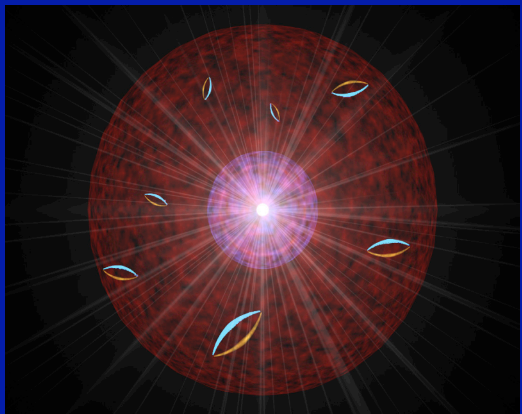
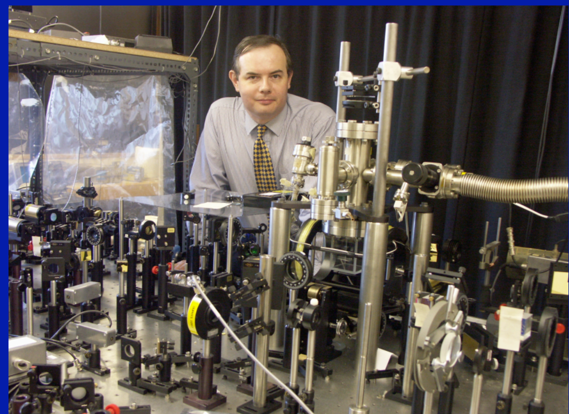
Electron Induced Processing

Applications and data needs





Nigel John Mason

ICAMDATA 2006

Electron Induced Processing;

Electron Induced Processes

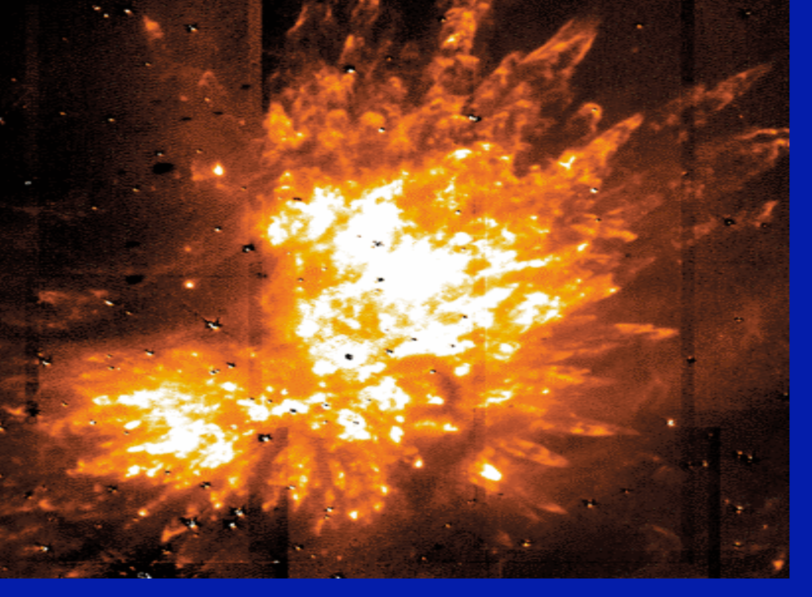
Atmospheric physics and planetary atmospheres

