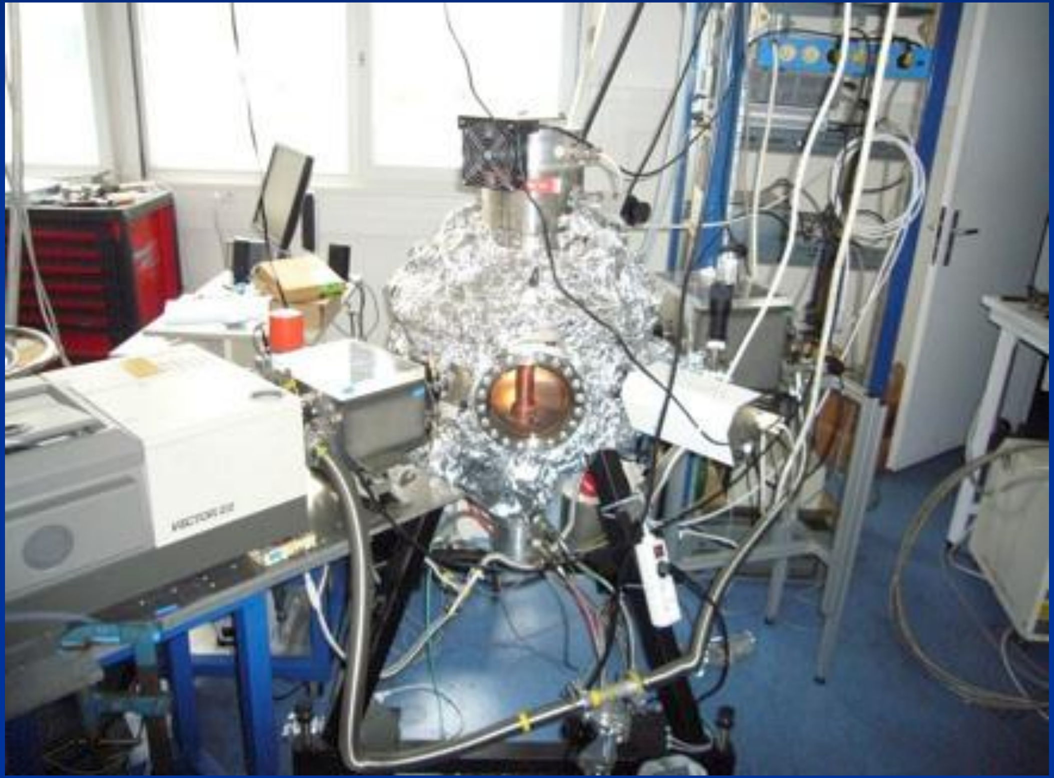
The set-up : SPICES

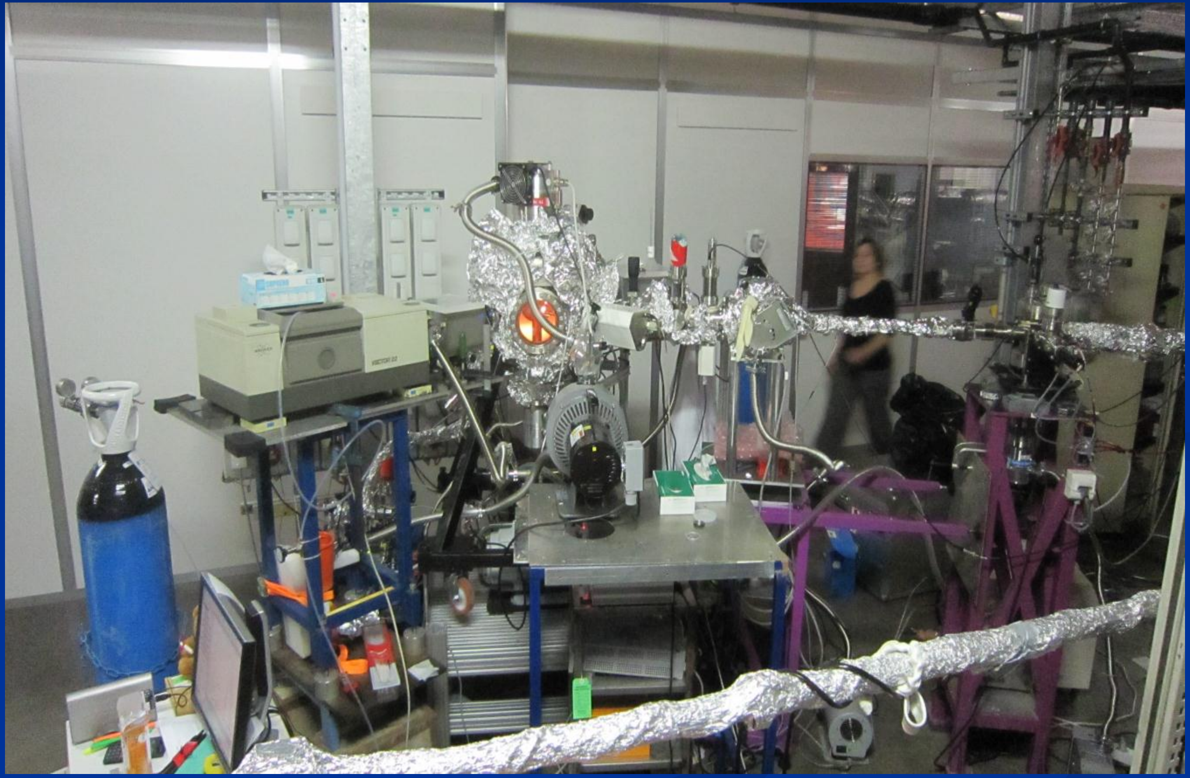


- Chamber under ultra-high vacuum
- Substrate temperature down to 13 K
- Ices grown by background deposition
- Detection via mass spectrometry for the gas phase and via Infra-Red for the ice composition
- Set-up transportable



Apparatus – SPICES on DESIRS beam line at the SOLEIL synchrotron facility

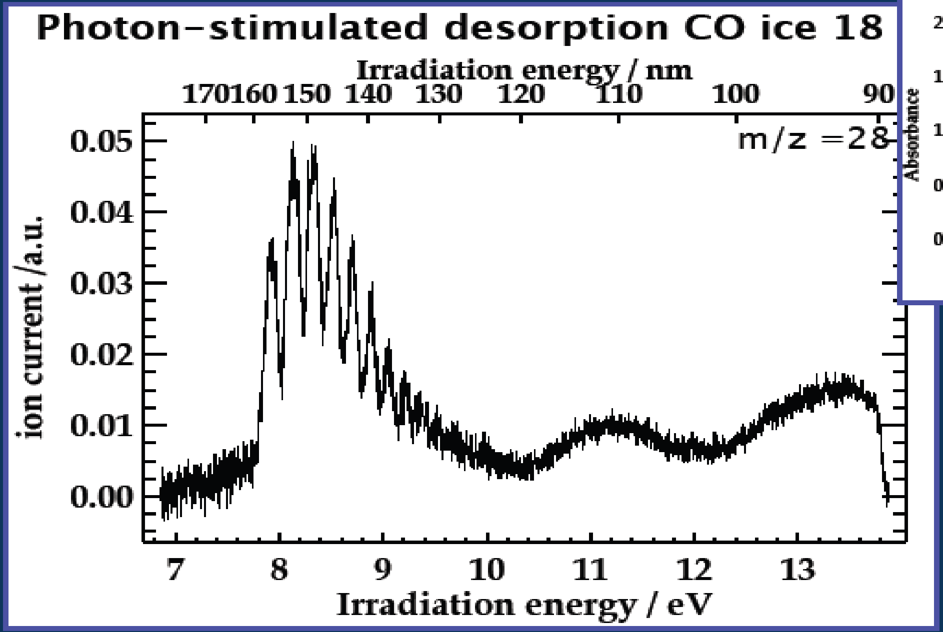


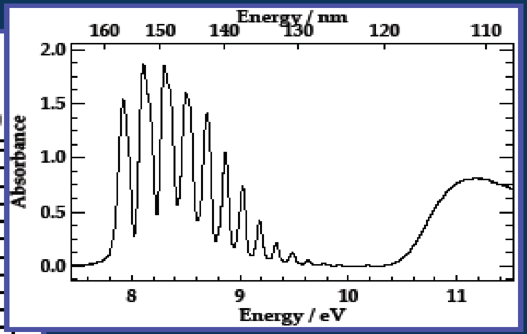


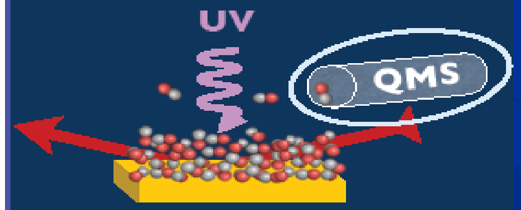
CO photodesorption

Results CO – QMS

- 10 ML CO at 18 K + Energy scan from 7 to 14 eV
- Photodesorption linked to absorption profile



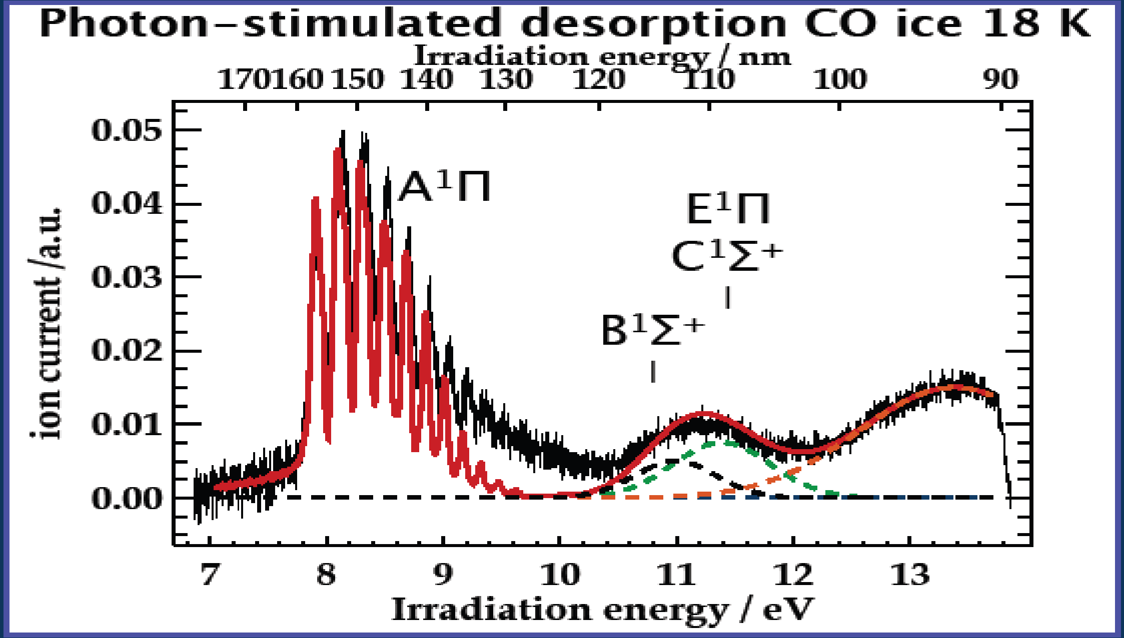




CO photodesorption

Results CO – QMS

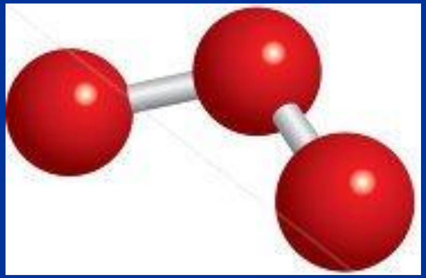
- Clear evidence for a direct mechanism
- Photodesorption highly wavelength sensitive
- Photodesorption rate as a function of irradiation energy



Fit using CO ice absorption data from
Mason et al. 2006
Lu et al. 2005

Ozone = biomarker of life ?

