Electron interactions with atoms, molecules, clusters and surfaces

What we know and what we need to know for next generation plasma technologies physics

Atomic and Molecular Data Needs for Plasma Applications Workshop.

April 13 – 15 2021

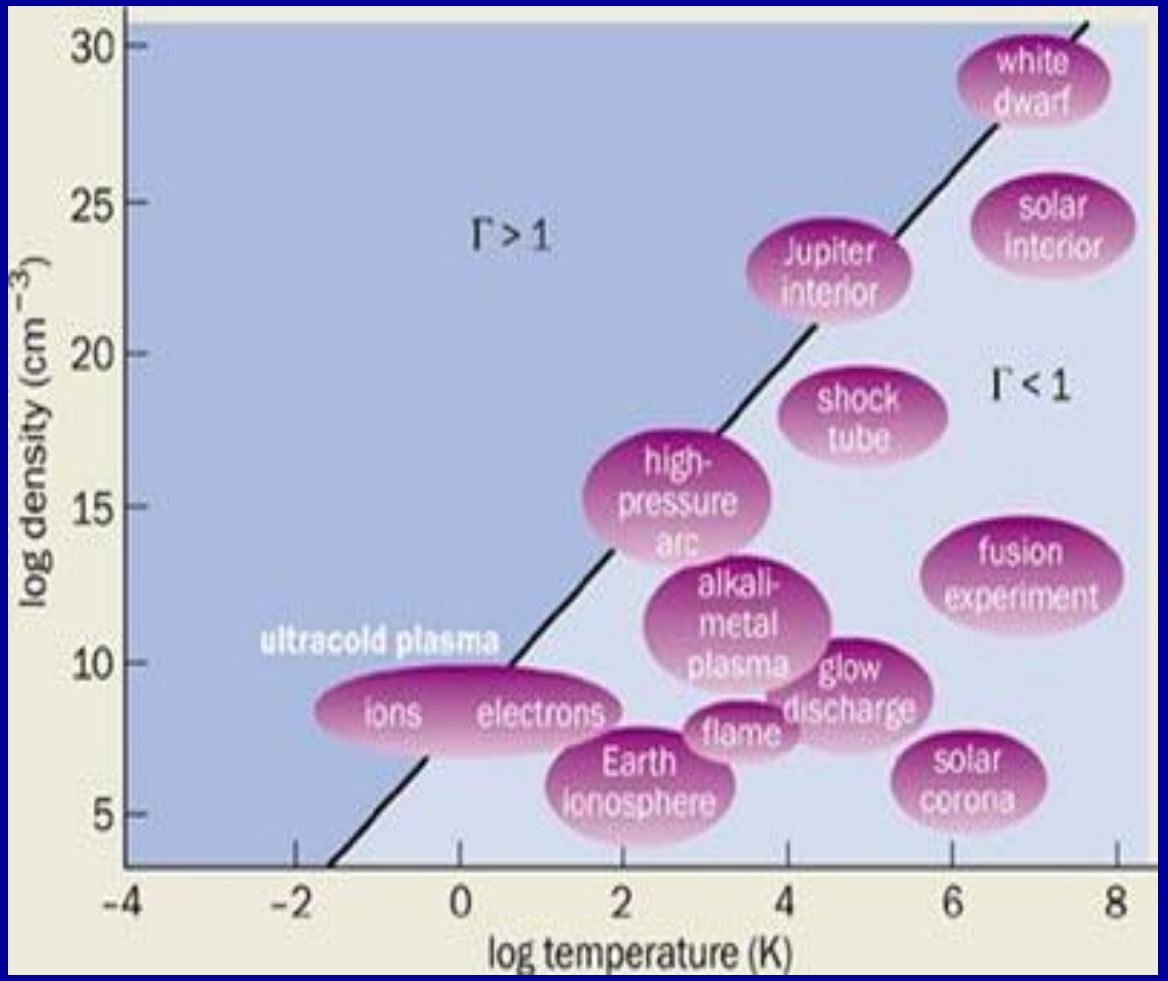
Nigel Mason
The University of Kent

University of Kent

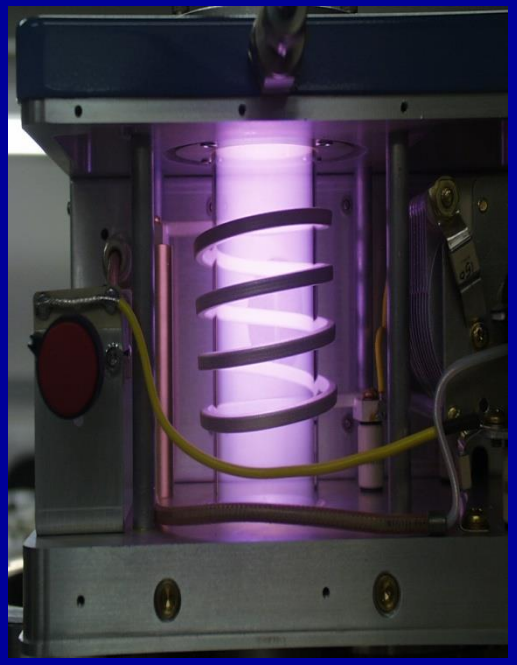
Plasmas cover a wide range

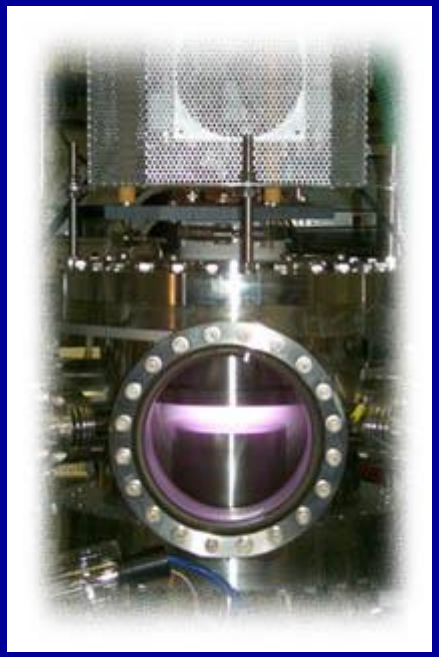
- Divide into three categories;

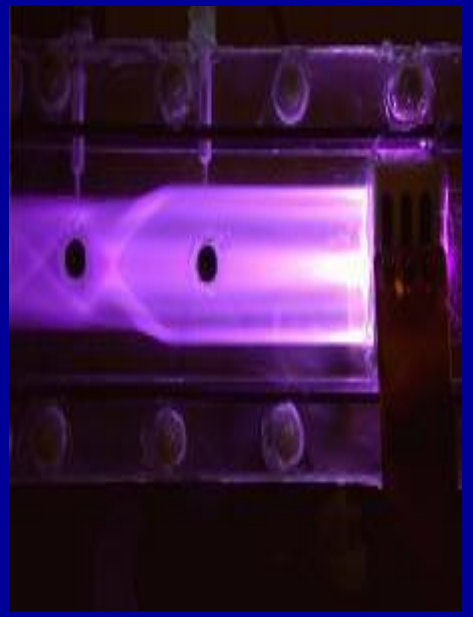
- **Low pressure**
- **Atmospheric plasma**
- **Fusion plasma**



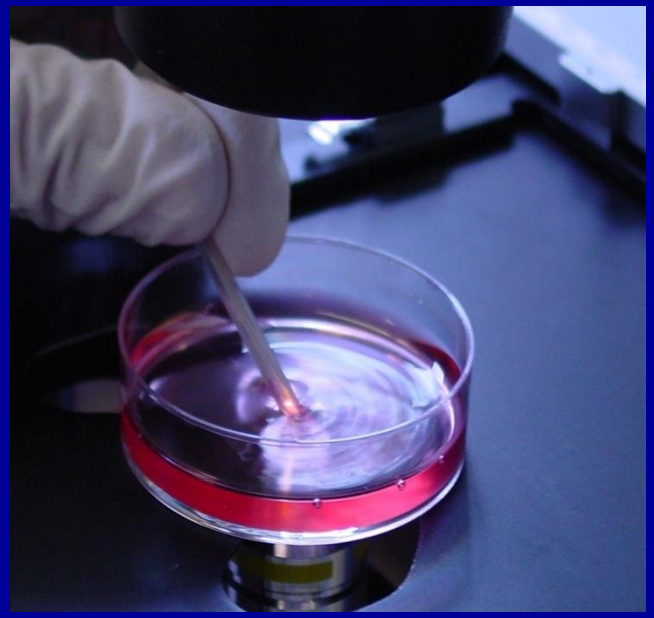
Technological plasmas in semiconductor industry, CVD, magnetrons and pollution abatement