Michael Brunger

Electron Induced Processes

Astrochemistry: Formation of molecules in Space

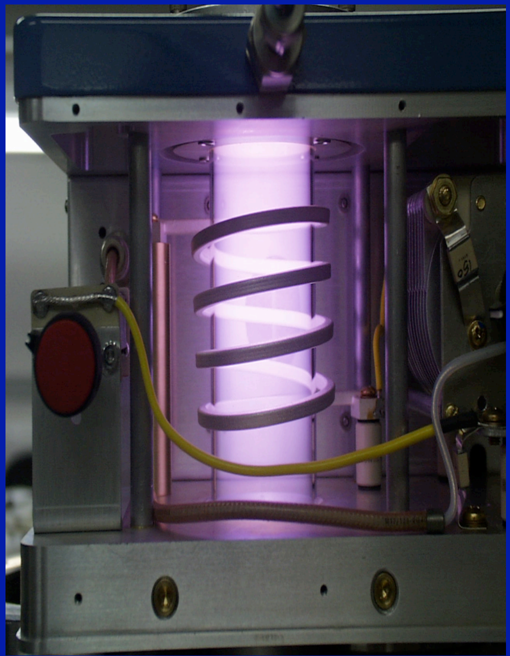
Kate Kirby & Amiel Sternberg

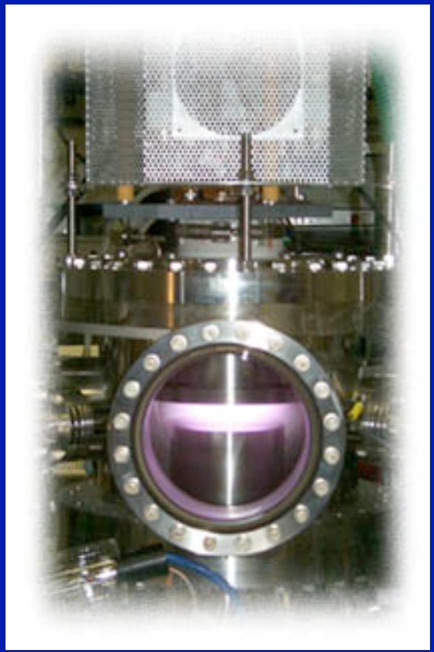


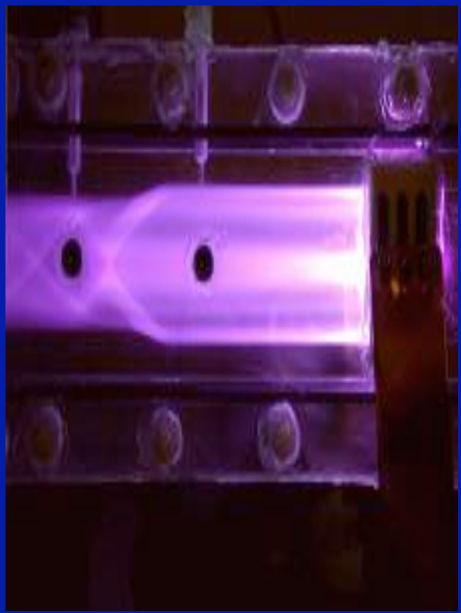
Electron Induced Processes

Semiconductor plasmas for manufacture of computer chips

Peter Ventzek



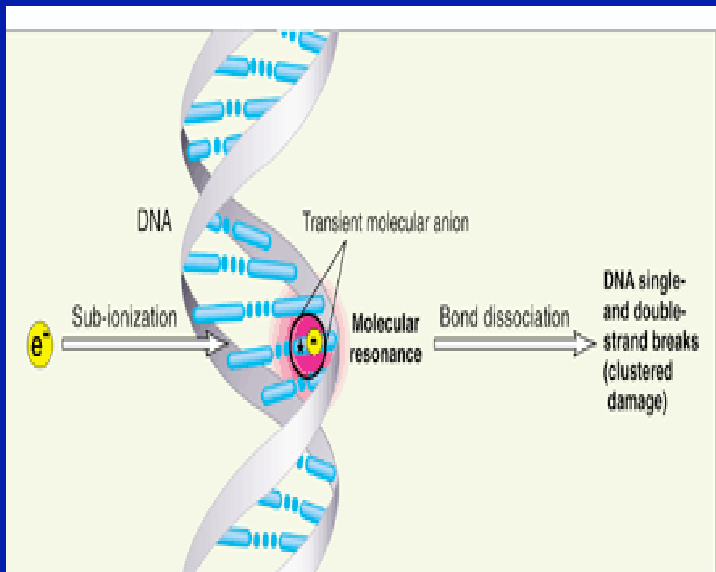




Electron Induced Processes

Radiation damage of DNA and cellular material

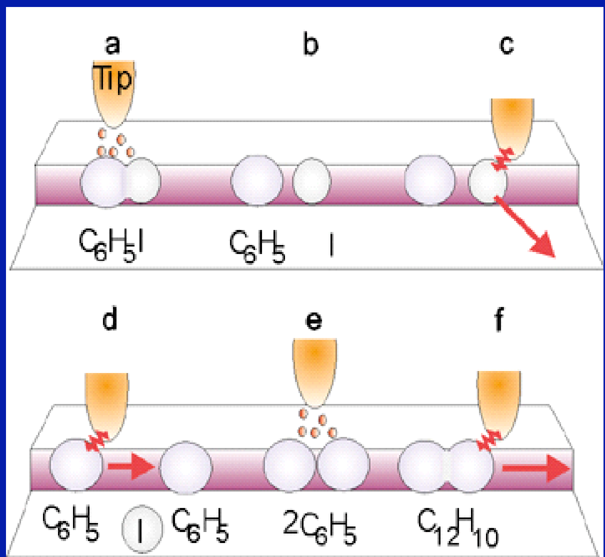
Verena Grill



Electron Induced Processing

Electron Induced Processing

Nanotechnology and surface engineering



Electron Induced Chemistry;

In this presentation I will describe;

- The role of low energy electrons in electron driven chemistry
- Show how such research can be applied to study fundamental problems in natural and industrial world
- Discuss the state of the database and indicate need for further data compilation AND ANALYSIS

Electron Induced Processing; Chemical Control at the Molecular Level

In Europe this research has been developed through collaborative programme Funded by EU

2002 Framework V Network EPIC 2002-2005
Electron and Positron Induced Chemistry

ELECTRON AND POSITRON INDUCED CHEMISTRY
EU Network Framework V
2002-2005

EU COST Action P9 **RADAM Radiation damage**

ESF Network **Collisions in Atom Traps (CATS) 2003-6**

ESF Programme **Electron Induced Processing at the Molecular Level (EIPAM)** 2004-2009

Electron Induced Processing ;

How do electrons trigger chemistry ?

By

- Exciting
- Dissociating or