- CO_2/methane/water needed for life so biomarker ?
- No have both biotic and abiotic sources
- Ozone was believed to be the BEST ***BIOMARKER***



Ozone formation

- Ozone is formed in a three body reaction since without a third body to stabilise the product ozone it would rapidly redissociate

- $O + O_2 + M \rightarrow O_3 + M$

Ozone Destruction

OH radicals destroy ozone in a catalytic cycle;

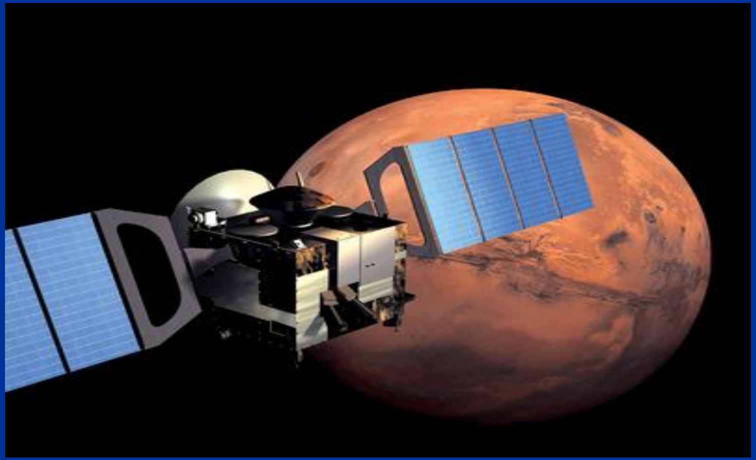
- $OH + O_3$ --> $HO_2 + O_2$
-

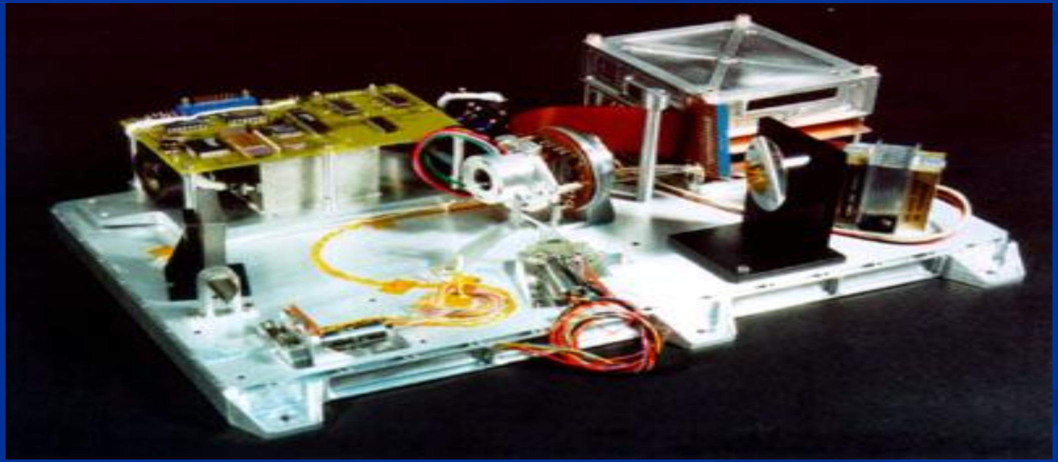
  $HO_2 + O_3$ --> $OH + 2O_2$

So can ozone be formed on other planets ?

- Yes is found on Mars

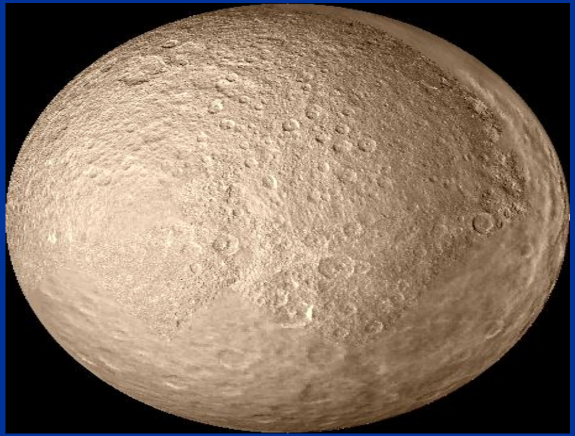
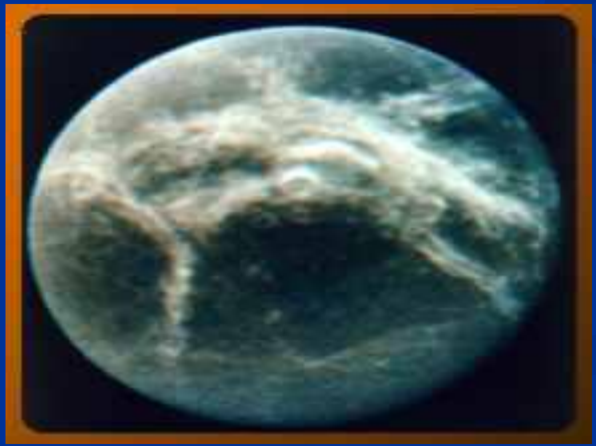
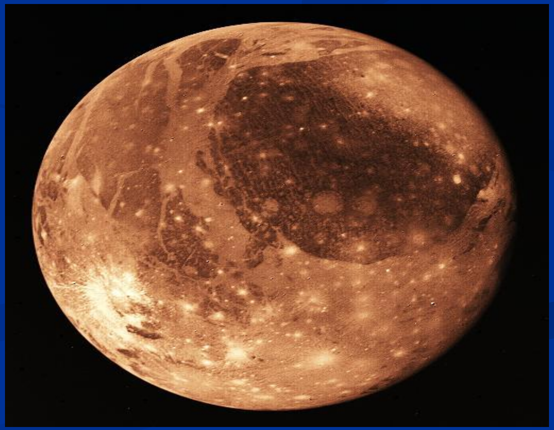
- SPICAM data from Mars Express



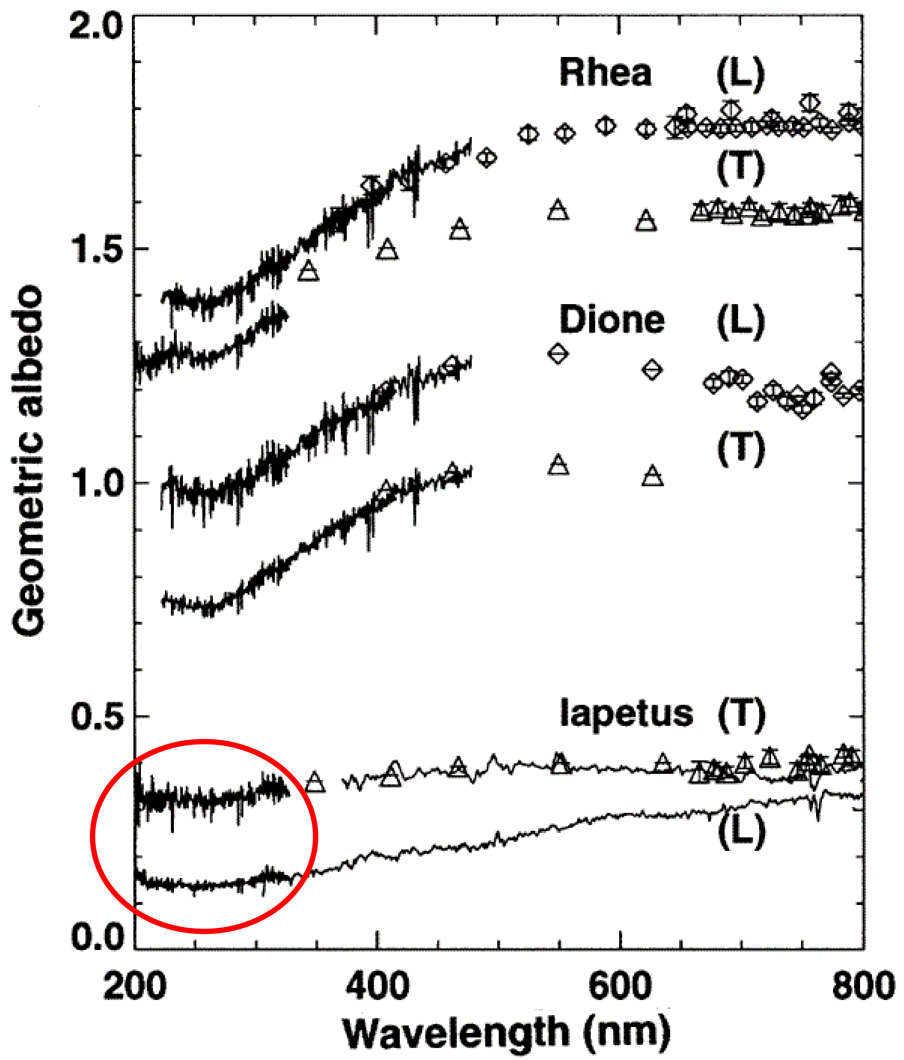


So can ozone be formed on other planets ?

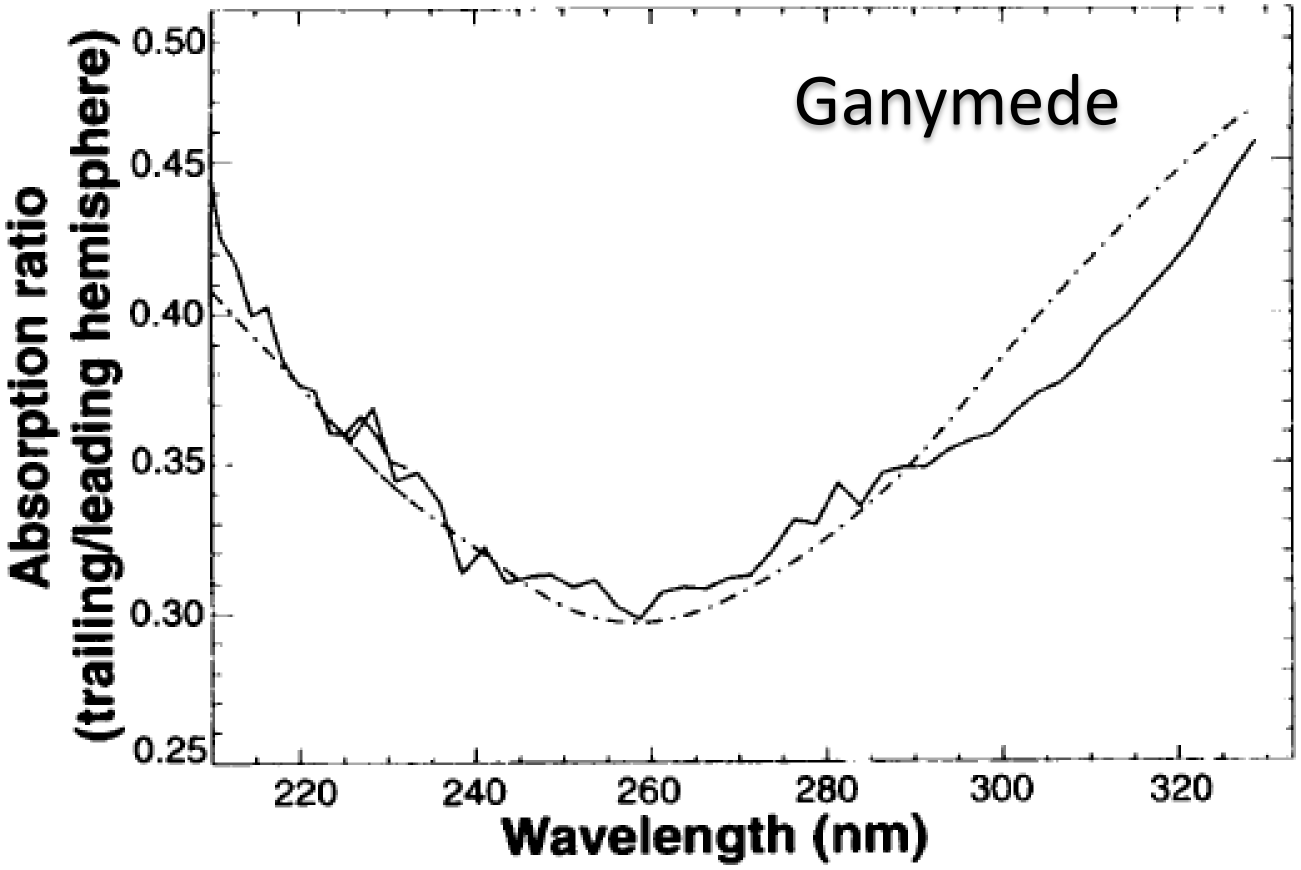
- Recently found on
- Ganymeade- moon of Jupiter
- Dione and Rhea moons of Saturn

Noll et al, Nature (1997)