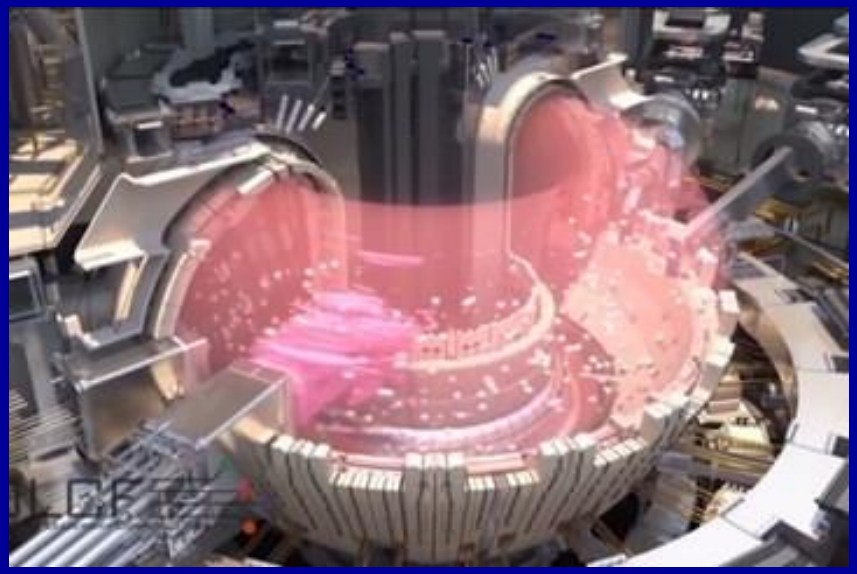


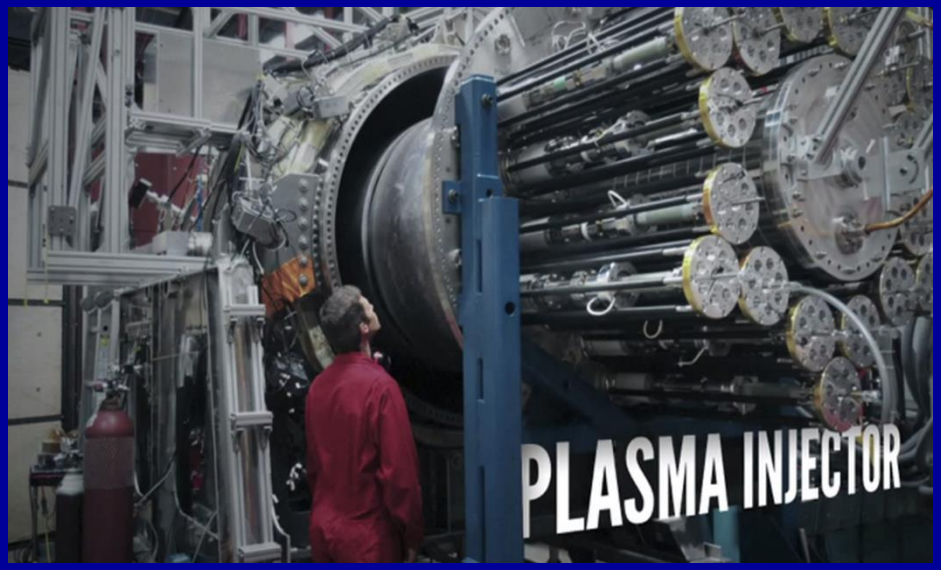


Atmospheric plasma plasmas
Biophysics and medical applications



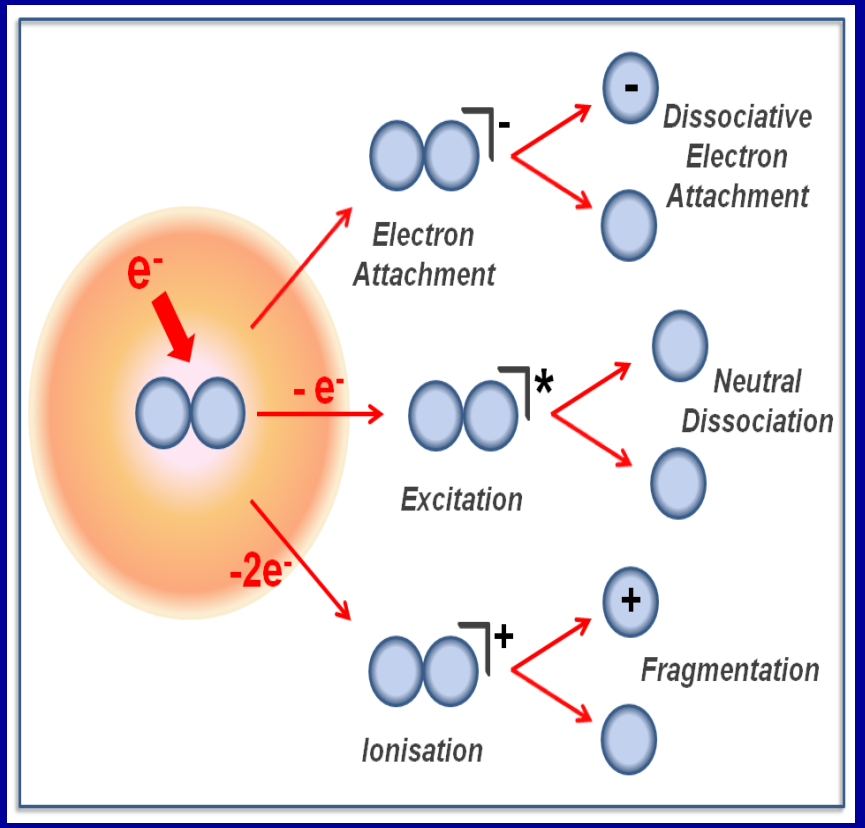
Fusion plasmas





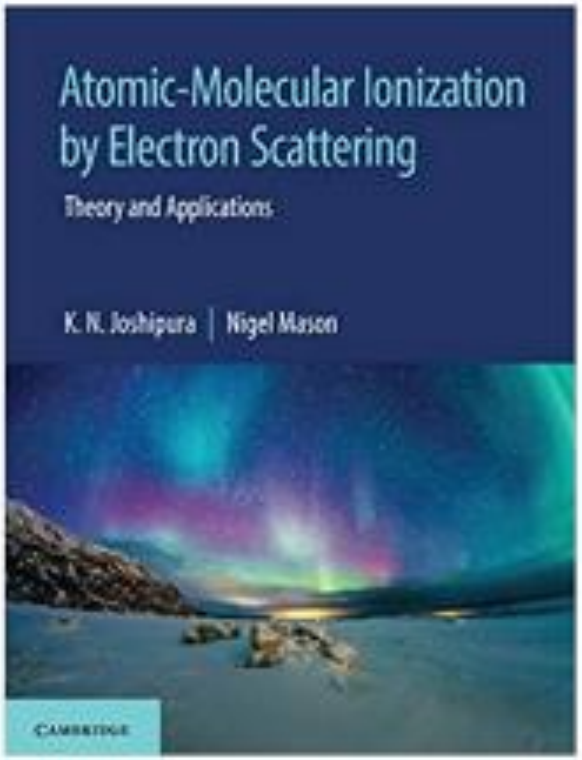
However, in order to understand all of these, we require knowledge of the fundamental processes – physical and chemical !

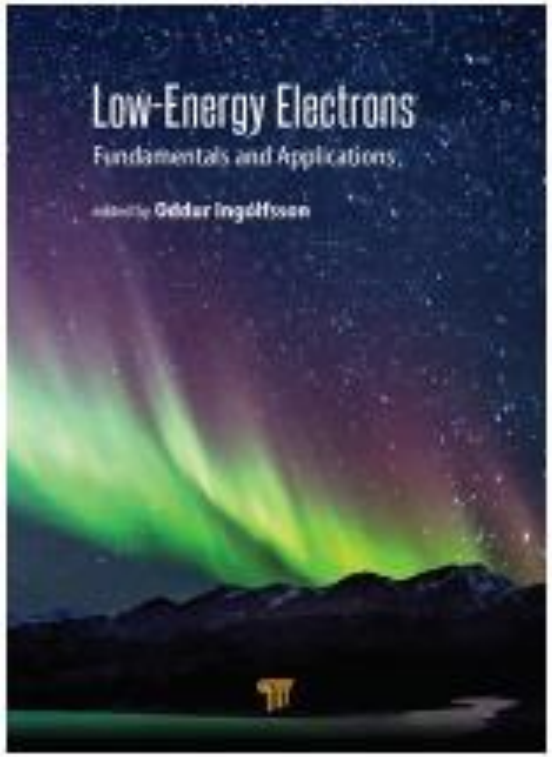
One of the most important set of processes are electron induced processes - previous talk



Reference Texts

- **Review of role of electrons in different applications**





Electron driven processes in plasmas
Database assessment

- **What data is needed ?**

- Energy resolved cross sections
- Average temperature dependent rate coeffs
- Dissociation/ionisation processes (including DEA, DR)
- Collisions with fragments (eg CF_3 and CF_2)
- Emission cross sections for diagnostics

So where are we now in electron studies ?

- Electron –molecule interactions
- Still poor c.f. atoms
- Difficulty remains complexity of targets – increasing complex ‘more electron rich’ (Cooper and Gorfinkiel talks)

- Still poor data for dissociation – drives chemistry

So where are we now in electron studies ?

Electron –molecule interactions

Total cross sections;

Accurate to some 5%

(allow for forward scattering)

Lowest energies few meV !

So where are we now in electron studies ?

Electron –molecule interactions

Elastic cross sections;

Accurate to some 10% - good standards

Angular range – can now measure 0 to 180°

So momentum transfer cross section data are improving

So where are we now in electron studies ?

Electron –molecule interactions

Inelastic cross sections;

Vibrational (but resolution and deconvolution)
(Deborah next talk)

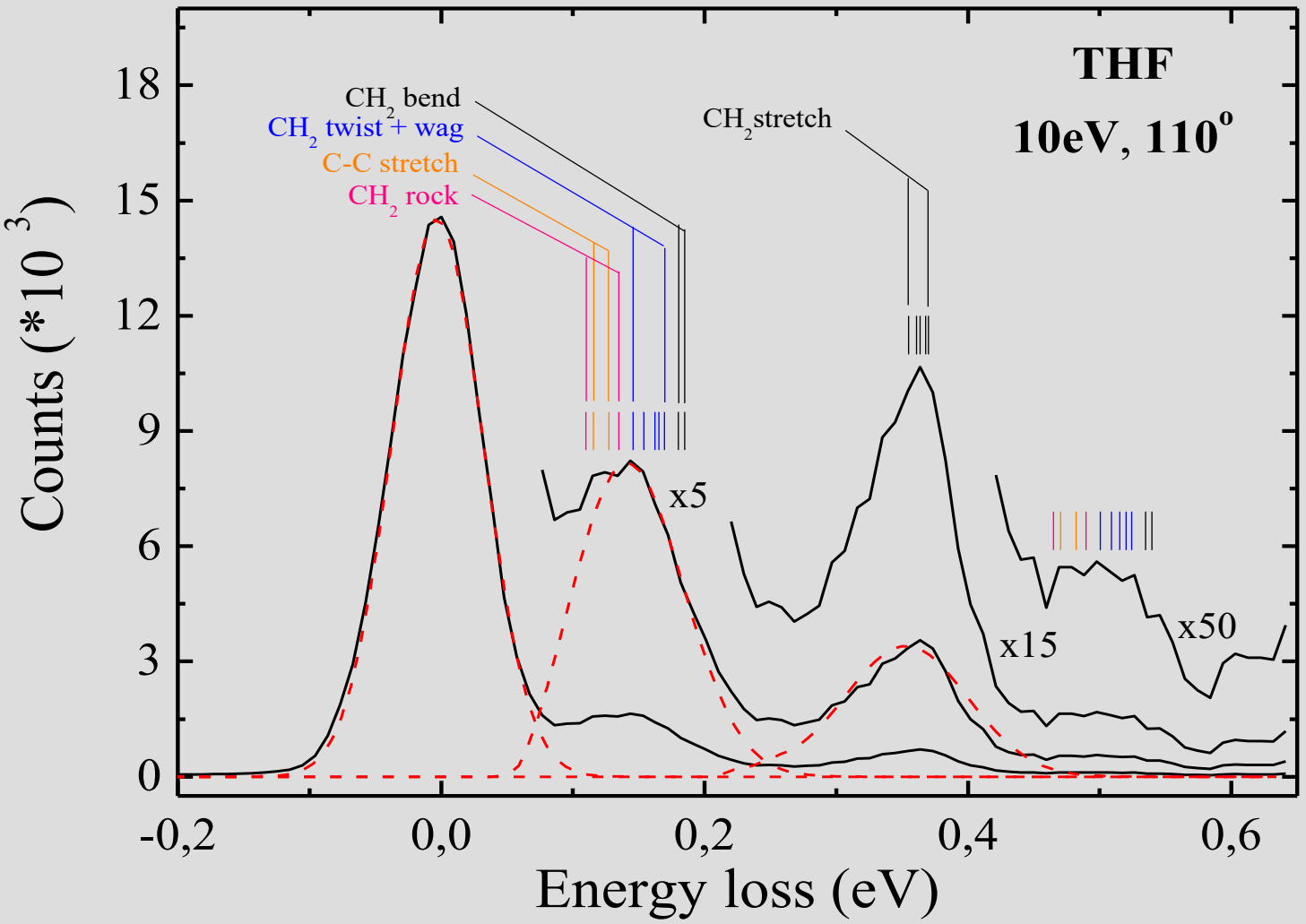
Excitation – still very poor despite importance

Rotational excitation…

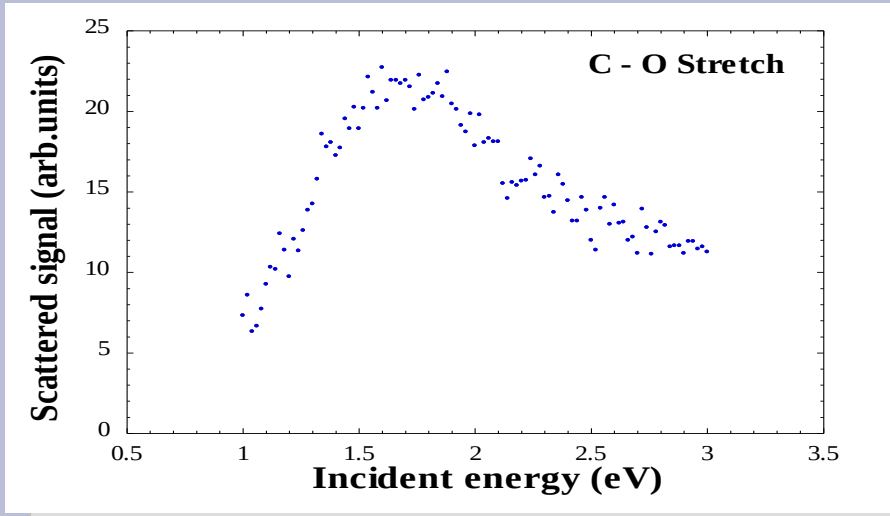
Swarm derived data vs beam data – still discrepancies

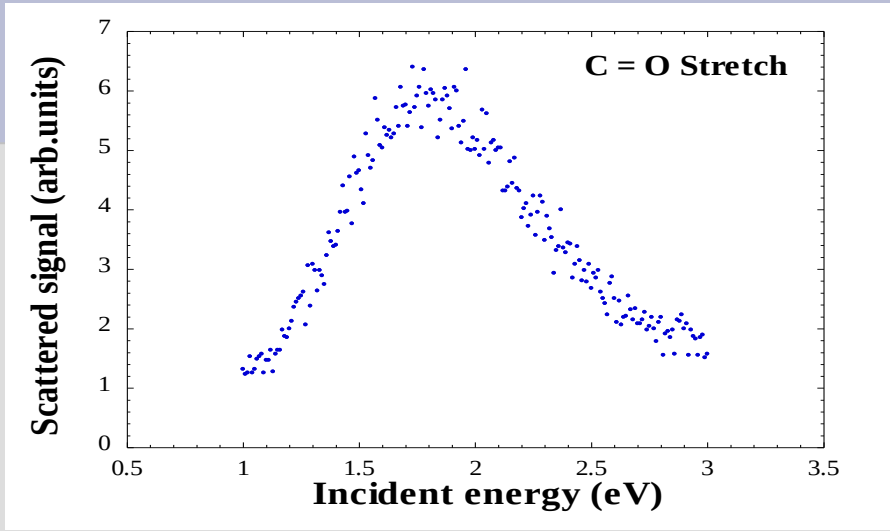
Vibrational excitation
Problem of deconvultion