- ionising molecules

with subsequent products being reactants in collisional chemistry

Electron Induced Processing; Chemical Control at the Molecular Level

Consider for example simple electron induced dissociation through an excited molecular electronic state.

$$e^- + M \rightarrow M\# \rightarrow X + R + e \qquad (1)$$

$$R + AB \rightarrow AR + B \qquad (2)$$

Example

Formation of glycine in the Interstellar medium

Glycine – What is it ? Why study it ?

NH2CH2COOH – The simplest amino acid
Amino acids of the building blocks of proteins
Higher homologues amino acids can be derived from glycine by replacing one hydrogen atom of the methylene group (CH2) by an organic group

- Amino Acids have been formed in laboratory experiments from UV irradiation of ice samples, e.g. Caro et al 2002 Nature 416, 403 - 406 (28 March 2002)
- Detected in Meteorite samples
  - In excess of seventy amino acids alone have been detected in the Murchison meteorite sample (Cronin, Cooper, and Pizzarello, 1995)

Cronin, J. R, Cooper G. W, Pizzarello S.,1995, Advances in Space Research,15, 91

Experimental Procedure

- Ice sample was prepared at 10 K by depositing binary gas mixtures of methylamine (CH_3NH_2; and carbon dioxide (CO_2) onto a cooled silver crystal.
- Ice thickness & column densities determined by Beer-Lambert Law
- Column densities of carbon dioxide and methylamine of $2.0\pm0.4 \times10^{16}$ cm^{-2} and $7.2\pm0.2\times10^{17}$ cm^{-2} respectively

5 keV Electron irradiation of methylammine and carbon dioxide ice makes glycine simple amino acid