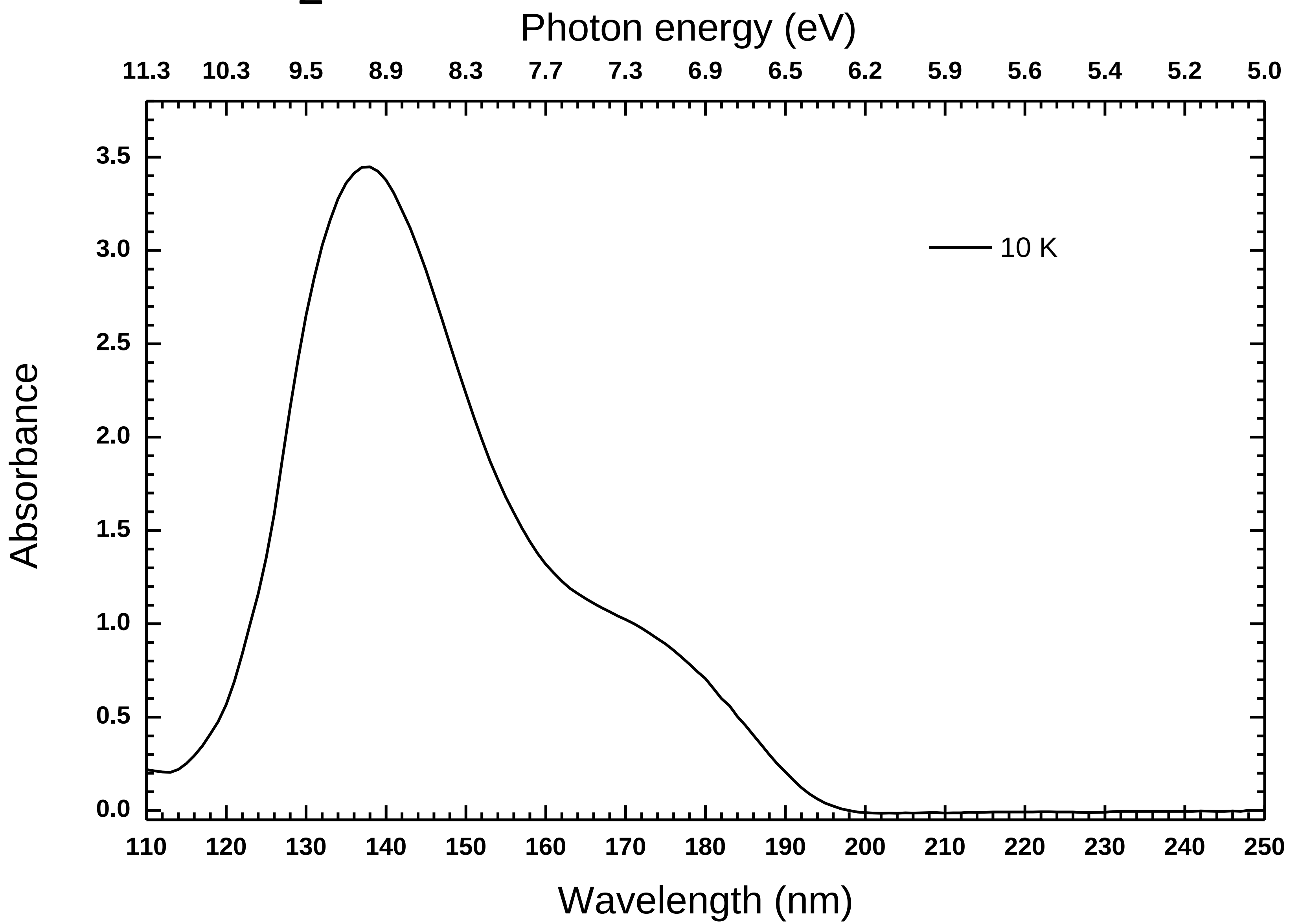
Noll et al, Science (1996)



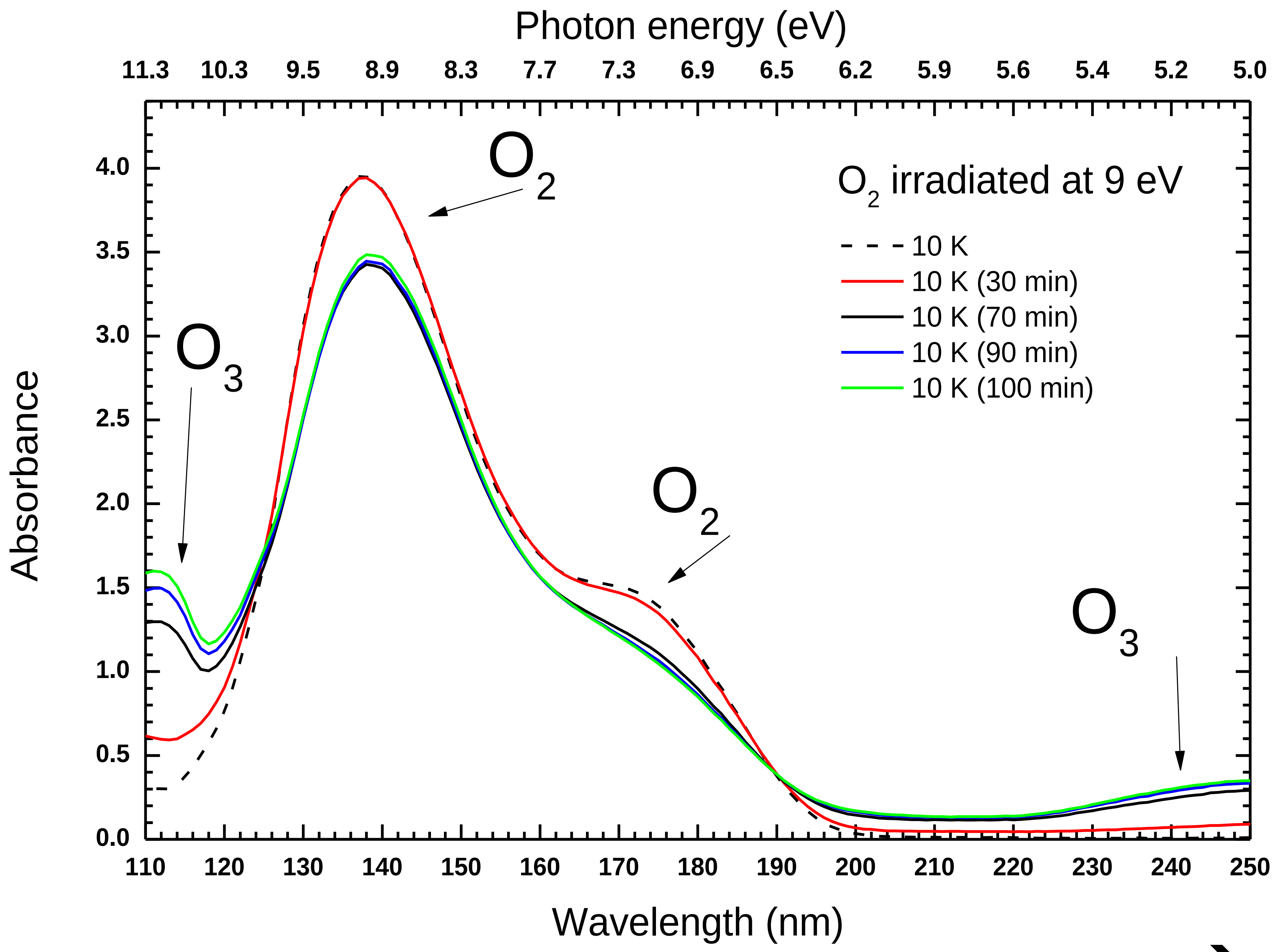
Solid ozone VUV spectra

- Solid ozone is unstable and explosive !
- So make in-situ by irradiating oxygen film
- Taiwan facility

VUV spectra - O_2

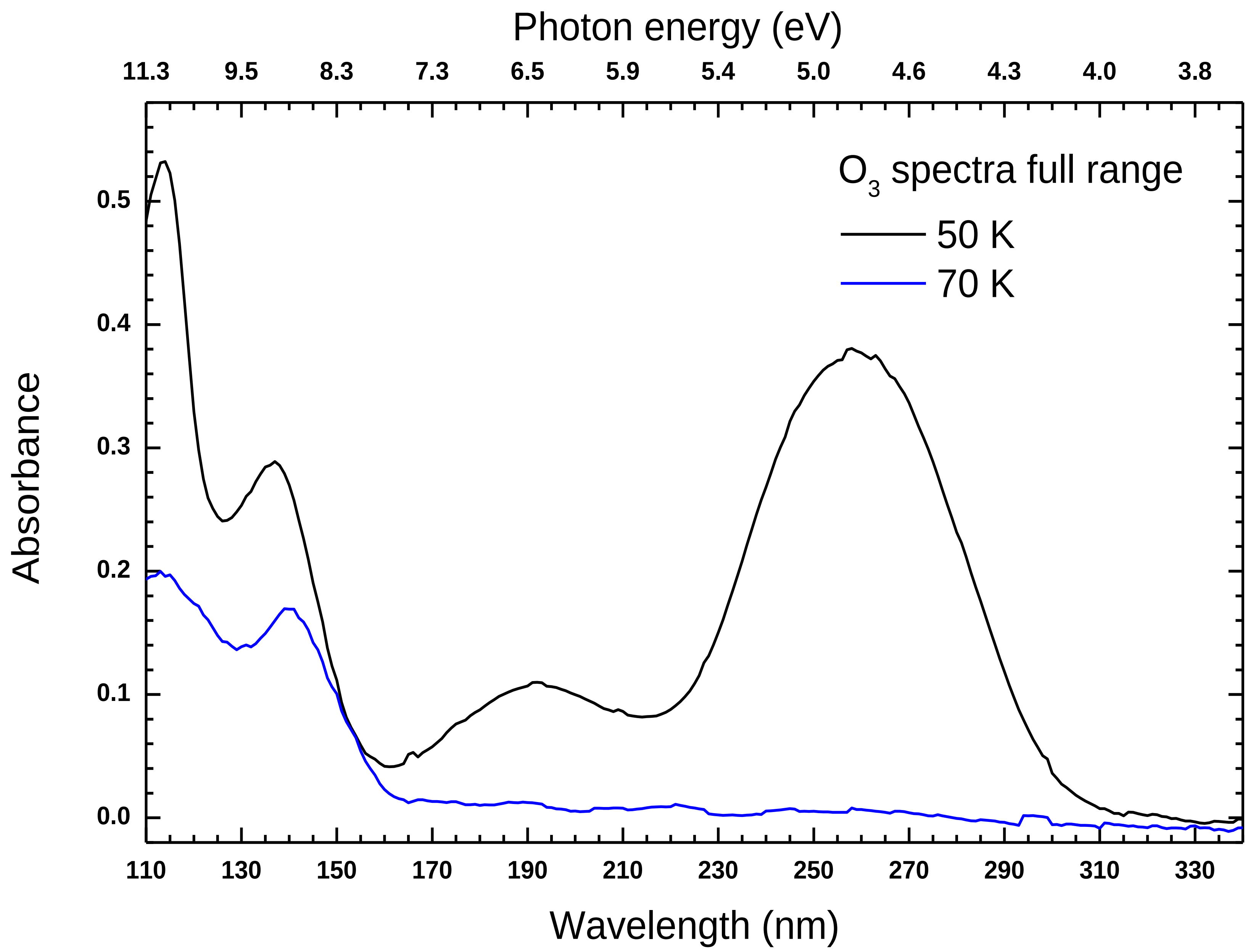


Cheng et al, Spec Chimica Acta:B, 2011.