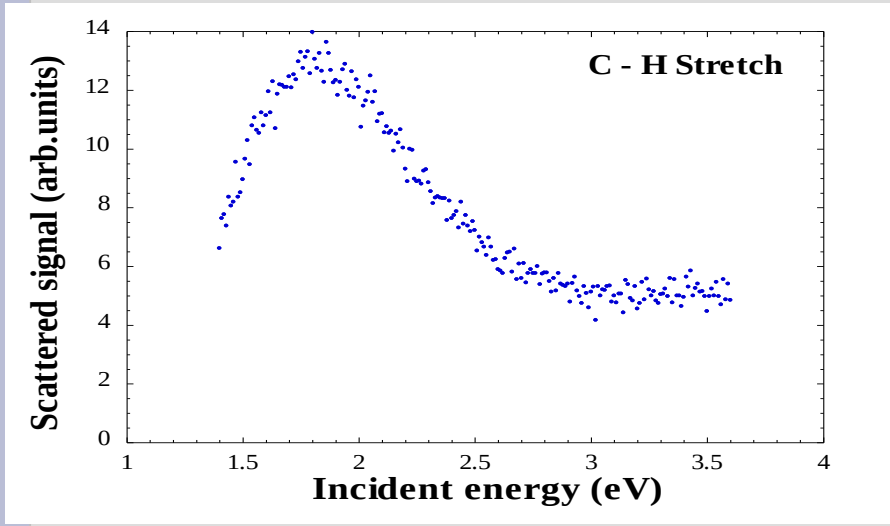
Energy loss spectra

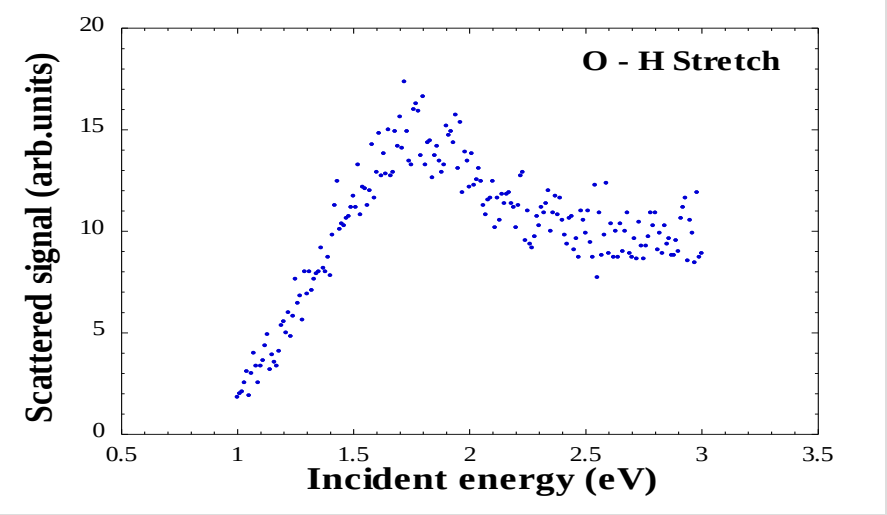


Vibrational excitation - HCOOH



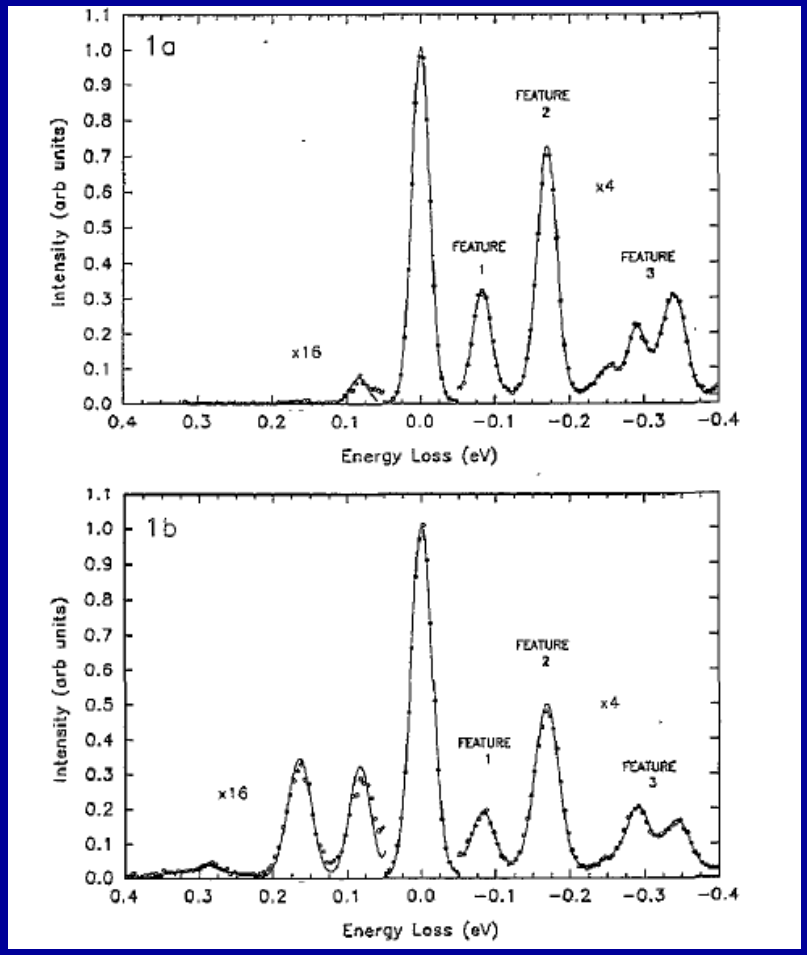






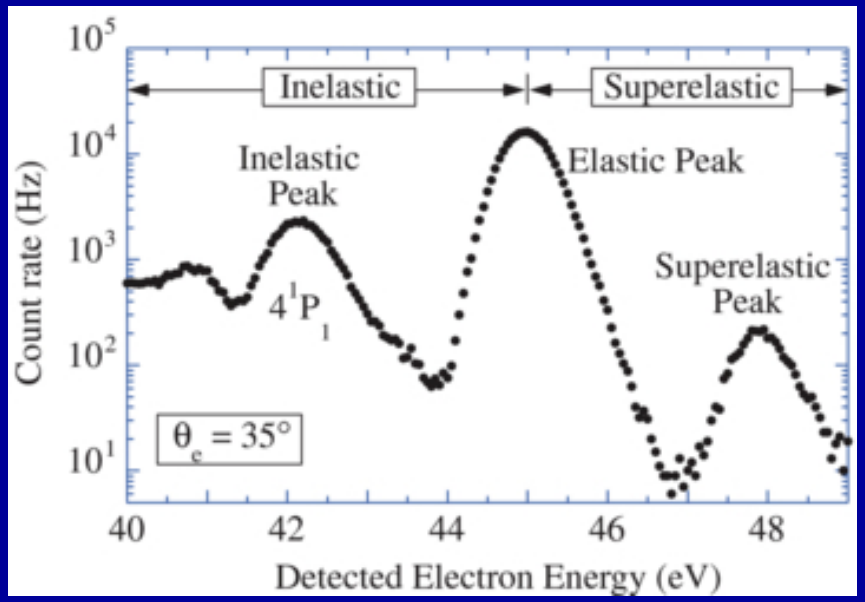
Electron scattering from vibrationally excited states

- Noted several times (e.g. Boegarts in CO_2 plasmas)
- Little/no data – expt or theory
- Expt electrons CO_2 40 and 400K Johnstone et al 1993 JPhys B 26 L147



Electron scattering from electronically excited states

- Important in applications (metastable states)
- Little/no data
- Expt DEA some
- Calculations possible (Gorfinkiel et al)



So where are we now in electron studies ?

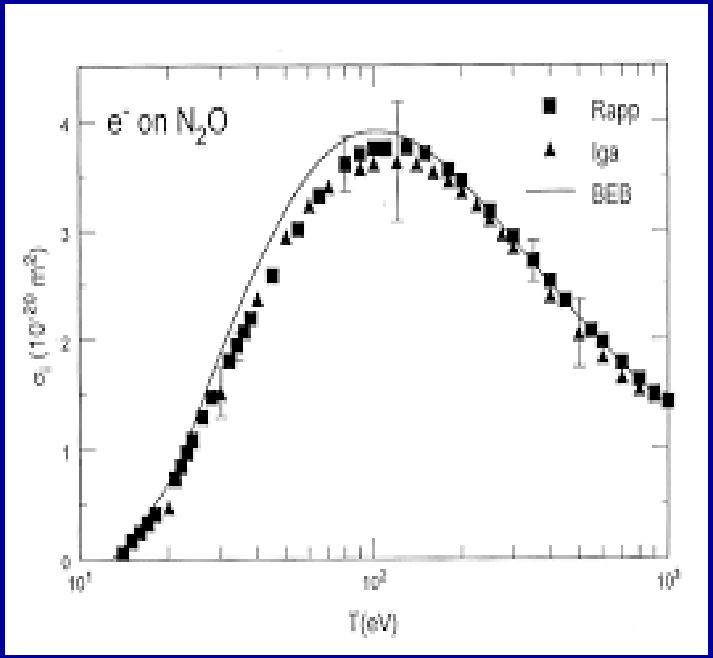
Ionisation - Gibson talk;

Total cross sections accurate to few %

Semi- empirical Theory

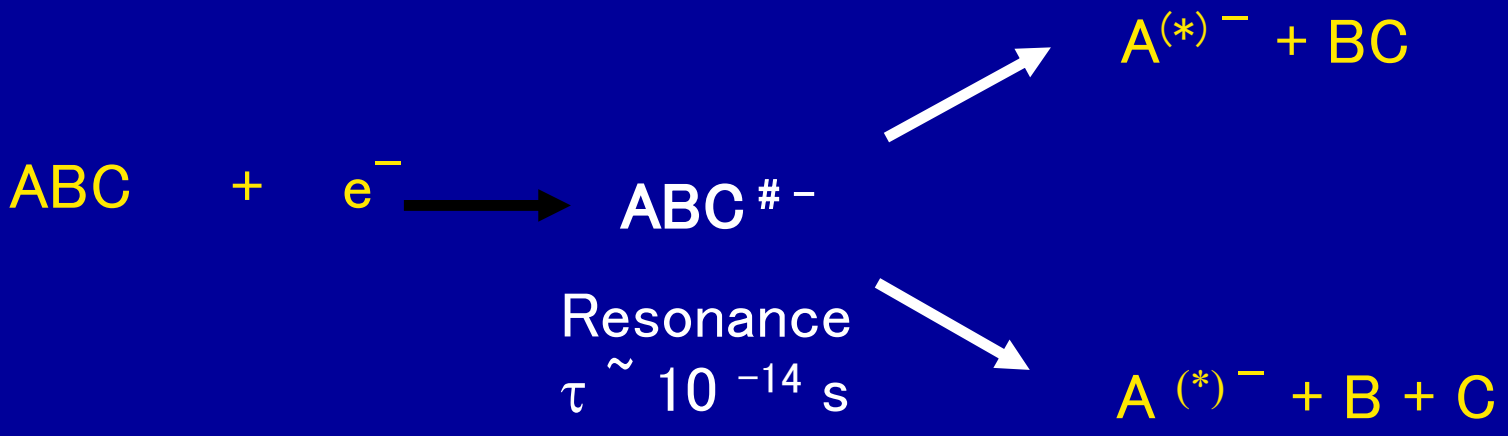
Branching ratios still need to be measured

Expt - Kinetic effects in products



So where are we now in electron studies ?

Dissociative Electron Attachment (DEA)



Production of Negative Ions in Plasmas

So where are we now in electron studies ?

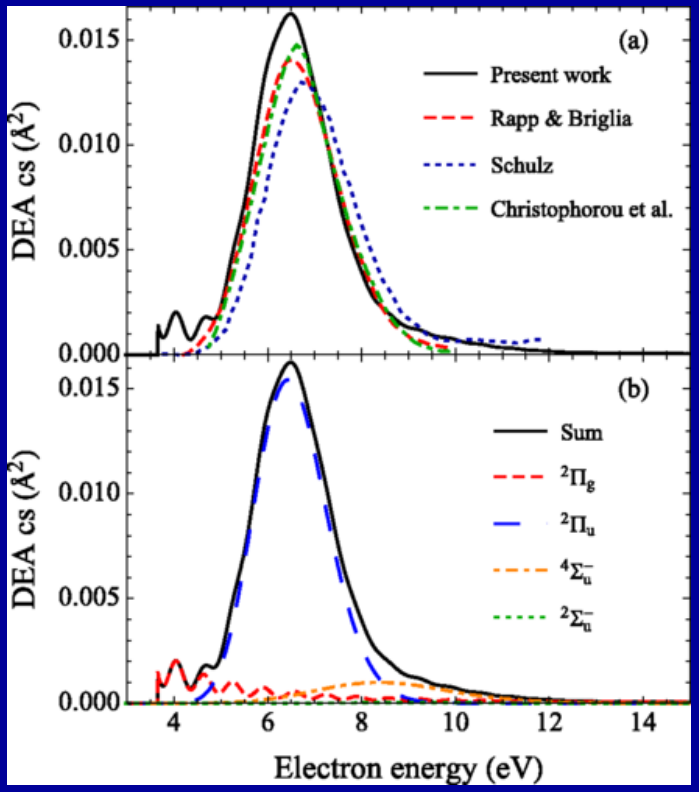
Dissociative Electron Attachment

Question as to how establish cross section

Few/no standards

Kinetic effects in products

Zero energy peaks !