Effects of Irradiation

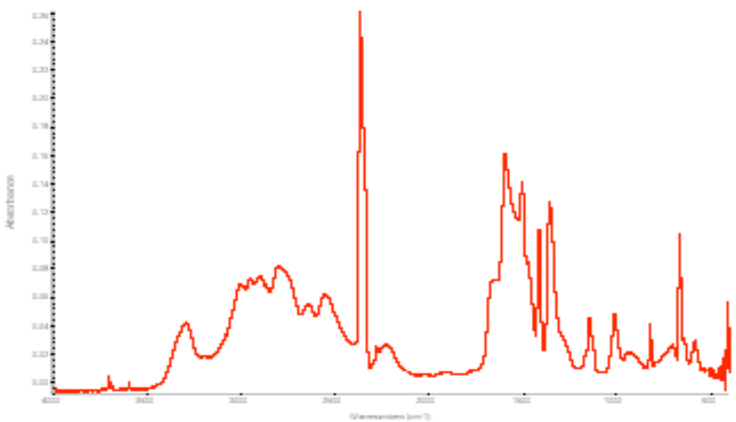


Figure 3 – Pristine CH_3NH_2 & CO_2 mixture

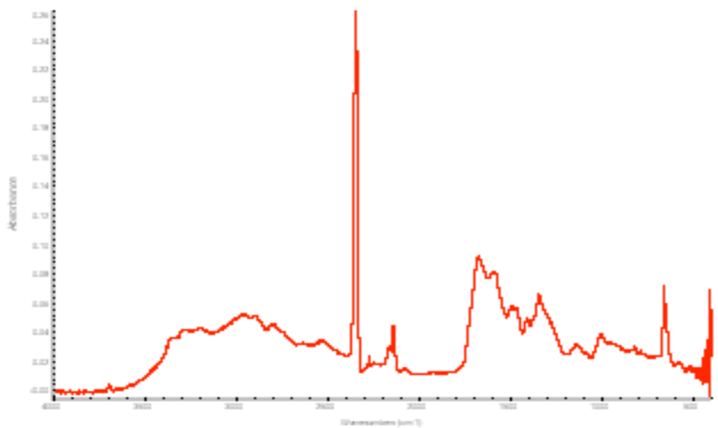


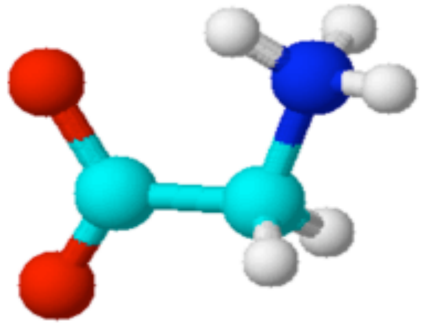
Figure 4 – 100 minute after irradiation of the mixture

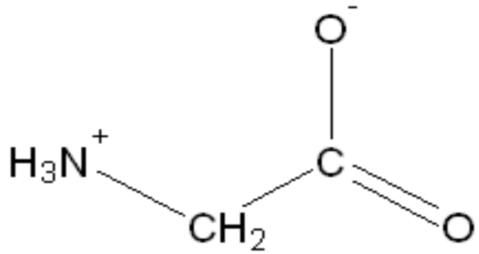
Forms of Glycine

- Zwittionic glycine

"A zwitterion is a dipolar ion that is capable of carrying both a positive and negative charge simultaneously"

E.G. $NH_3^+CH_2COO^-$

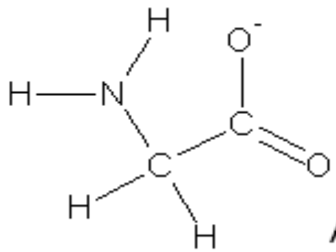




Zwittionic Glycine

- Anionic

Negatively charged, e.g. $NH_2CH_3COO^-$



Anionic Glycine

Methods of forming glycine

$CH_3NH_2 \rightarrow CH_2NH_2 + H$

$H + CO_2 \rightarrow HOCO$

$HOCO + CH_2NH_2 \rightarrow NH_2CH_2COOH$

$NH_2CH_2COOH + CH_3NH_2 \rightarrow CH_3NH_3^+ + NH_2CH_2COO^-$

Or

$CH_3NH_2 \rightarrow CH_3NH + H$

$H + CO_2 \rightarrow HOCO$

$HOCO + CH_3NH \rightarrow CH_3NHCOOH$

$CH_3NHCOOH + CH_3NH_2 \rightarrow CH_3NH_3^+ + CH_3NHCOO^-$

Electron Induced Processing

Glycine was an example of high energy electrons

'Blasting' molecules apart but

At low energies electrons can do surprising things !