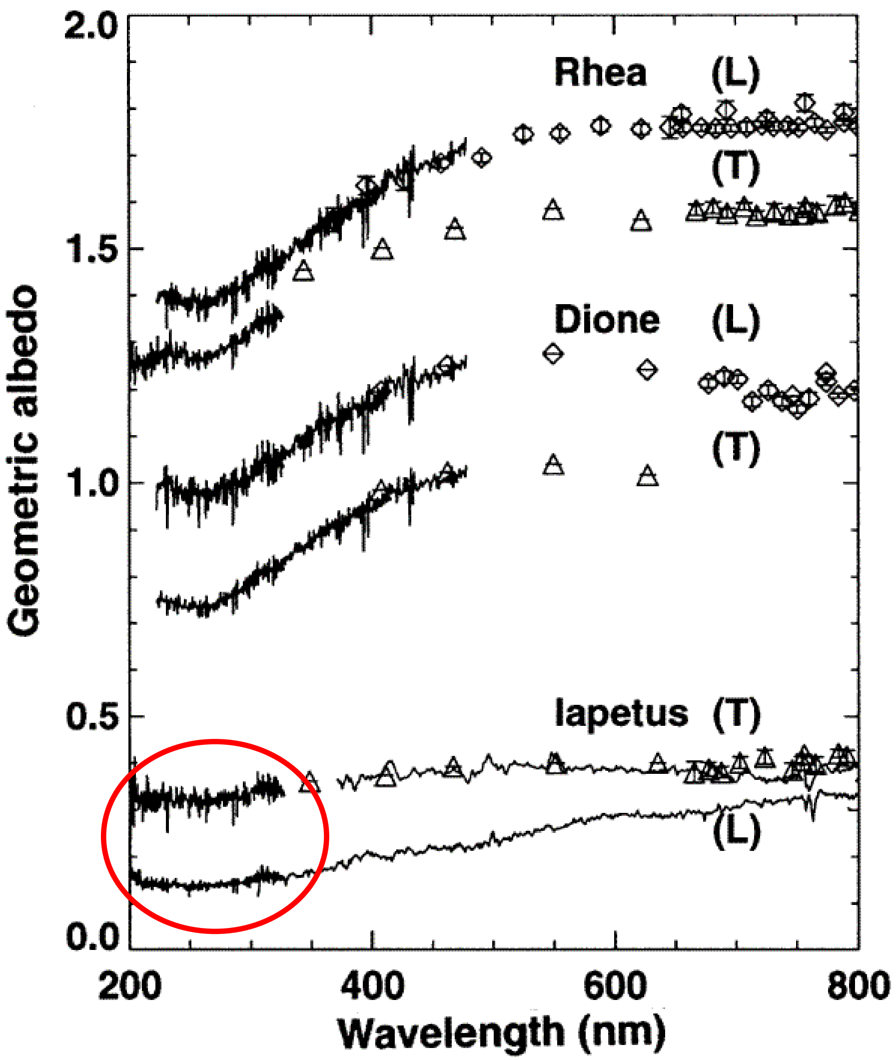
Sivaraman et al, Chem Phys Lett, 2014

$O_2 \rightarrow O_3$



Photon energy (eV)
11.3
9.5
8.3
7.3
6.5
5.9
5.4
5.0
4.6
4.3
4.0
3.8
O3 spectra full range
50 K
70 K
Absorbance
0.5
0.4
0.3
0.2
0.1
0.0
110
130
150
170
190
210
230
250
270
290
310
330
Wavelength (nm)

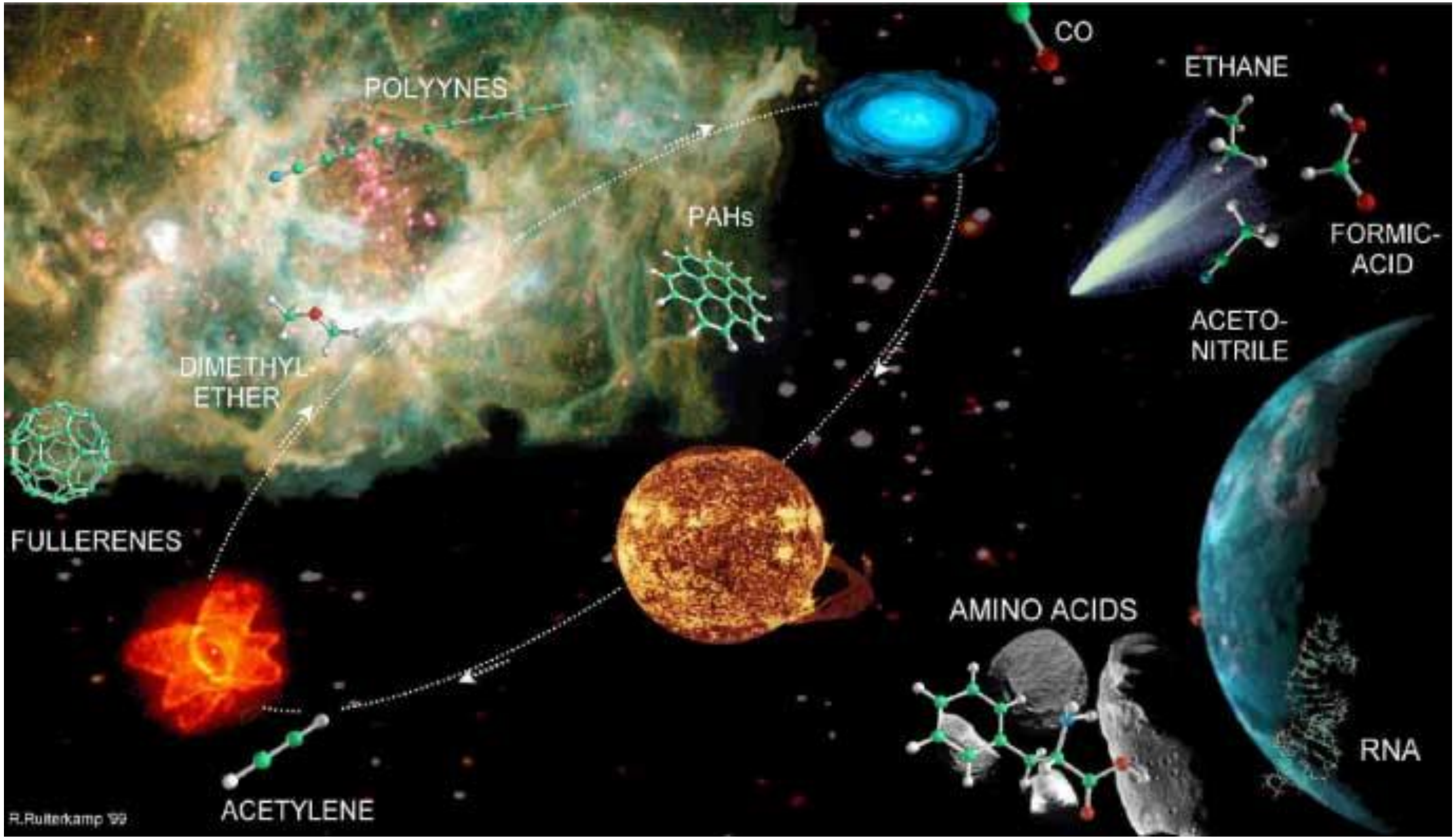
Noll et al, Nature (1997)



Other molecules

– So far discovered

– and to be discovered (ALMA)



ASTROCHEMICAL ICES DATABASE

ACID

ACID Login Registration

Astrochemical Ices Database

MOL-PH Group,

Space and Atmospheric Sciences Division

Physical Research Laboratory

Ahmedabad, India

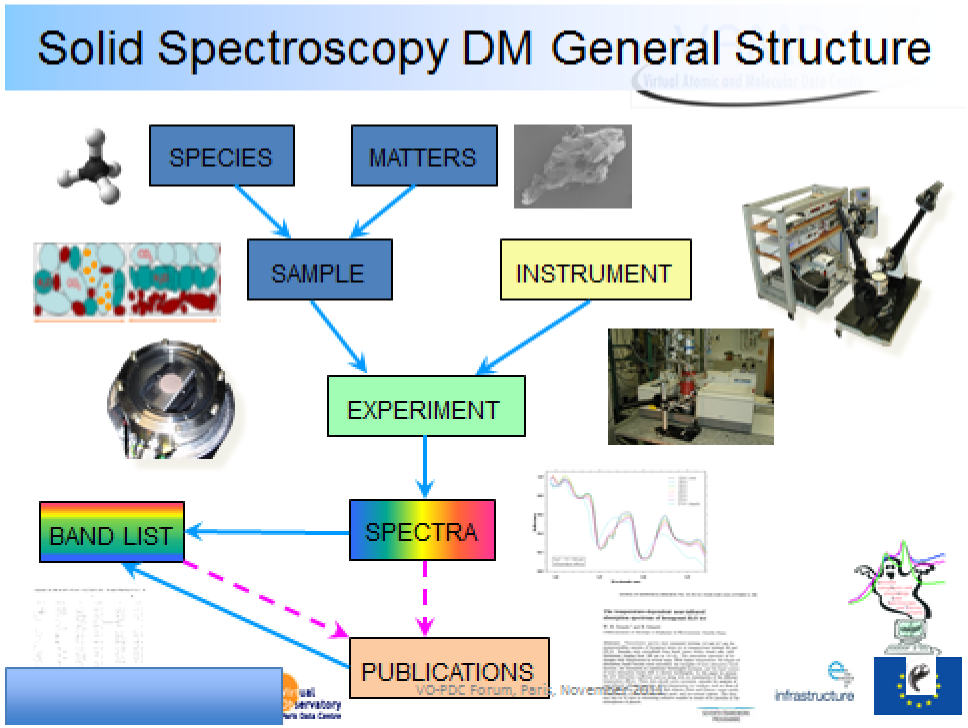
The Astrochemcial Ices Database is a spectral repository for infrared and vacuum ultraviolet spectra of astrochemical ice analogs.

To refer and download spectra or the data file, please obtain an user id by registering your details. Thank you!

Collect and deposit in ACID1 database

- Comparison with gas phase data
- Seek absolute cross sections
- Compare with IR spectra (phase changes)

- Develop SSHADE database as part of Europlanet RI



europlanet 2020

VAMDC

Virtual Atomic and Molecular Data Centre

http://www.vamdc.eu (.org)

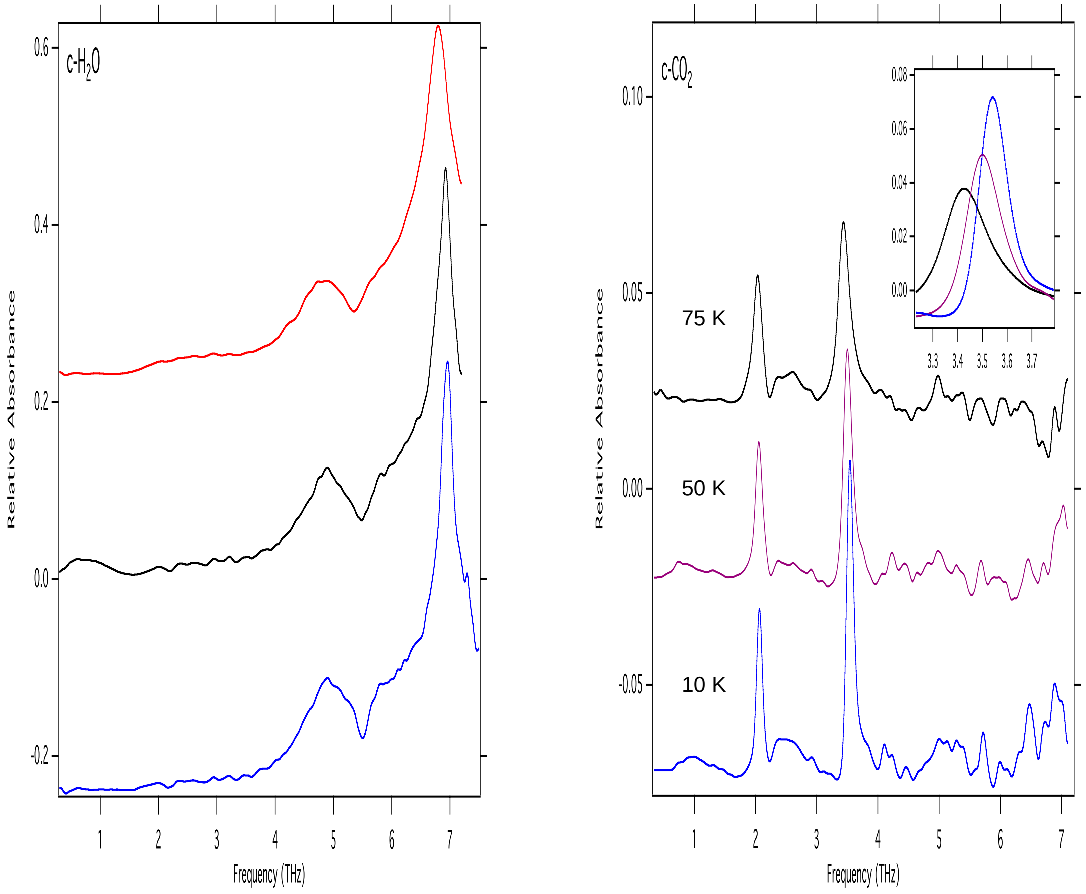
Coordinator: Marie-Lise Dubernet

Observatoire de Paris,

Université Pierre et Marie Curie

And in the future !

- **THz ice spectroscopy**
- Sergio Ioppolo
- THz spectra of: (left panel) crystalline water ice deposited at 150 K; (right panel) crystalline CO2 ice deposited at 75 K.