So where are we now in electron studies ?

Dissociation to neutrals particularly radicals

Ground state products – in its infancy

Still testing expt methodologies

No standard (..... CF_2)

Kinetic effects in products

So where are we now in electron studies ?

Dissociation to excited states

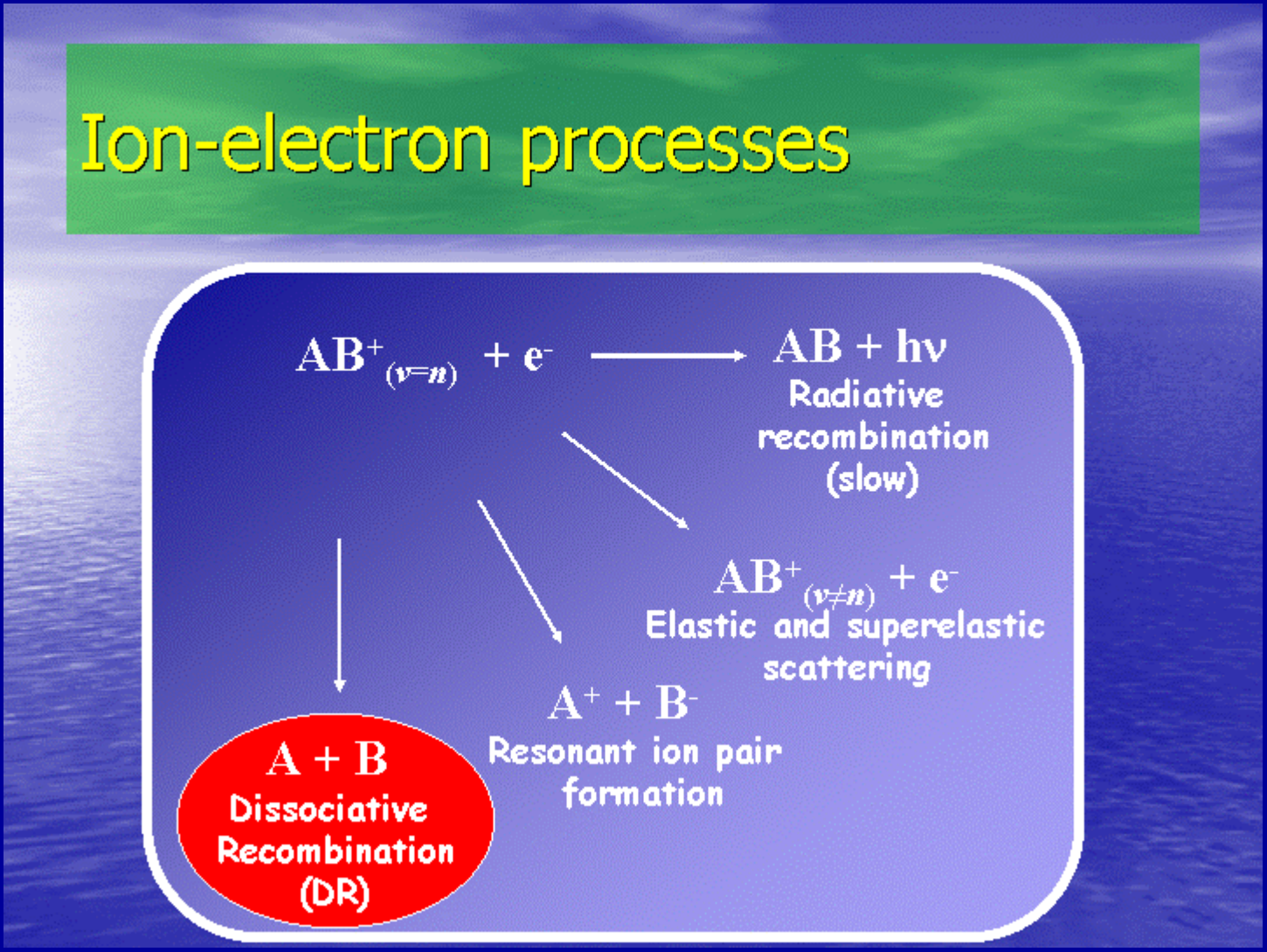
Fluorescence– lots of (old) data but

Detector calibrations

Role of cascade

Kinetic energy – Doppler broadening

So where are we now in electron studies ?



So where are we now in electron studies ?

Dissociative recombination – highlighted in astrophysics H_3^+ or HeH^+

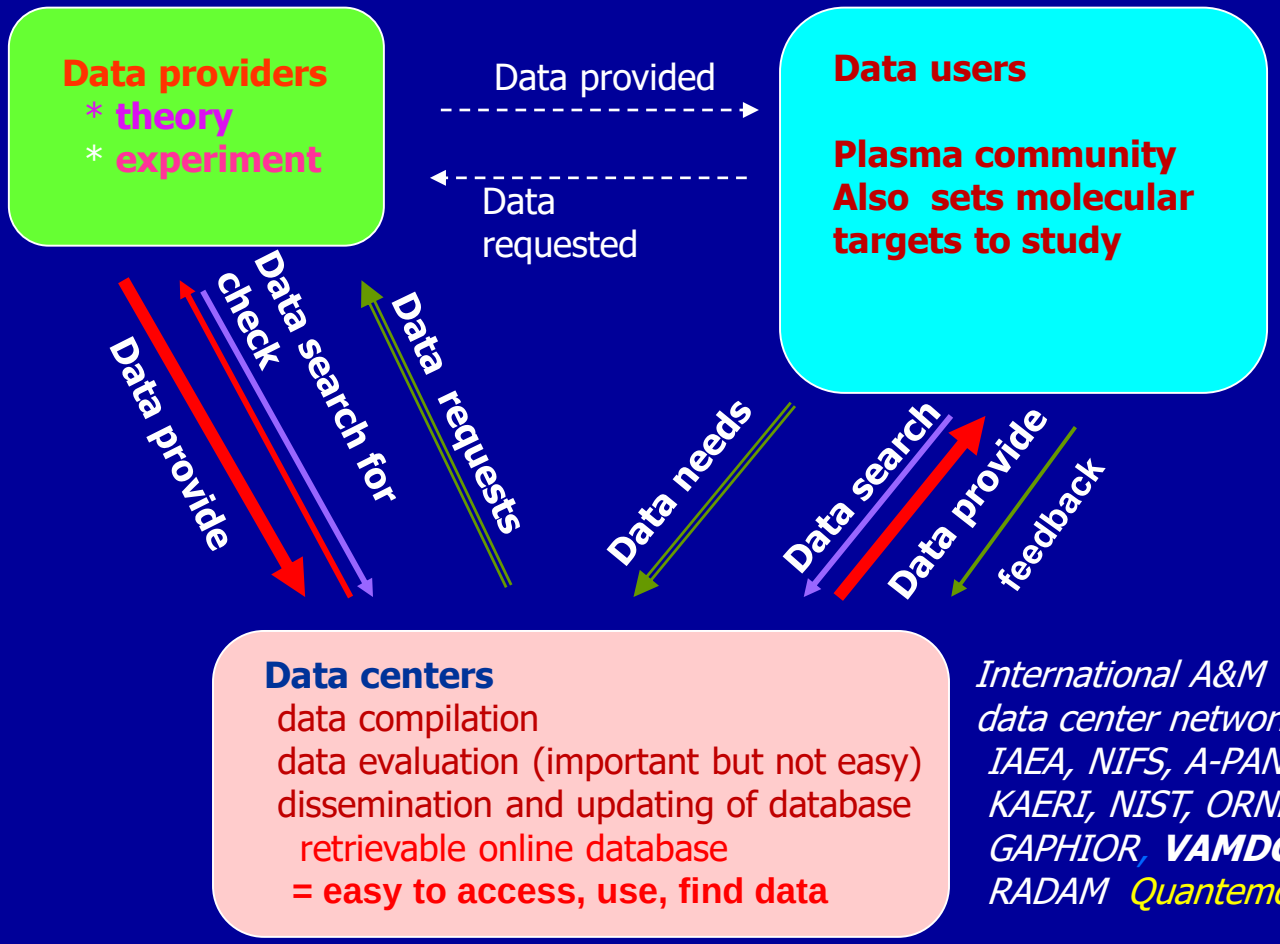
Electron storage rings (Desiree Stockholm ELISA Aarhus)

Theory – Tennyson talk

Summary electron molecule database

- Needs lots of data
- The Experimental crisis – too few experimental (and theoretical) groups and getting fewer….
- Rebuild community for 2020 – 2030 or lose it

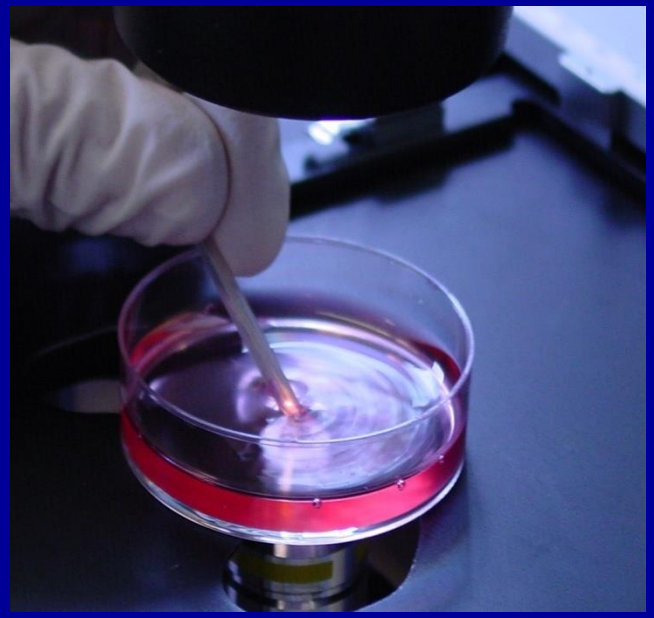
Need Databases with data, Uncertainties and recommendations



CLUSTERS - a common state of matter ?

- Important in atmospheres e.g. water dimers
- Seen in other planetary atmospheres e.g. Titan
- Atmospheric pressure plasma discharges

Plasma Discharges and medical applications

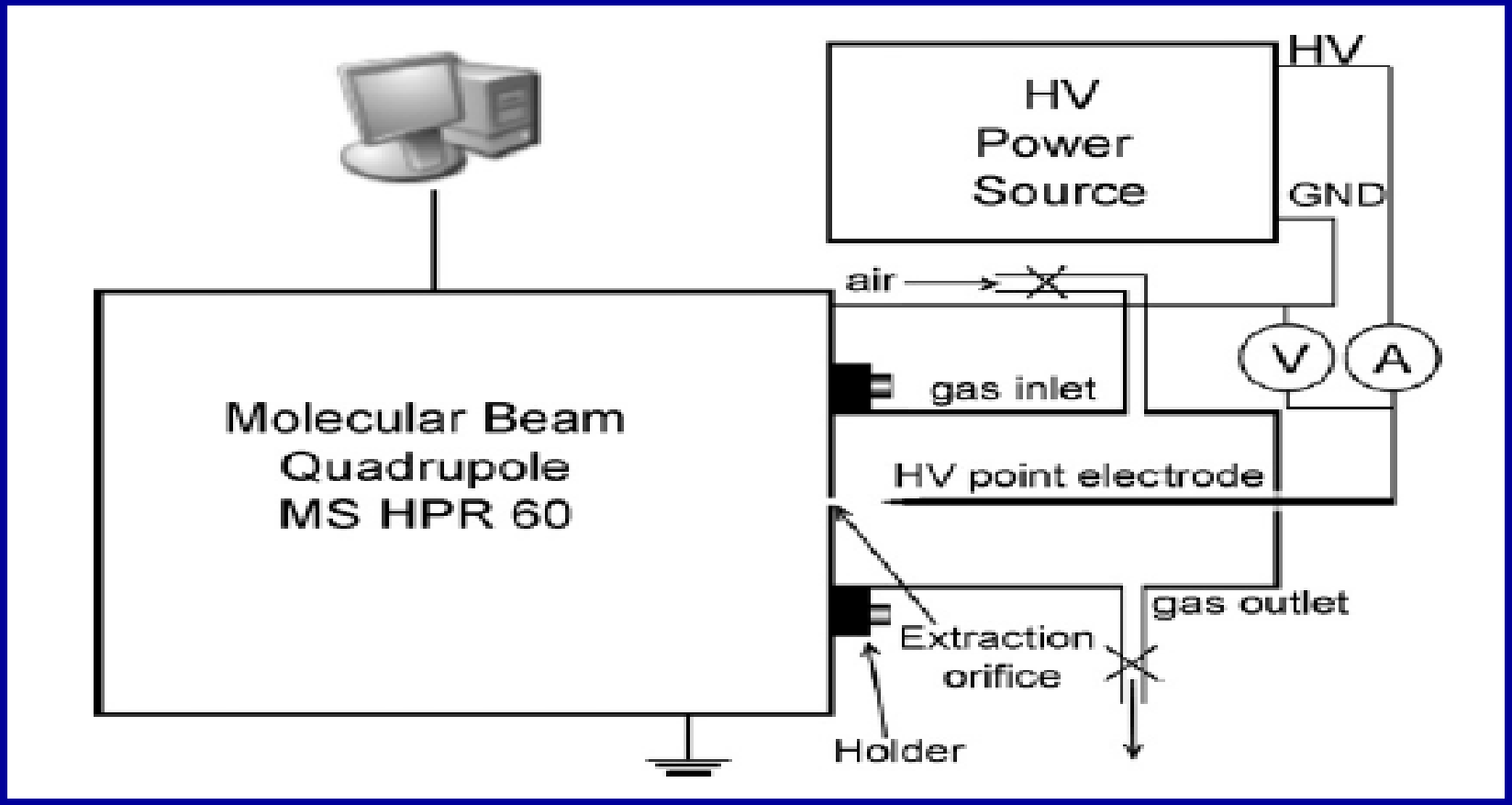


What about clusters ?