Electron Induced Processing

At low energies electrons can do surprising things !

- They can 'stick' to the molecule
- To form a **negative ion** or 'resonance'
- But only for a very short period of time (10^{-14} s)

- Then the electron detaches
- Leaving molecule excited or not (elastic scattering)
- But this process can also lead to the dissociation of the molecule

This is the process of
Dissociative Electron Attachment (DEA)
Ann Orel

Electron Induced Processing

Dissociative Electron Attachment (DEA)

$ABC + e^- \longrightarrow ABC^{\#-}$

Resonance $\tau \sim 10^{-14}$ s

$\nearrow A^{(*)-} + BC$

$\searrow A^{(*)-} + B + C$

Applications of DEA (some !)

- DNA damage
- Heterogeneous Chemistry (e.,g., Atmospheric Chemistry)
- Production of Negative Ions in Plasmas

Electron Induced Processing

Dissociative electron attachment therefore provides a method for breaking up molecules at low energies

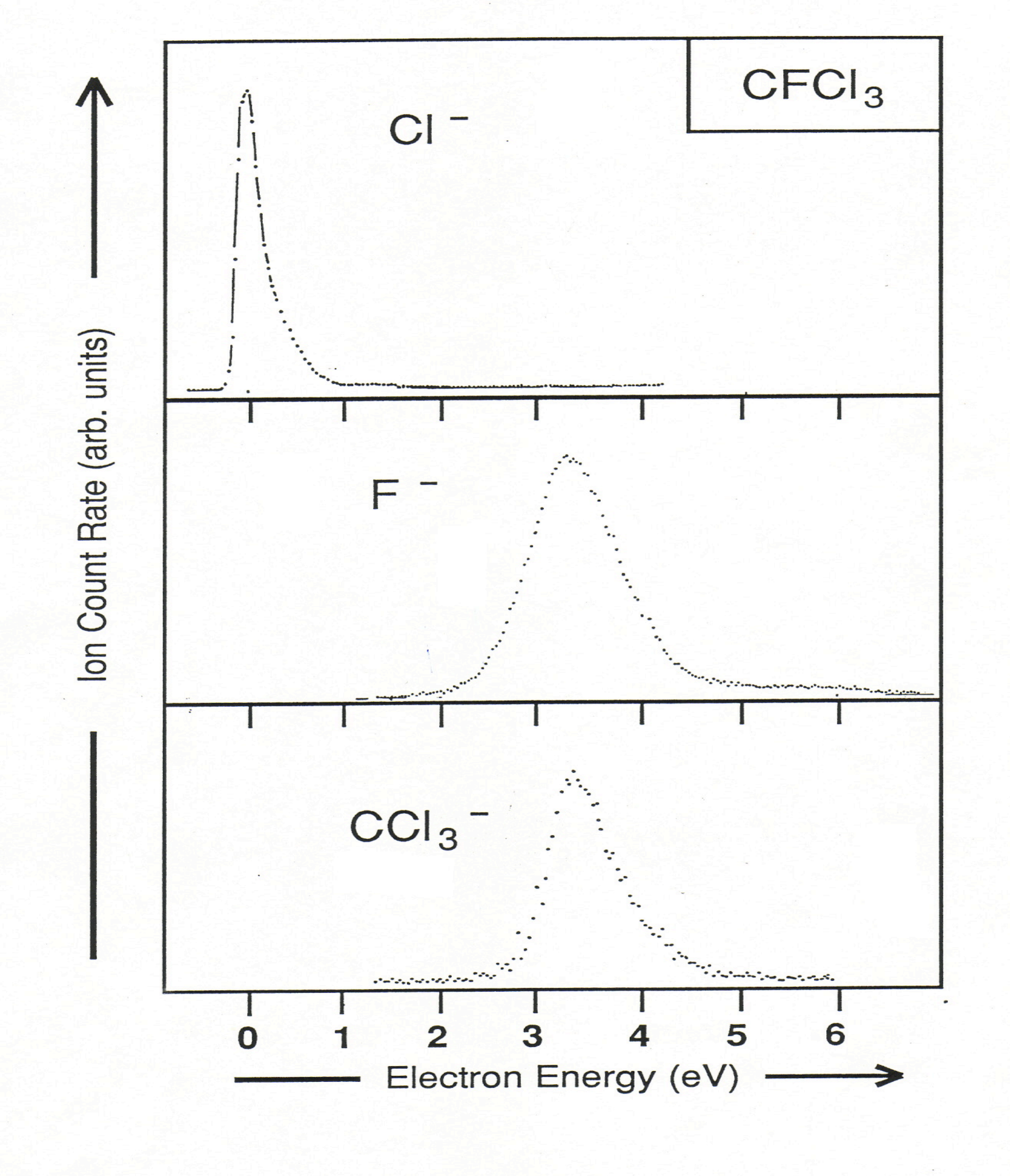
Energies lower than the chemical bond energy !!!