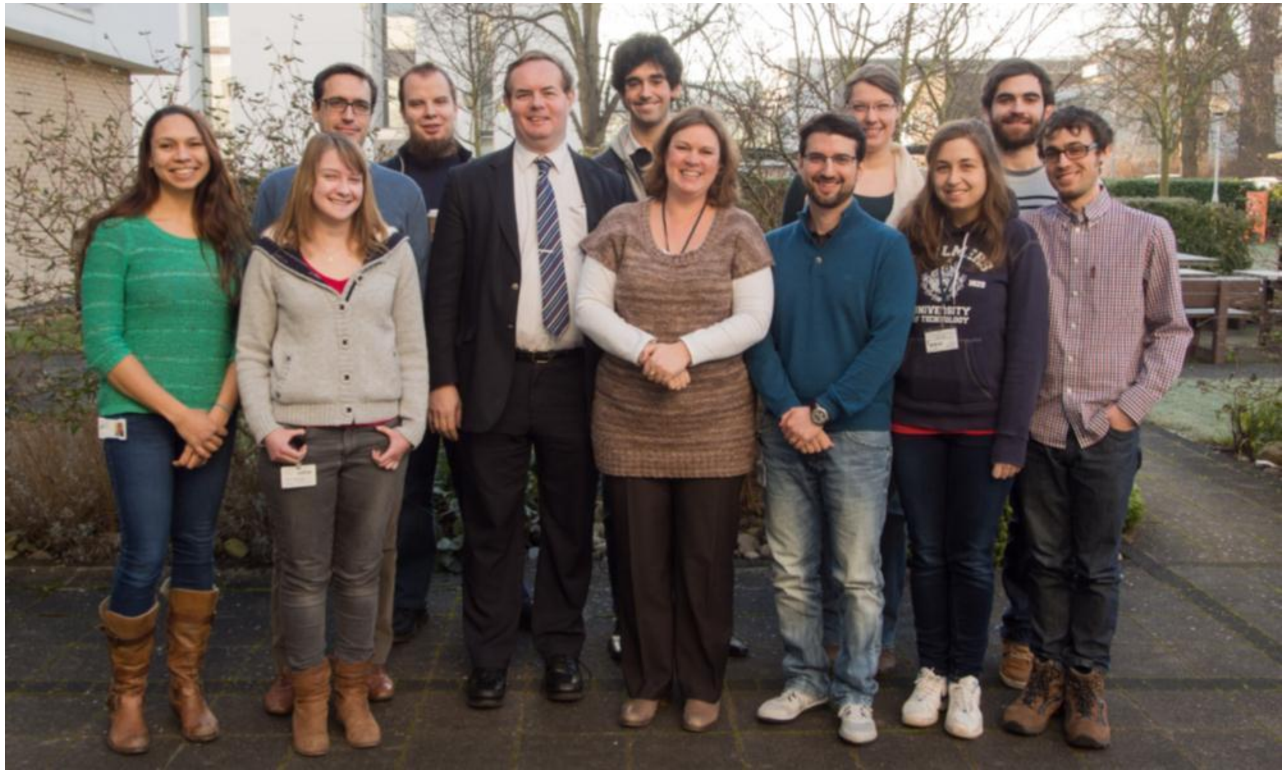


Conclusions

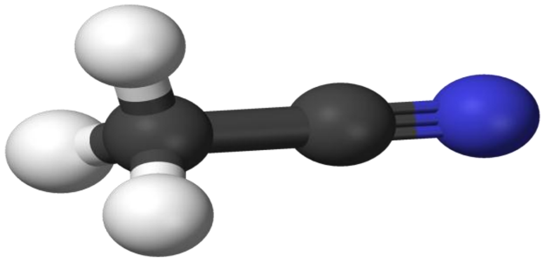
- Spectral database of astrochemical /planetary ices is being compiled
- Such spectra reveal interesting (and complex) morphology
- See Anita Dawes talk tomorrow on benzene/water ices

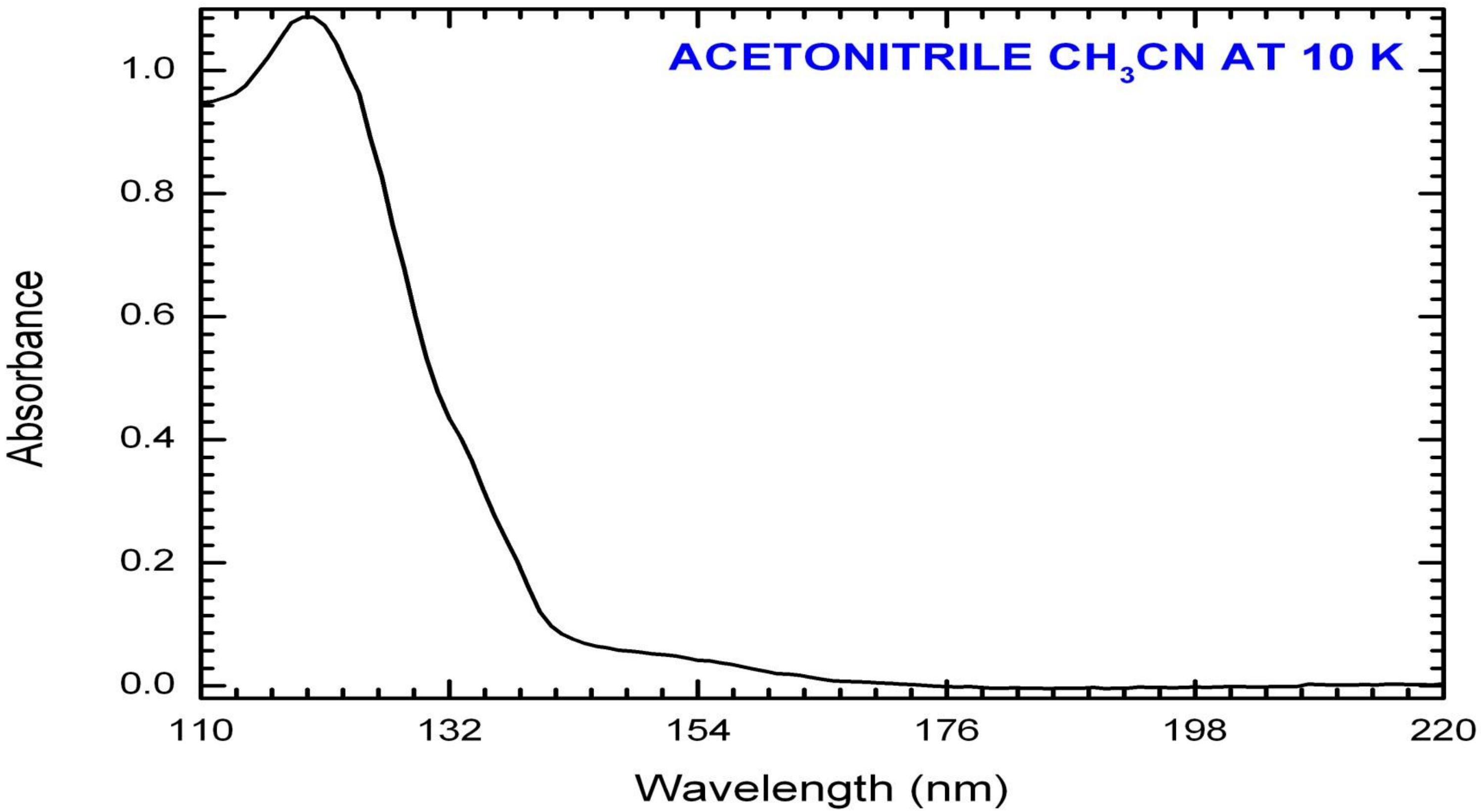
and finally ..

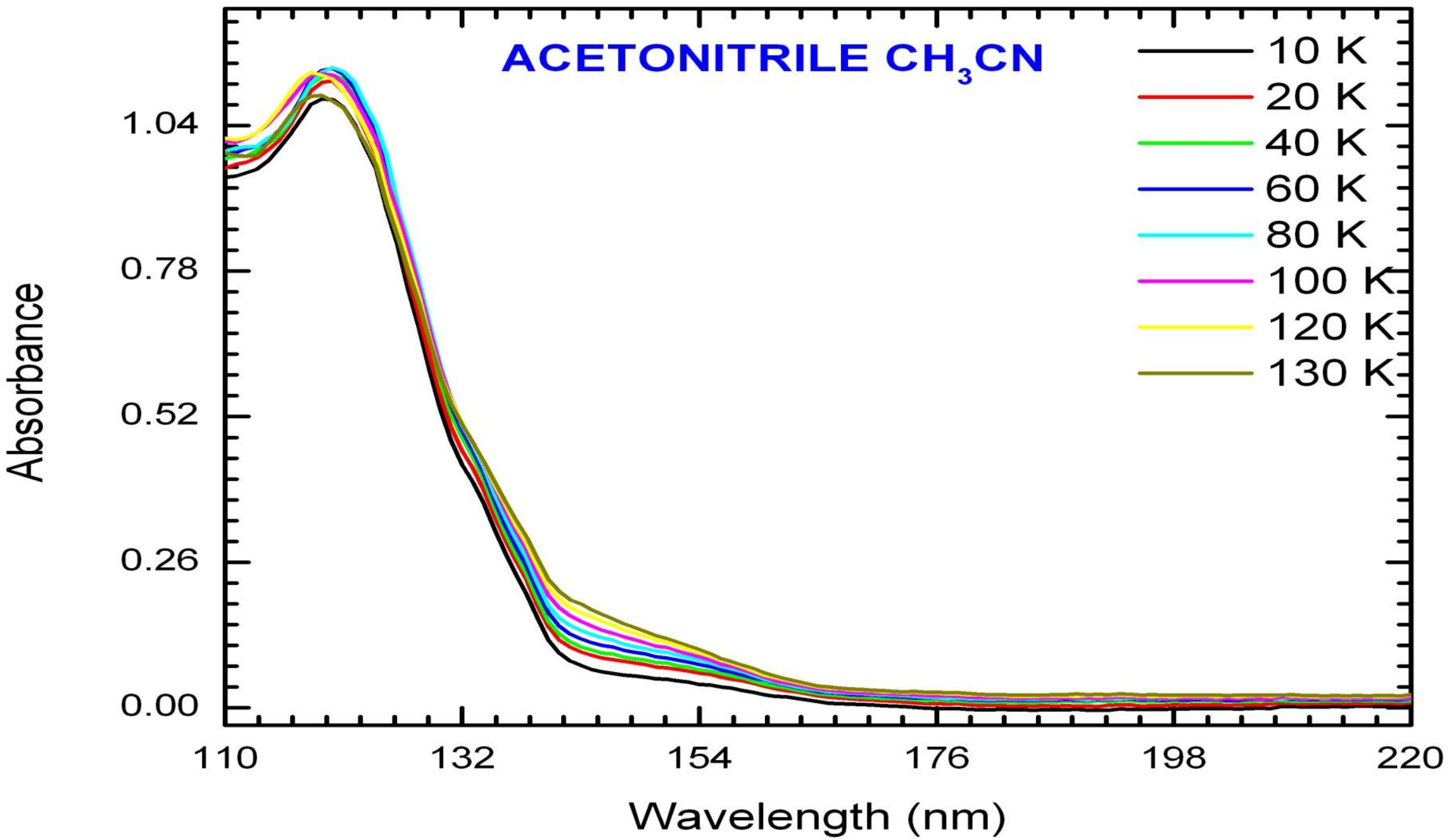
- Bhala Sivaraman
- Binu Nair
- PRL India



ACETONITRILE (CH_3CN)