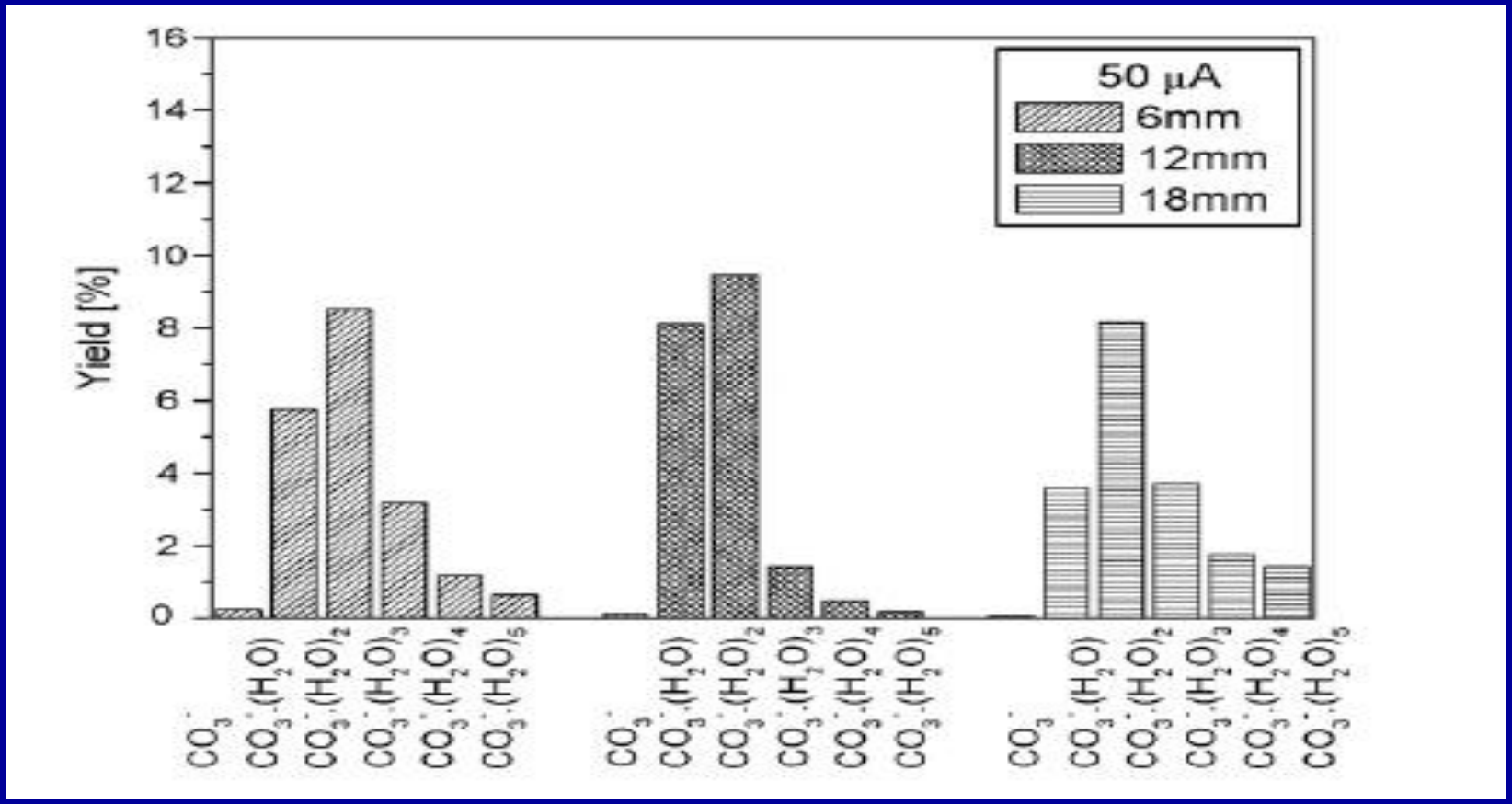
- Indeed key role in atmospheric discharges

- Particularly the role of water/humidity !
- (**Maguire** talk)

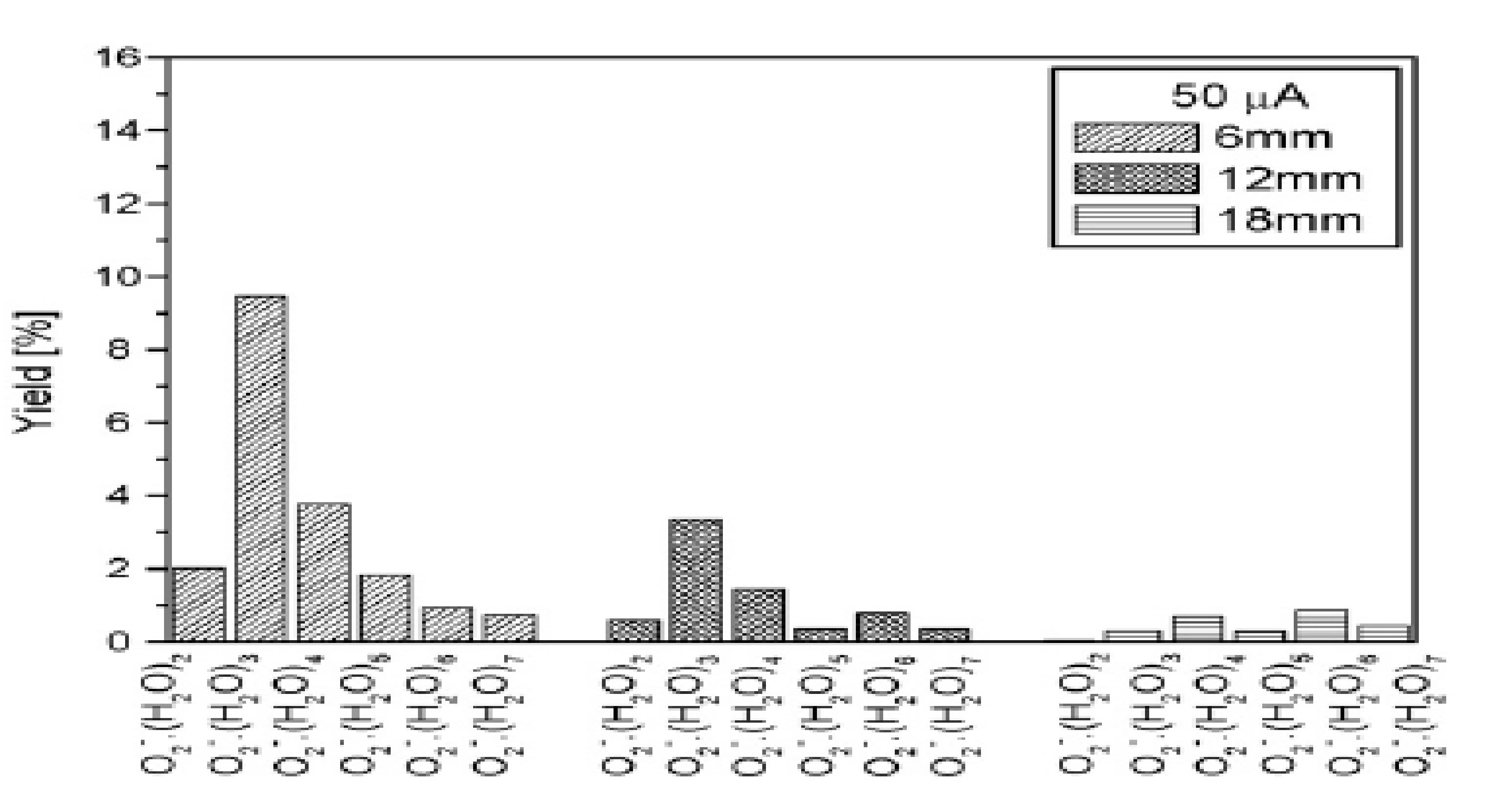
Mass analysis of ions in atmospheric plasma (Hiden)



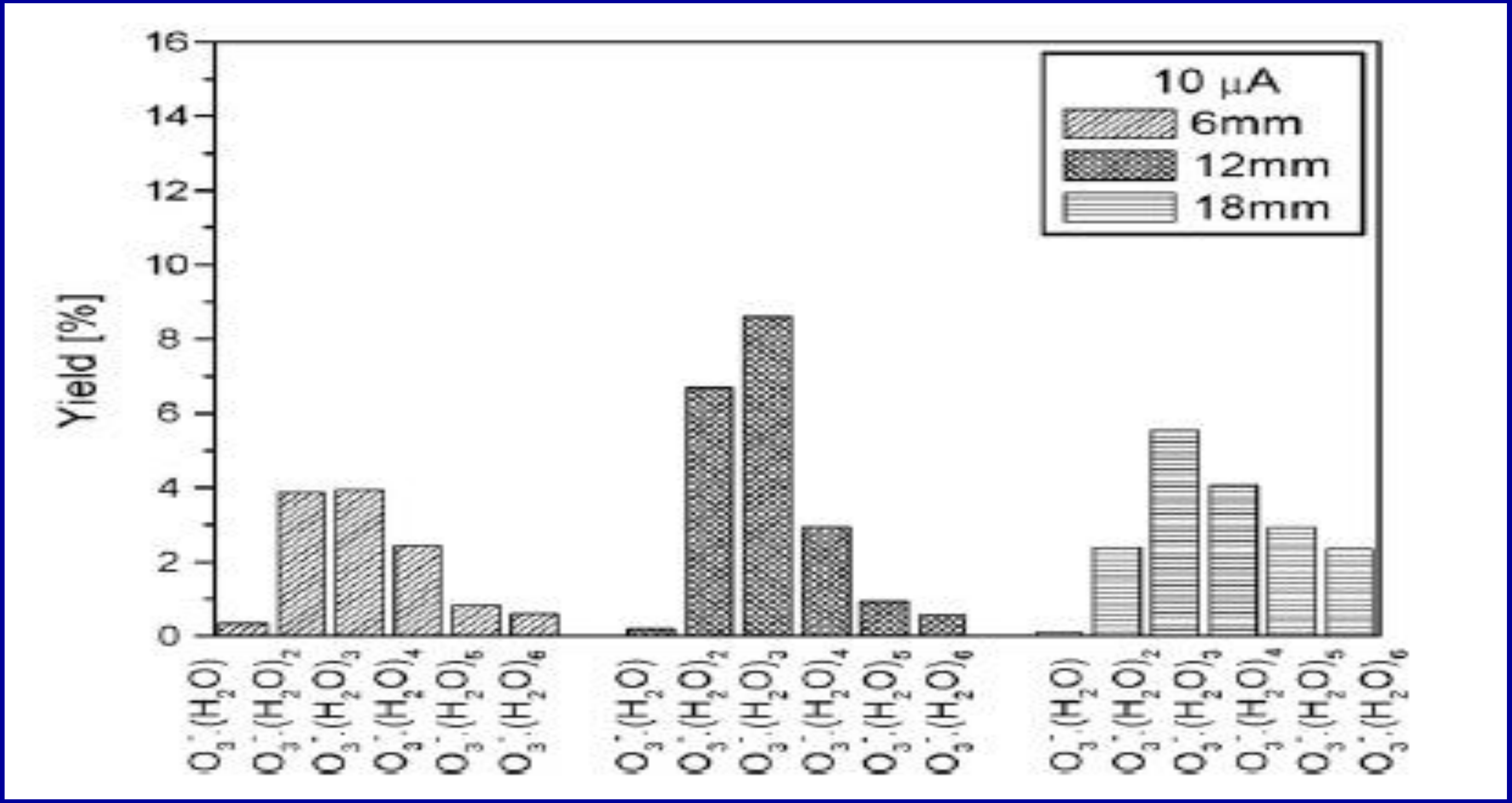
Mass analysis of ions in atmospheric plasma --- coronal discharge in air All are clusters no monomers



Mass analysis of ions in atmospheric plasma --- coronal discharge in air All are clusters no monomers



Mass analysis of ions in atmospheric plasma --- coronal discharge in air All are clusters no monomers



So cluster chemistry dominates !
And key role of water !!!