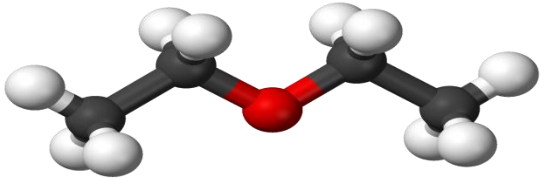


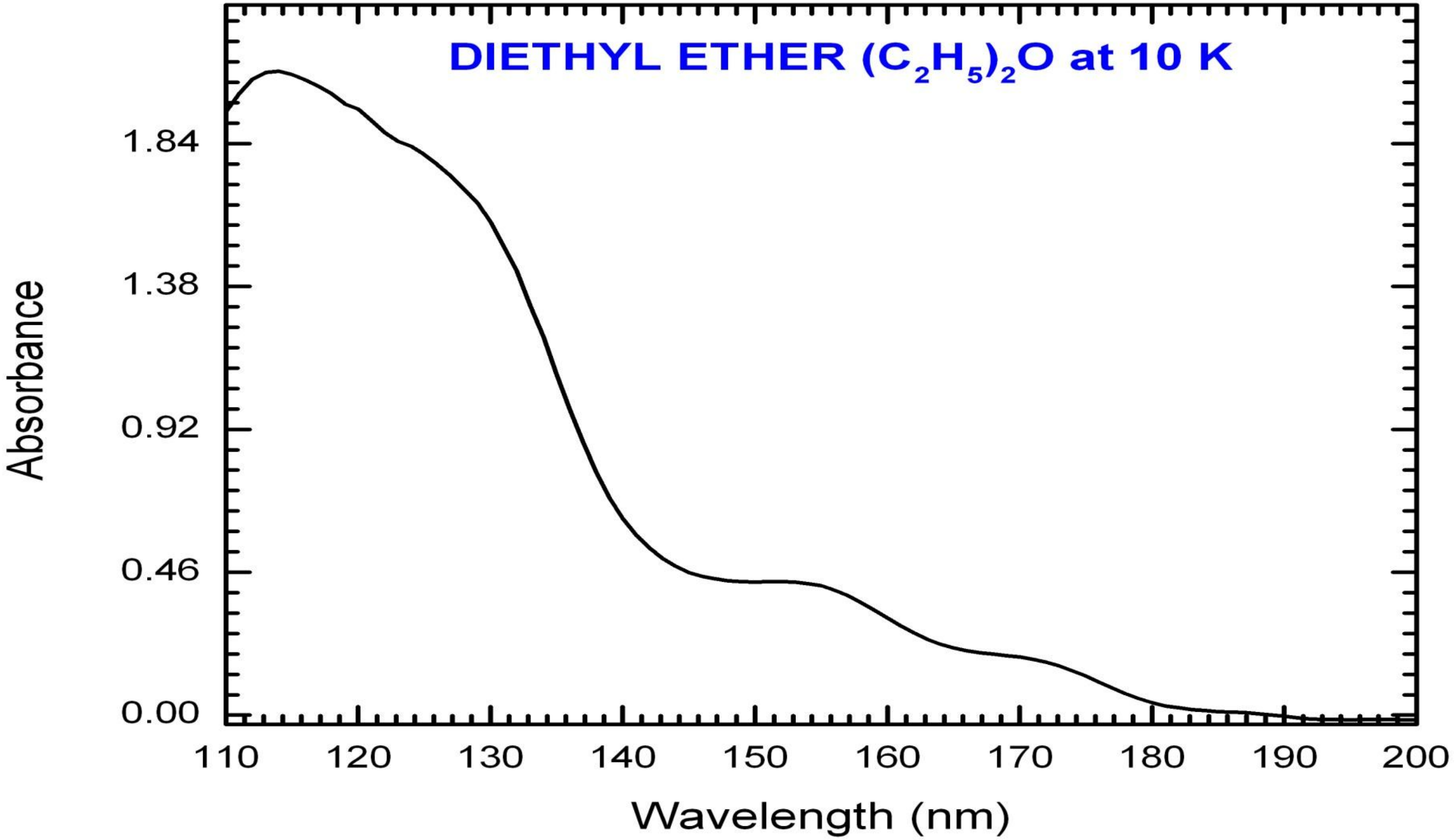


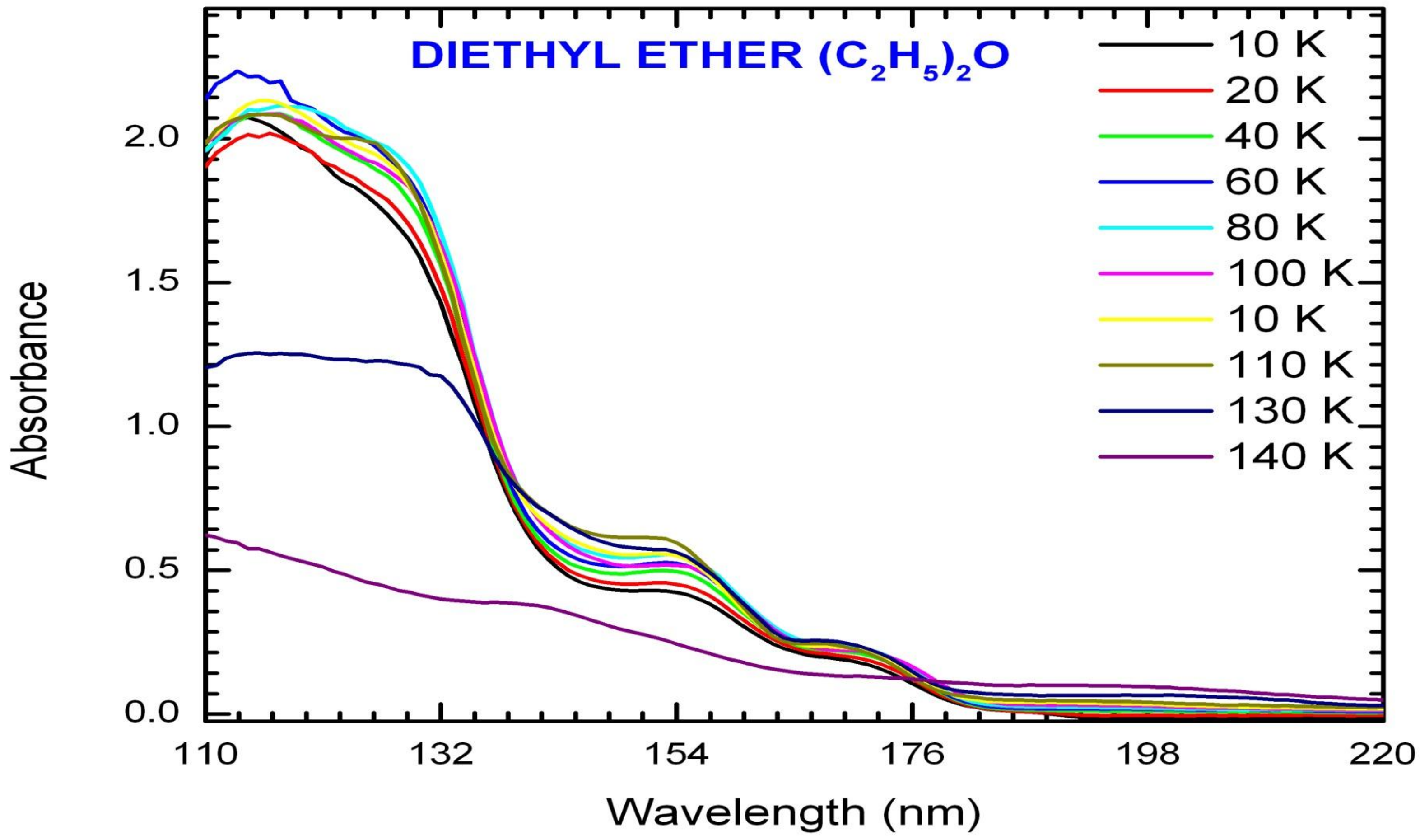


ACETONITRILE CH_3CN
10 K
20 K
40 K
60 K
80 K
100 K
120 K
130 K
Absorbance
1.04
0.78
0.52
0.26
0.00
110
132
154
176
198
220
Wavelength (nm)

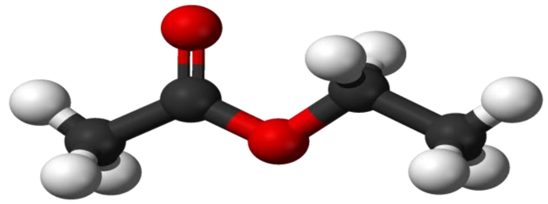
DIETHYL ETHER $(C_2H_5)_2O$

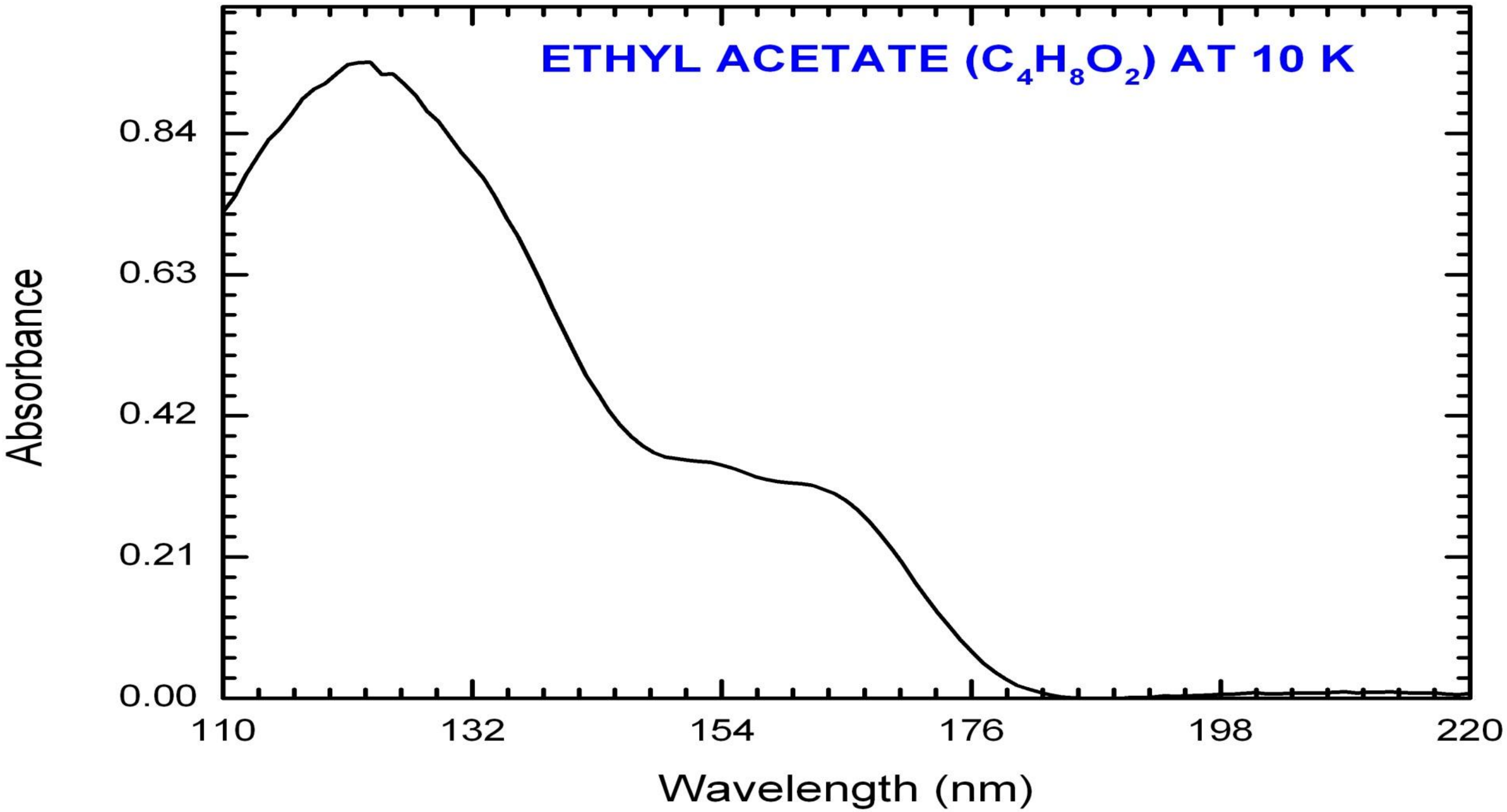




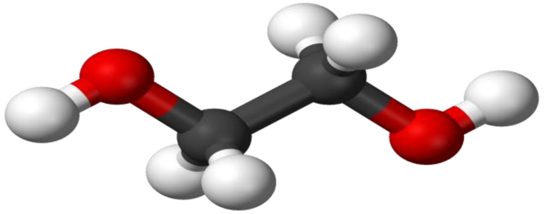

DIETHYL ETHER $(C_2H_5)_2O$
10 K
20 K
40 K
60 K
80 K
100 K
10 K
110 K
130 K
140 K
Absorbance
0.0
0.5
1.0
1.5
2.0
110
132
154
176
198
220
Wavelength (nm)

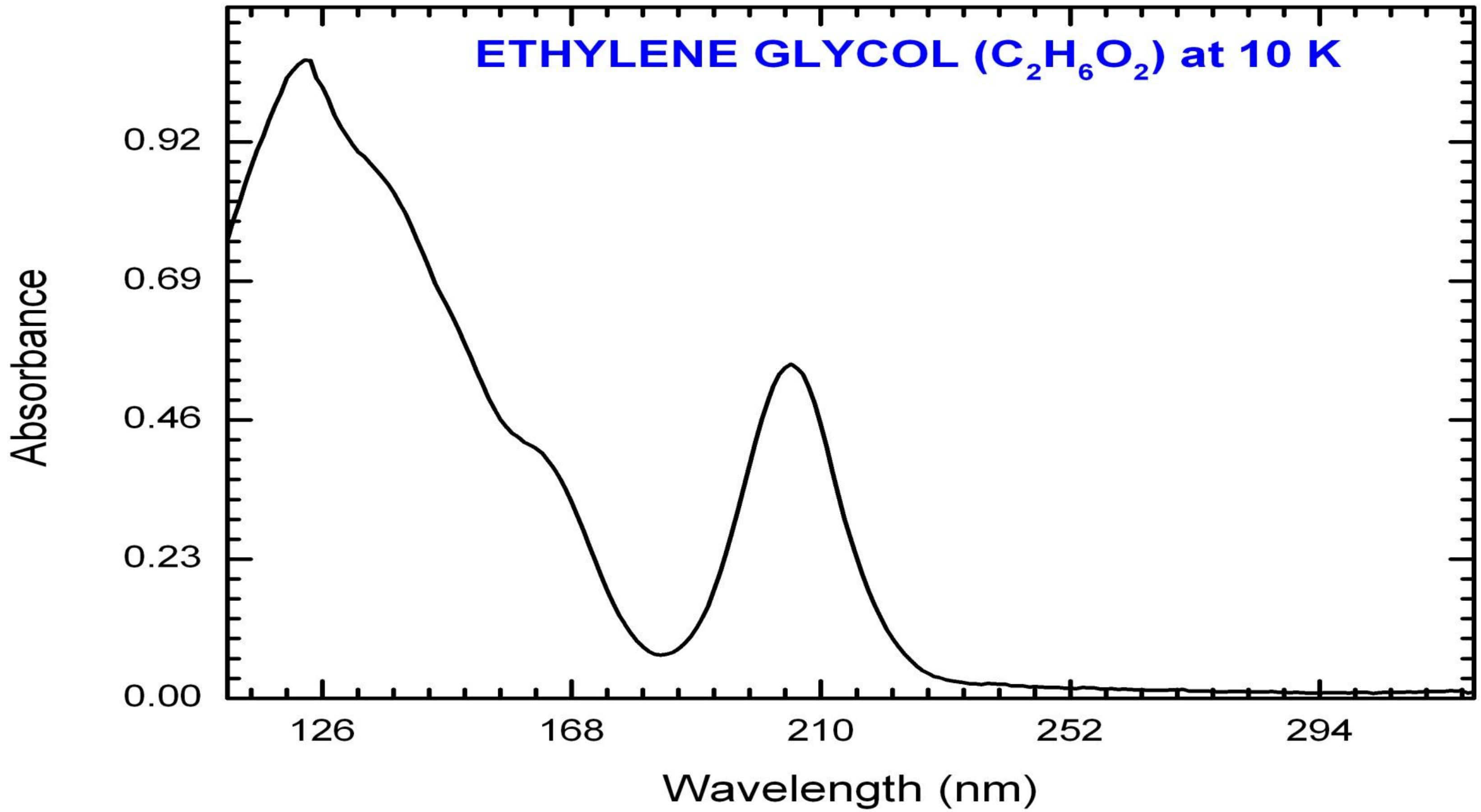
ETHYL ACETATE ($C_4H_8O_2$)



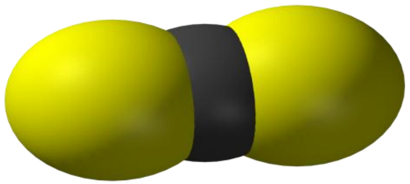


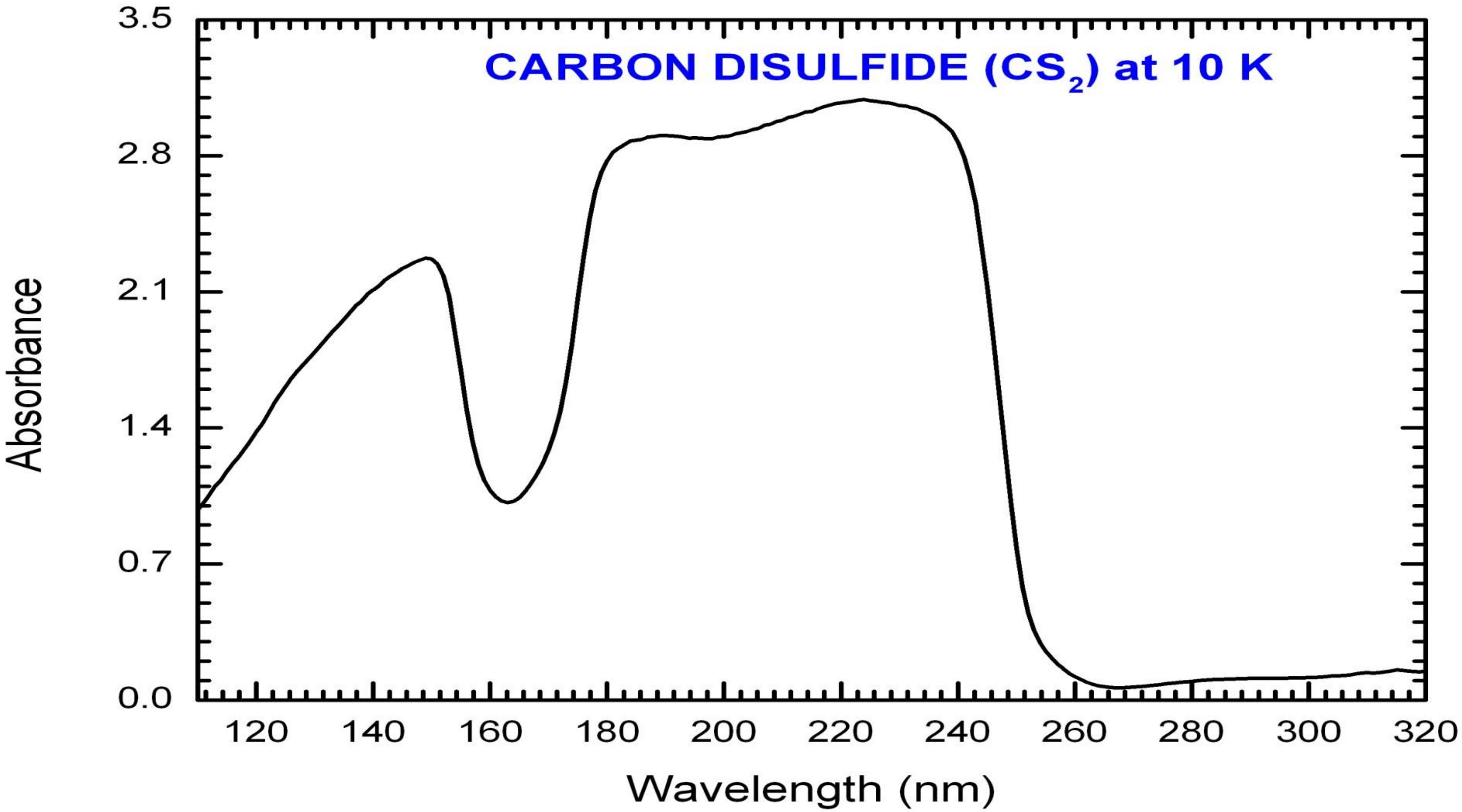
ETHYLENE GLYCOL ($C_2H_6O_2$)

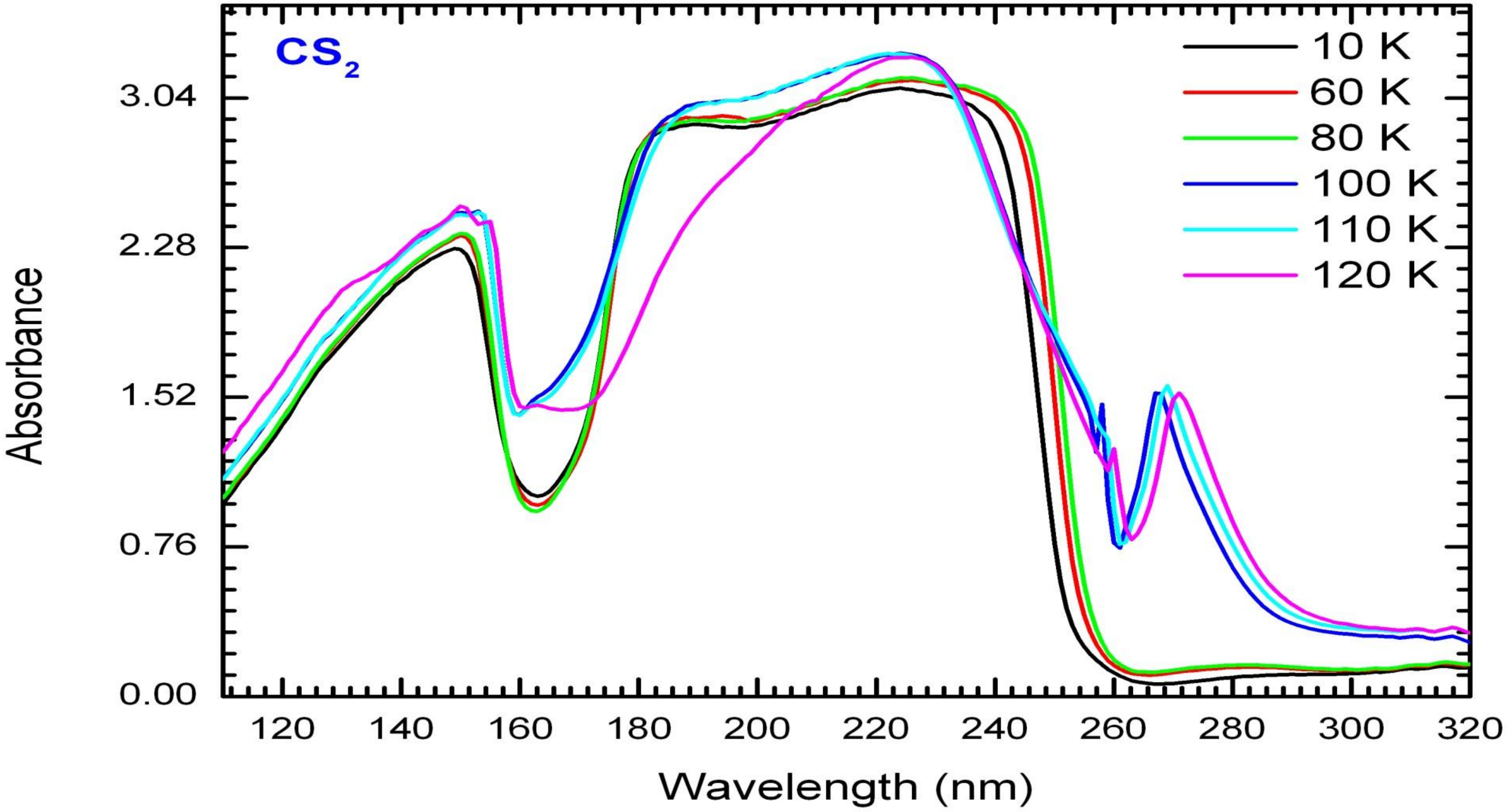




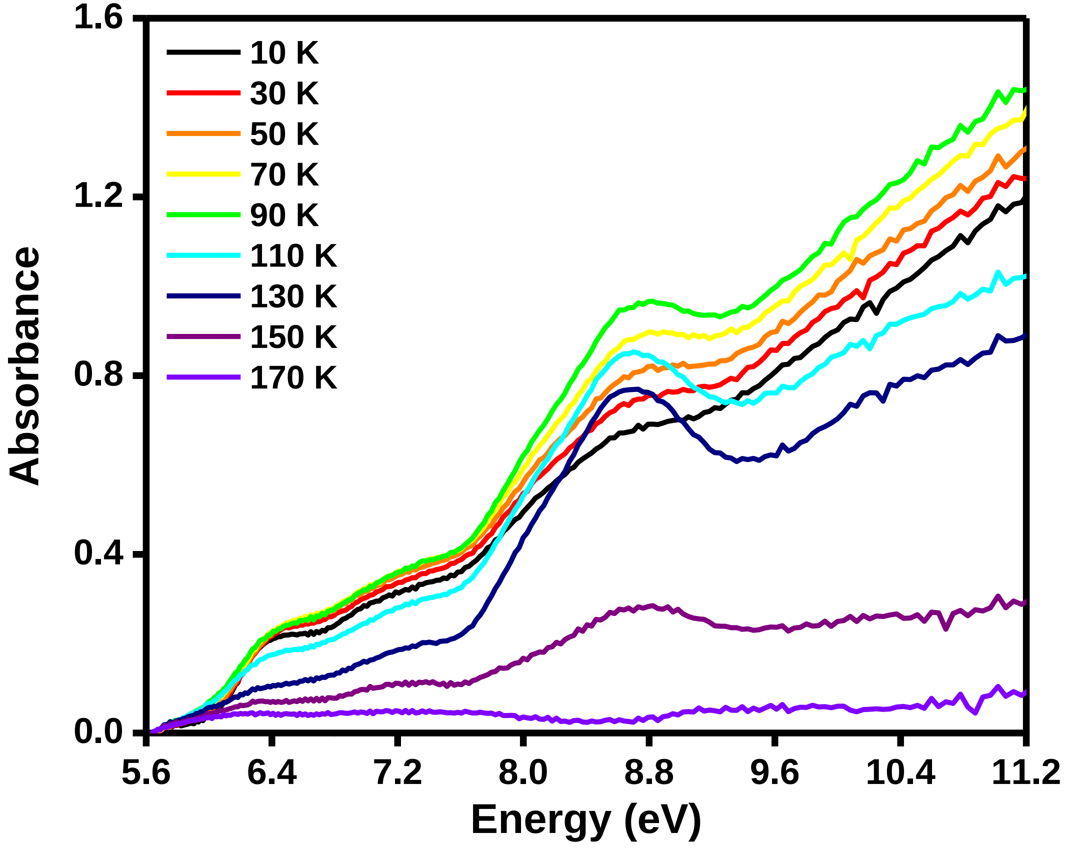
CARBON DISULFIDE (CS_2)