Clusters formed

$$O^- + CO_2 + M \rightarrow CO_3^- + M$$

$$CO_3^- + H_2O + M \rightarrow CO_3^- \cdot H_2O + M$$

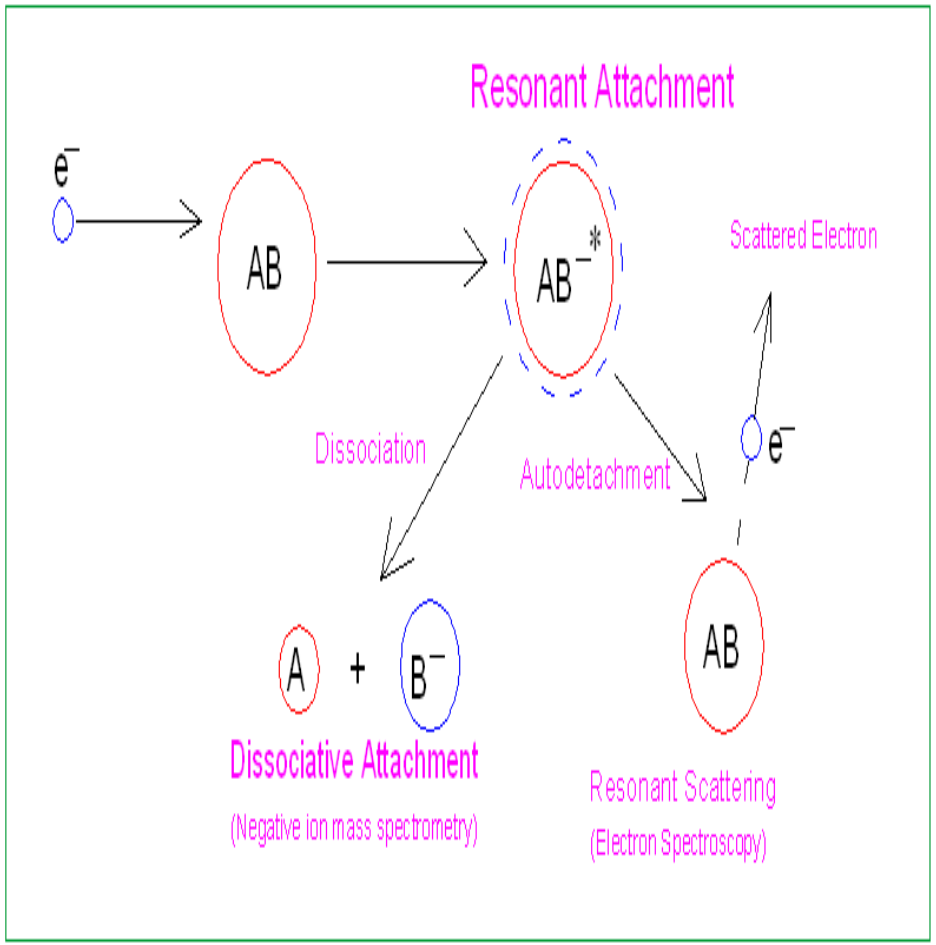
$$CO_3^- \cdot H_2O + H_2O + M \rightarrow CO_3^- \cdot (H_2O)_2 + M$$

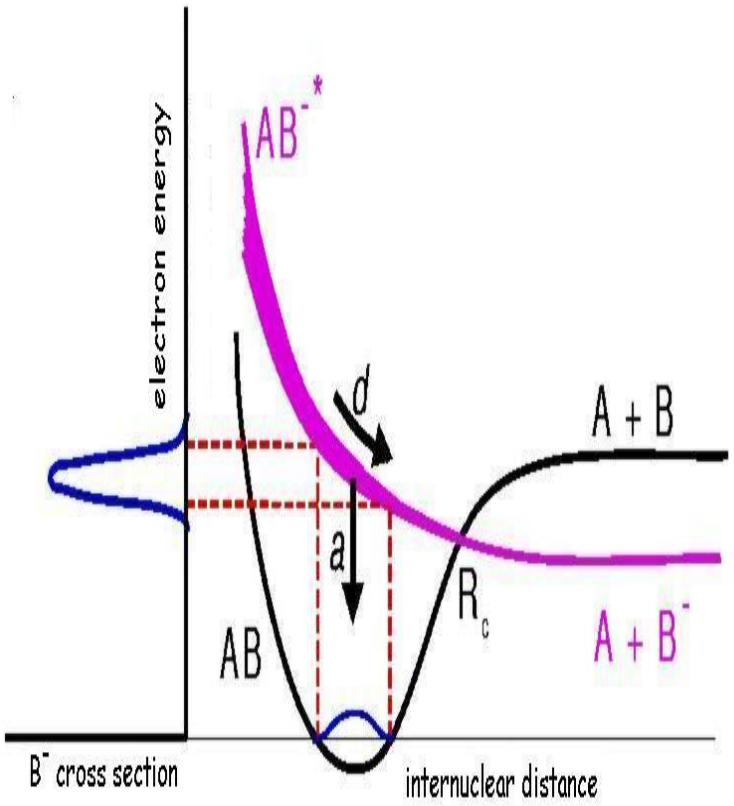
Anions cluster to water molecules easily

Open questions

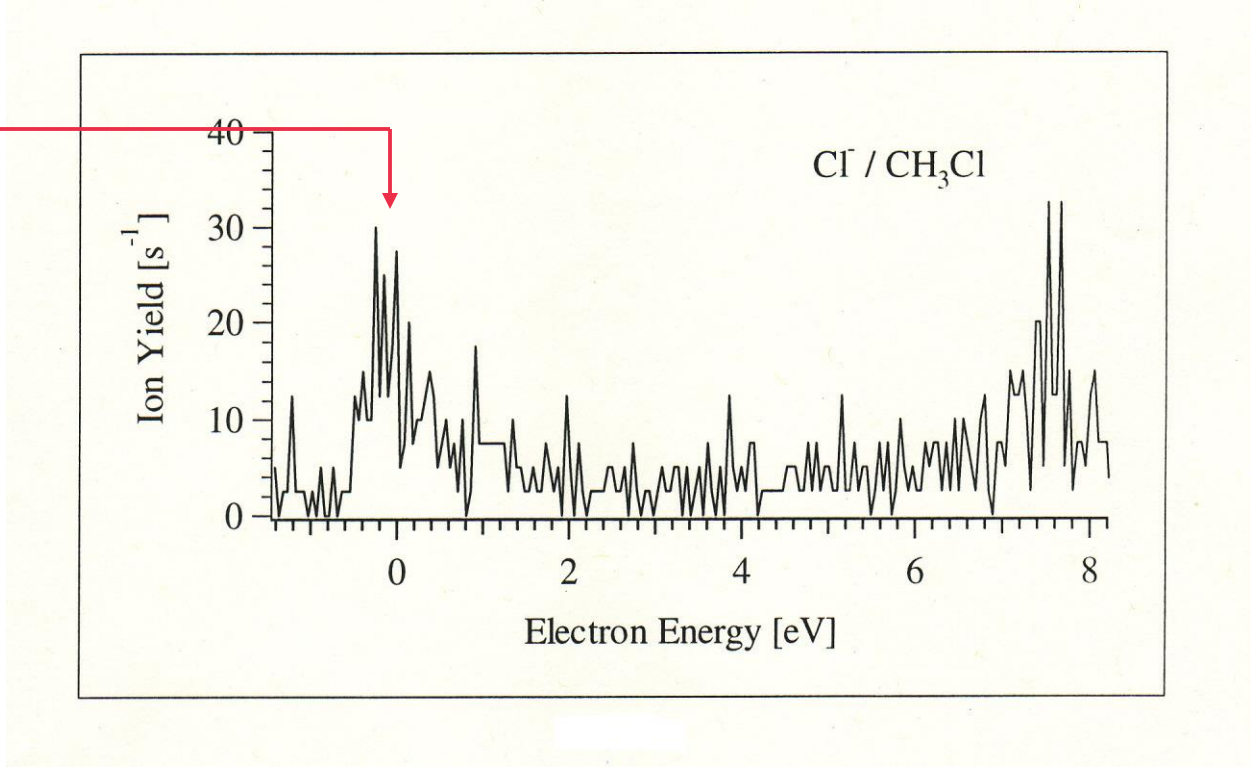
- What are reaction rates ? Or cross sections for formation of such anion clusters?
- Structure and stability of anionic clusters ?
- Influence of humidity and temperature ?

Process of Dissociative Electron Attachment





from impurity

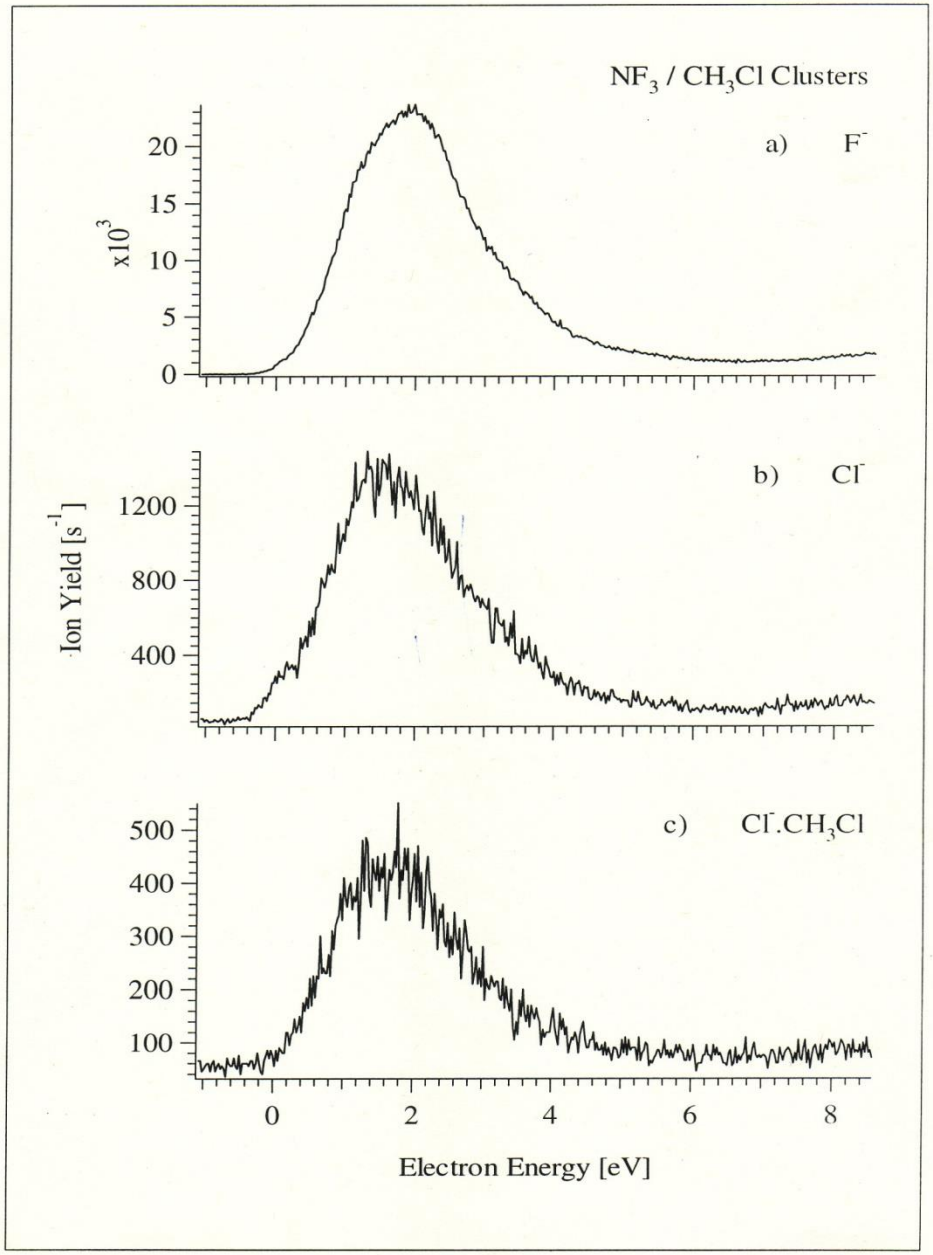


$e^- + CH_3Cl \rightarrow CH_3 + Cl^-$

$\sigma < 10^{-23}$ cm^2 (unmeasurably small)

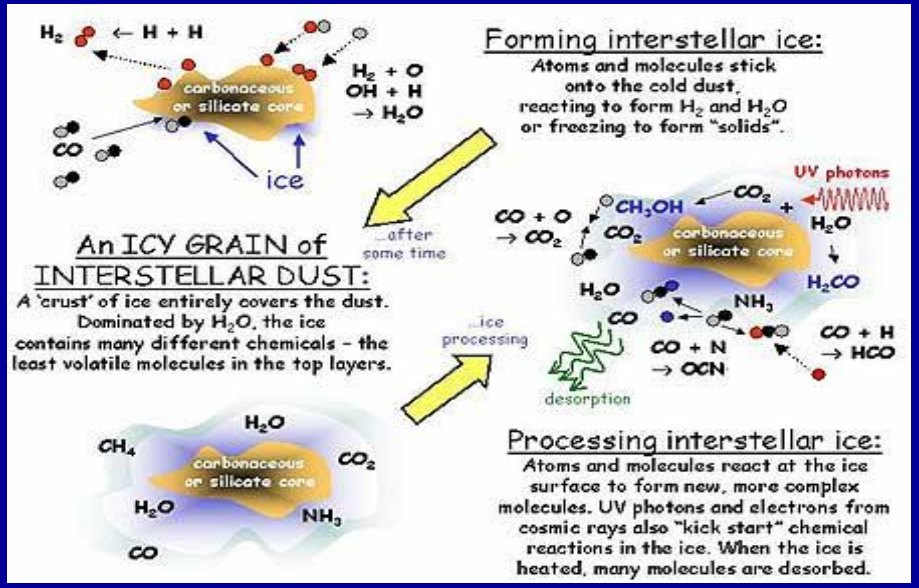
Nucleophilic Displacement (S_N2) Reaction in the cluster NF_3/CH_3Cl

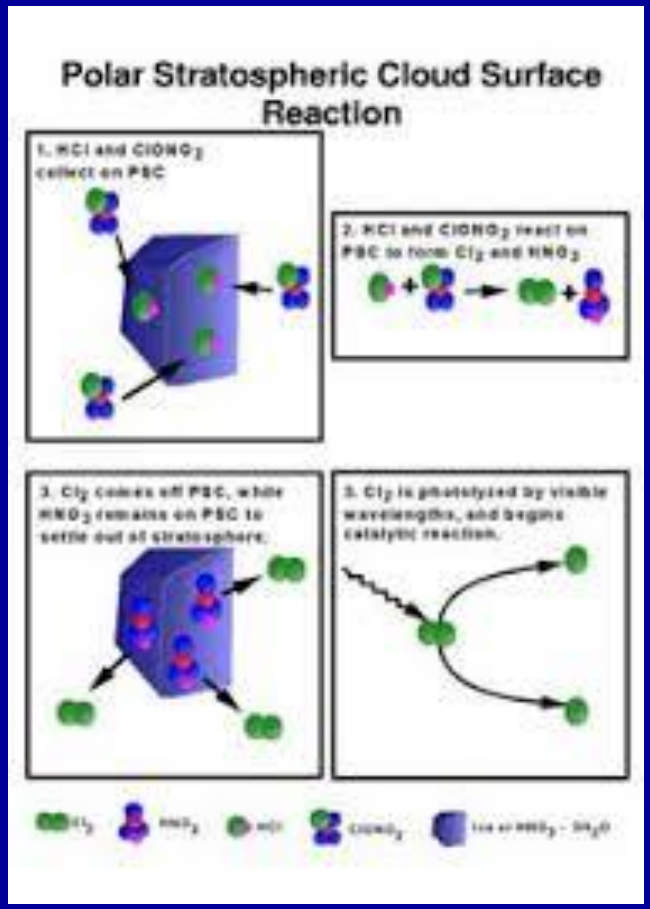
$F^- + CH_3Cl \rightarrow CH_3F + Cl^-$



What about surfaces ?

- **Role of heterogeneous chemistry**
- **Stratospheric ozone depletion**
- **Interstellar chemistry**





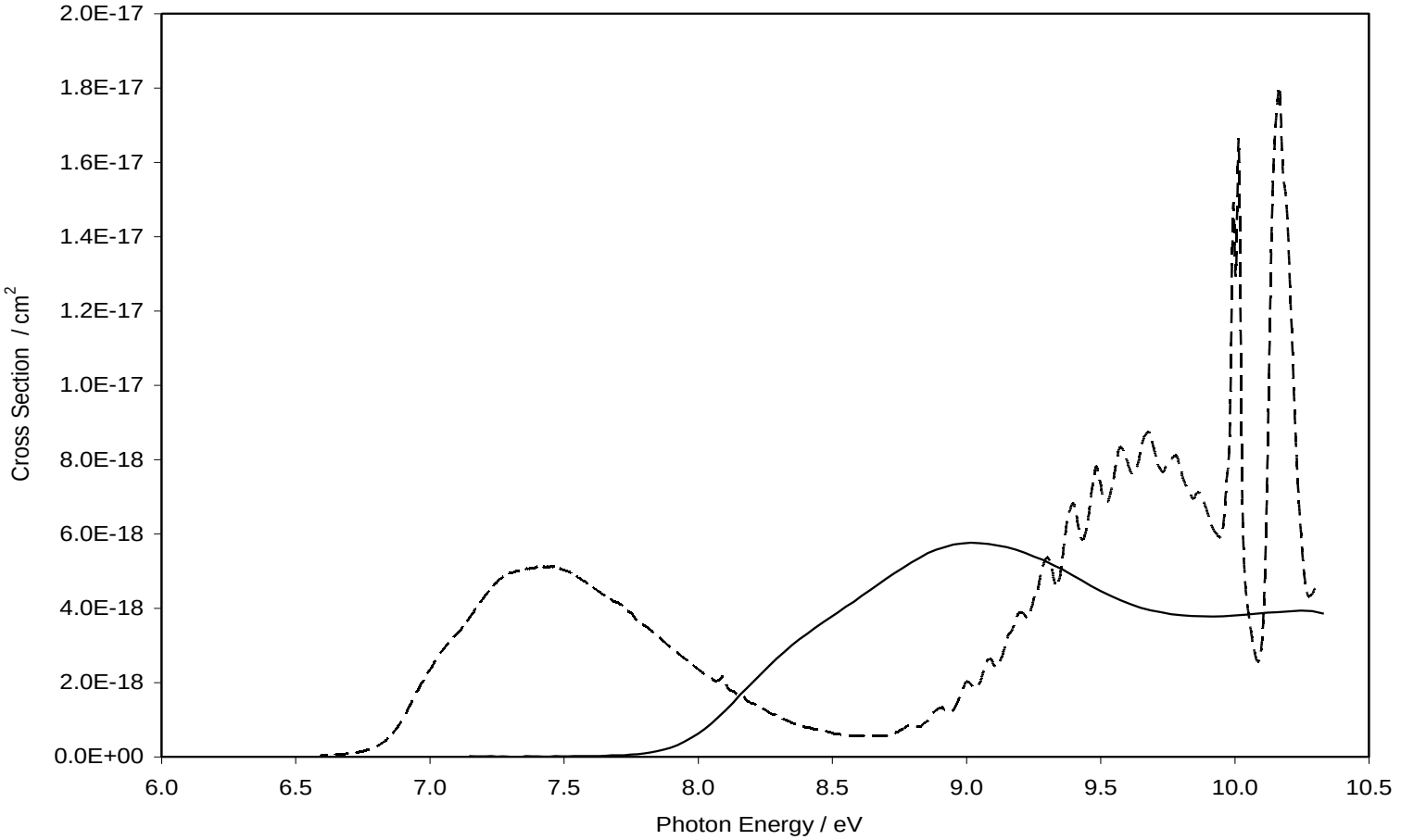
Open Questions

Surface studies

- How to define a cross section on a surface ?
- Role of molecular orientation
- Role of morphology
- Note Shift in energy levels and electronic states leads to changes in all Electron processes !

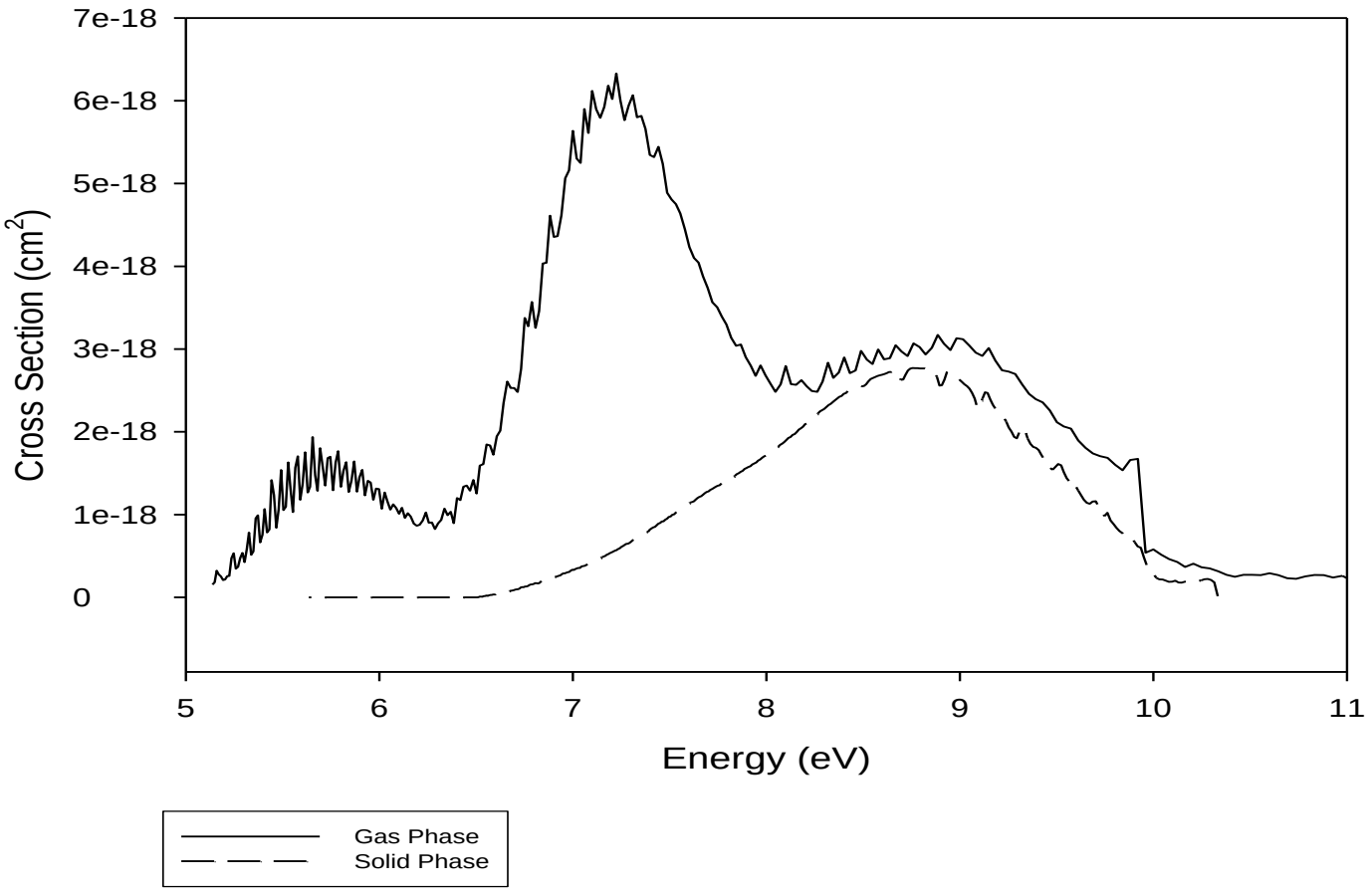
Water ice

Note : Blue shift in the solid phase



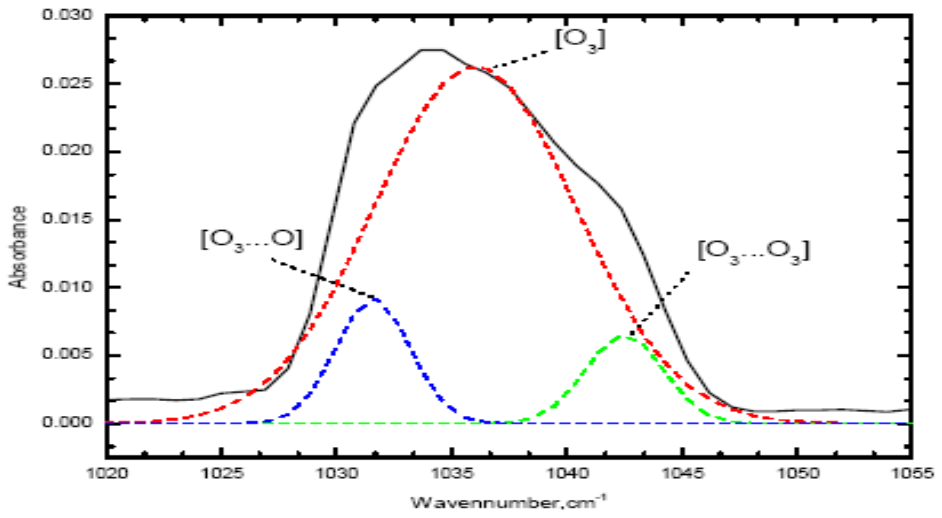
Comparison of gas and solid phase Methylamine