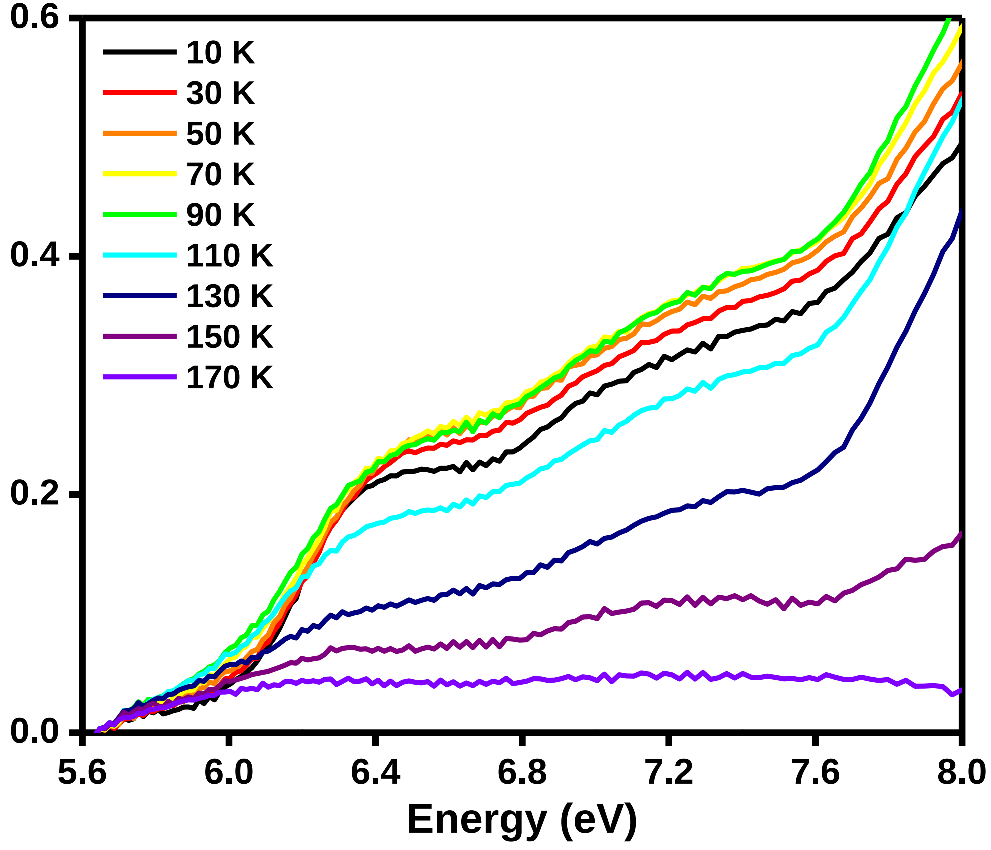





CS2
10 K
60 K
80 K
100 K
110 K
120 K
Absorbance
3.04
2.28
1.52
0.76
0.00
120
140
160
180
200
220
240
260
280
300
320
Wavelength (nm)

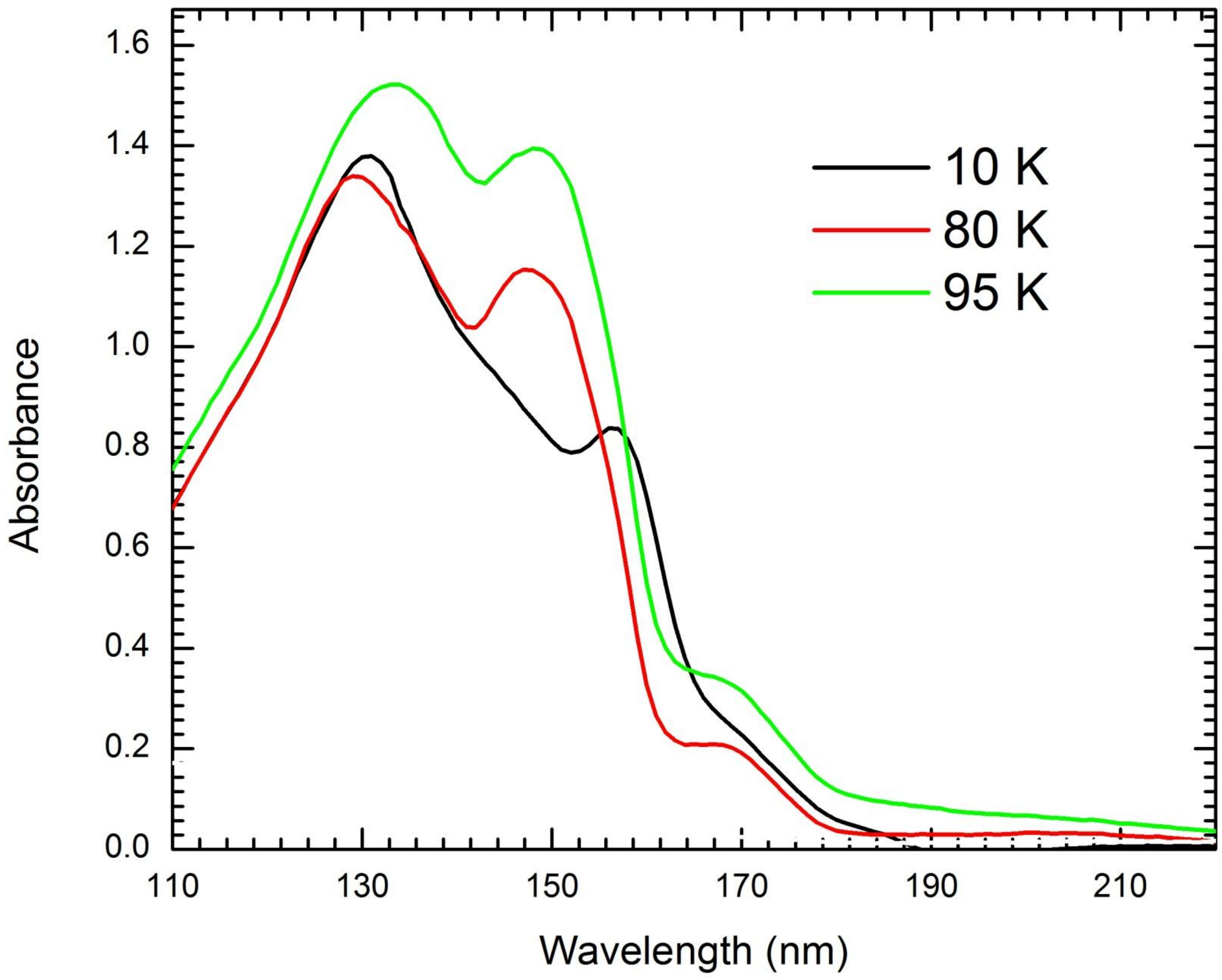
Ethanethiol (CH_3CH_2SH) - Discovery in 2014



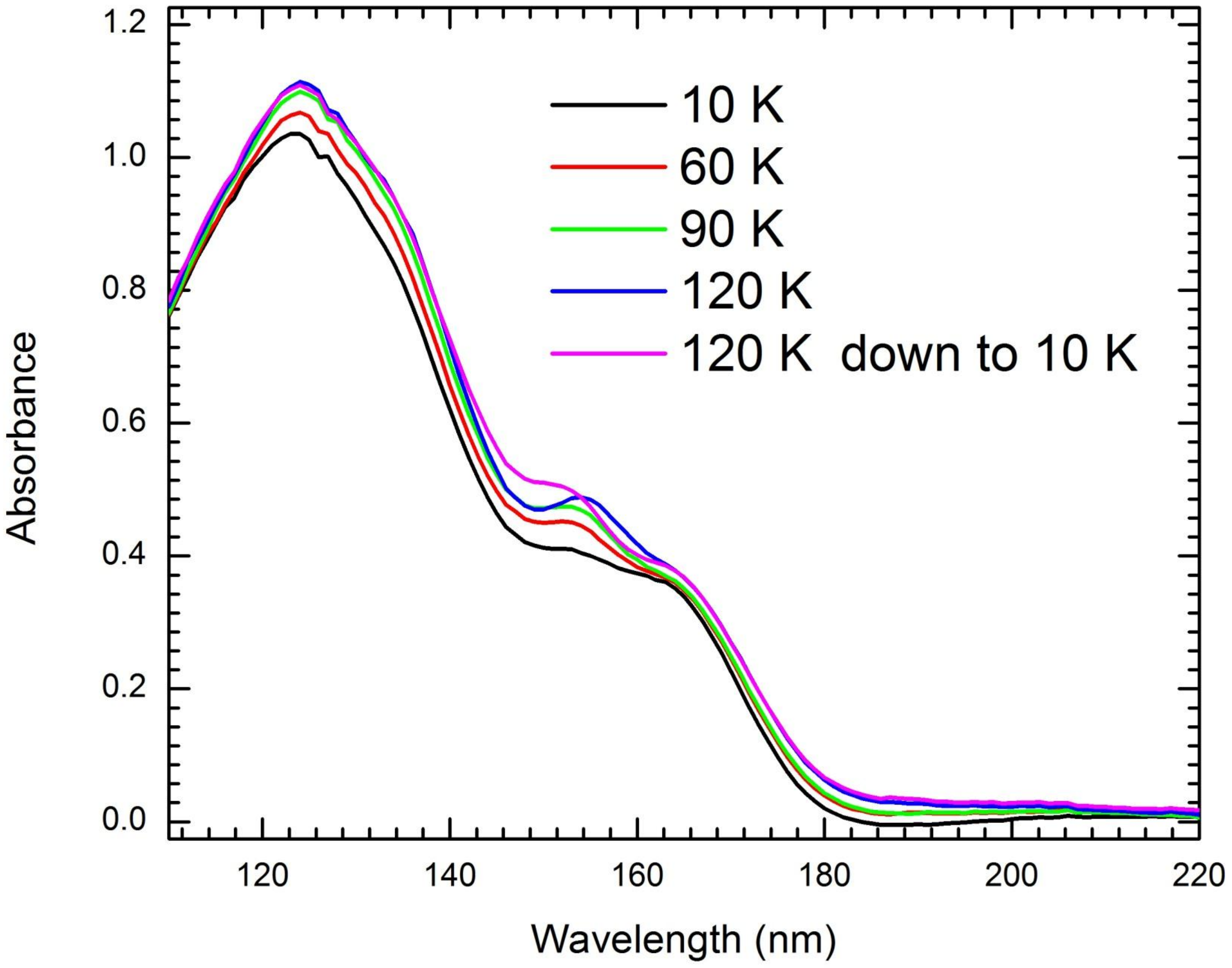


Bhuin, Sivaraman et al, JCP- Communications, 2008

Dimethyl ether



Ethyl acetate



Ethylene glycol