Note absence of low lying bands in solid phase



Electron Induced Chemistry

- Give some examples of how electrons irradiating ice can induce synthesis.
- **Simplest system -- irradiation of oxygen ice**
- **Create ozone but IR spectra shows complexes**



Oxygen ice films

- Oxygen deposited on cold surface (25K) VUV spectra suggests $(O_2)_2$ formed

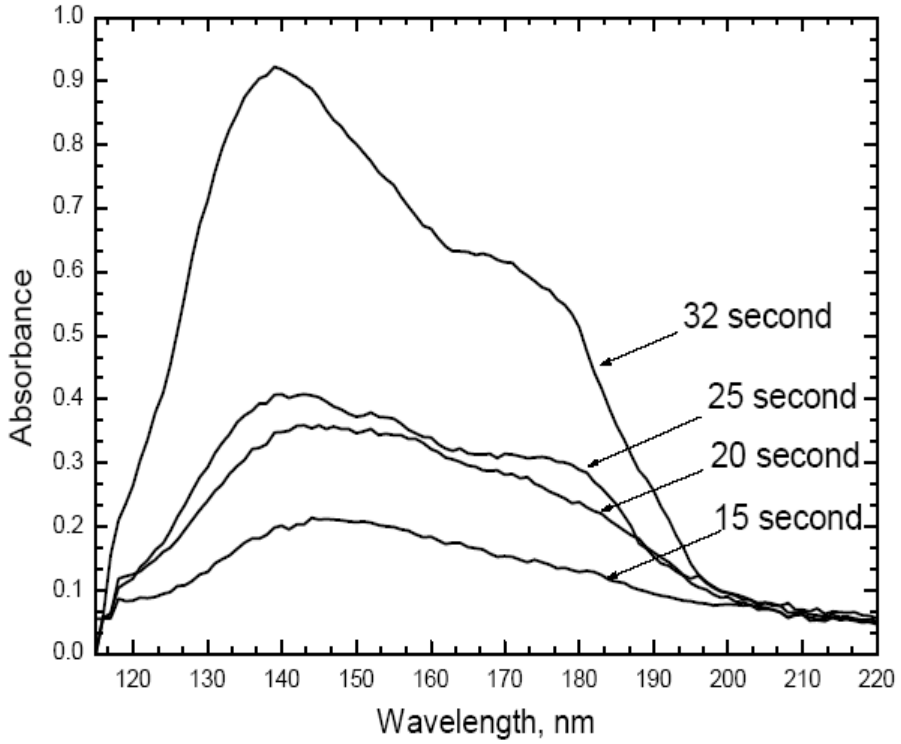
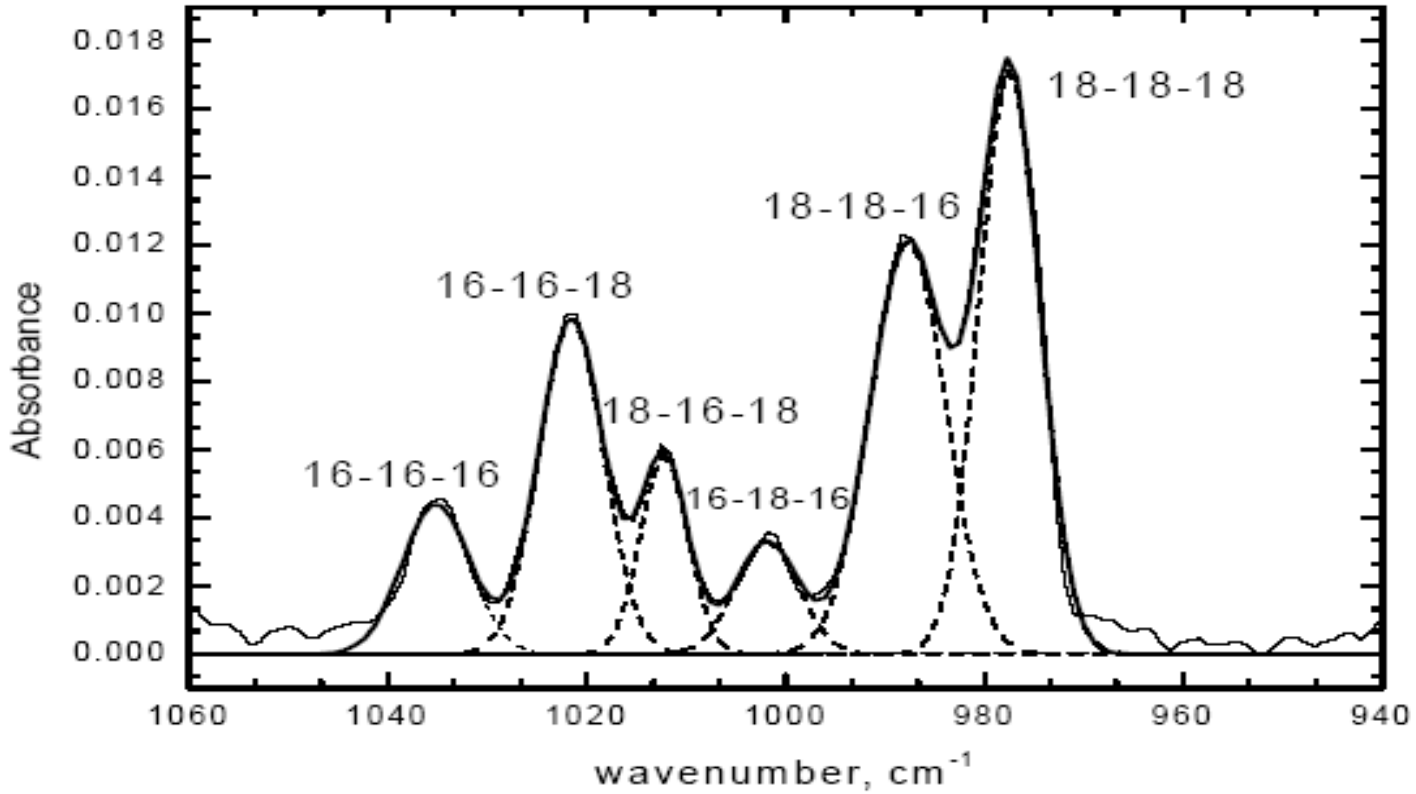


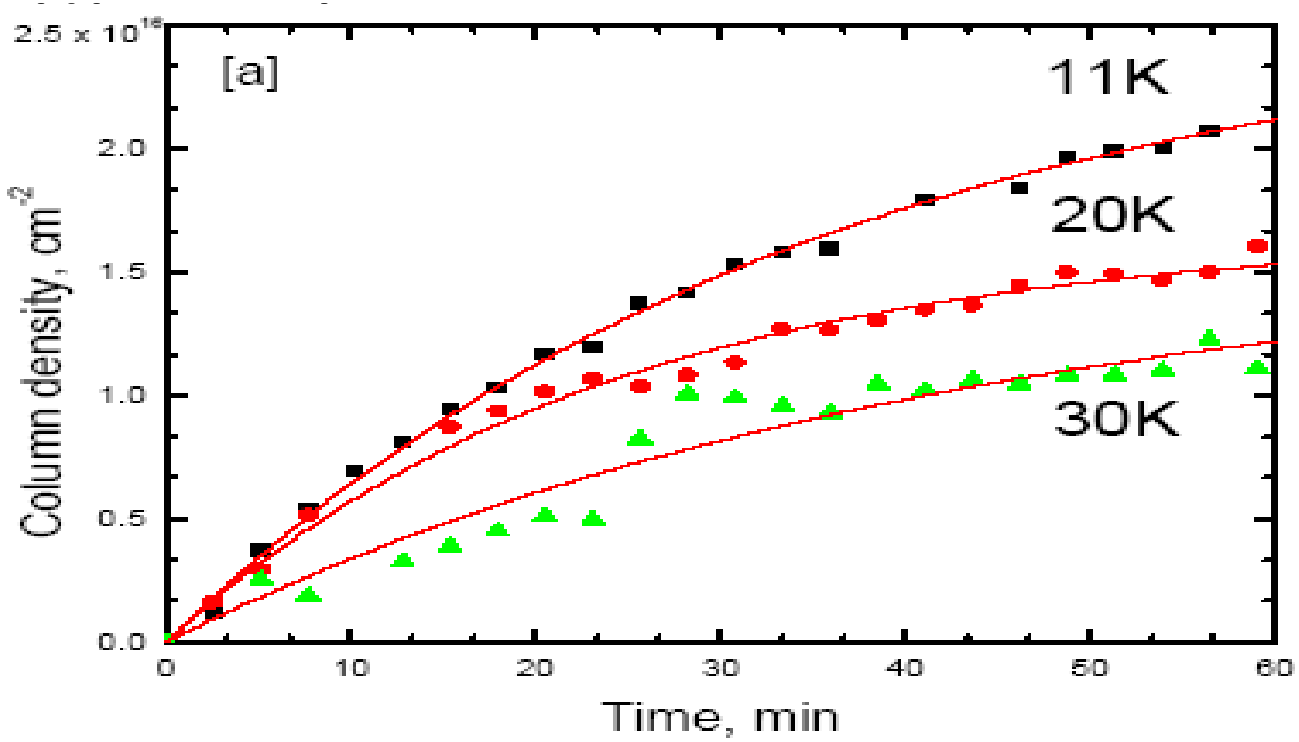
Figure 5.4: VUV spectra of solid oxygen at different thicknesses kept at ~25 K.

Formation of isotopomers (11K)



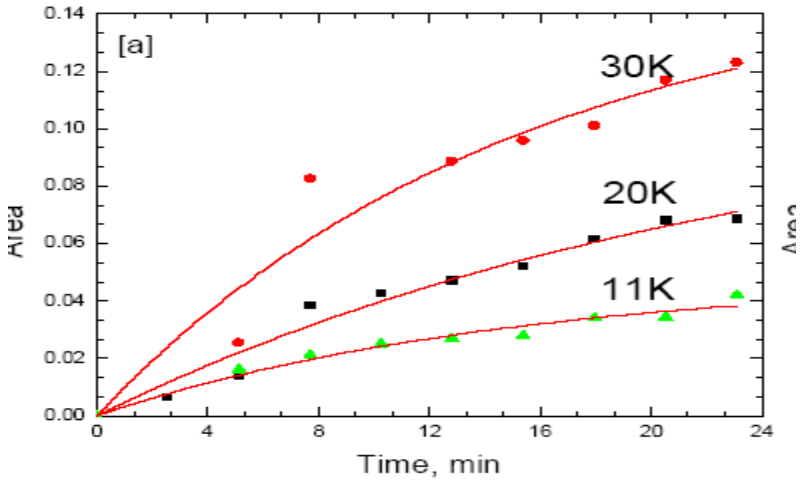
Ozone monomer synthesis

Temperature dependence ;

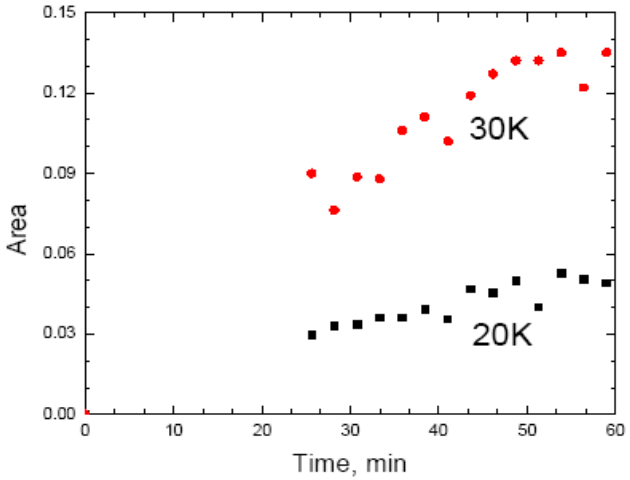


Ozone complexes

- **O_3 - O**



O_3 - O_3



Ozone monomer synthesis

- Inter cluster chemistry !

- As temperature rises clusters unstable so reduce to monomers – no inter cluster chemistry so reaction rate / production of Ozone FALLS

$$(O_2 \ldots O_2) \rightarrow (O_2 \ldots O \ldots O) \rightarrow (O_3 \ldots O)$$

Low temperature molecular synthesis through clusters

- At low temperature the electron induced chemistry is an inter- cluster process
- Similar effects seen in CO_2 and N_2O films
- Strong T dependence such that above 30K dimers/clusters are not formed so diffusion processes occur.

Conclusions

- Rich chemistry observed.
- Our knowledge of formation and chemical reactivity of clusters remains incomplete
- Reactions on surfaces still largely studied case by case – no predictions little theory.

Conclusions

- We need a lot of data (with uncertainties!)
- Experimental work is limited and needs to be supported/regenerated.
- Theory will have to produce bulk of data but also limited community and challenges.
- Use of machine learning and AI should be explored.
- More meetings like this to create community to be encouraged

Malta October 2021 - Covid permitting if not online

- Celebrate centenary of Ramsauer/Townsend experiment

- Applications and New Horizons of electron interactions