Hence electrons can initiate chemistry

Electron Induced chemistry

- Electrons used to ‘tune’ the products of a reaction
- Through selective bond dissociation different energy different pathways

Electron Induced Processing



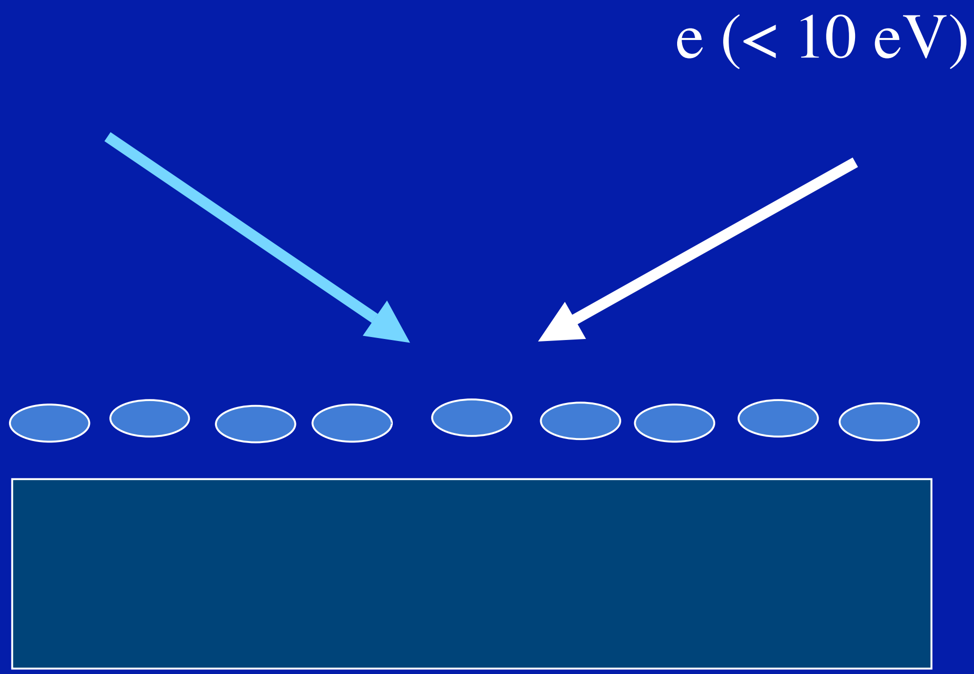
Selective C-Cl bond cleavage at 0 eV

Selective C-F bond cleavage at 3.2 eV

Illenberger et al Berlin

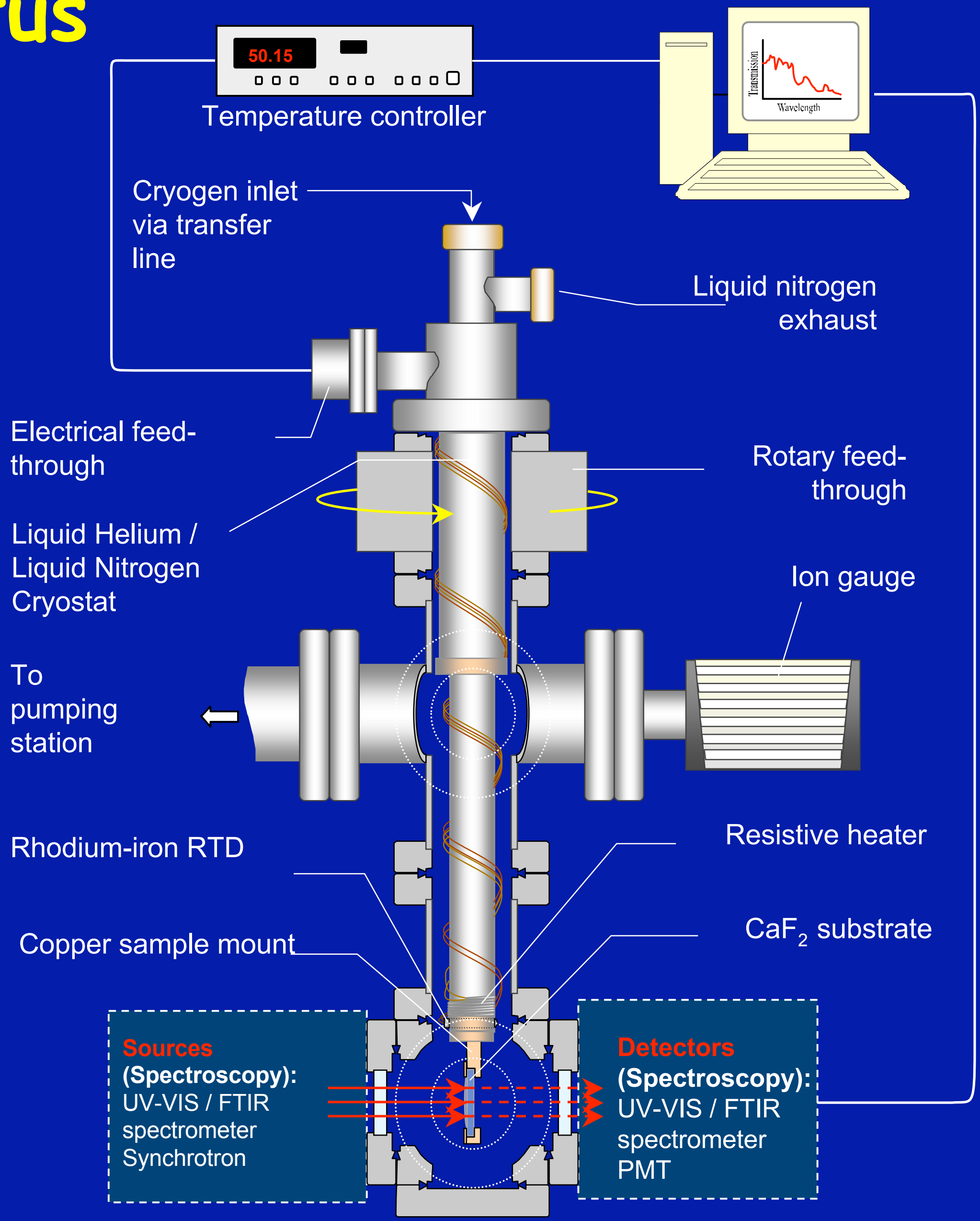
Electron Induced Processing

Can use electrons to process molecular films



Portable Apparatus

- HV (UHV) chamber:
  - P~10^{-7}-10^{-10} mbar
- CaF_2 substrate for transmission spectroscopy
  - 120 nm – 10 μm
- Temperature:
  - LN2 / LHe cryostat
  - >30 K
  - Rh-Fe sensor
  - Resistive coax. Heater
- 4 ports
  - Sample deposition
  - Spectroscopy
  - Irradiation
- Transmission spectra recorded vs. wavelength / frequency



Electron Induced Processing

Convert layer of molecular oxygen to ozone

Electrons breakup O_2 to form O atoms

O atoms react with other O_2 on the surface

'Chapman reaction' $O + O_2 + M \rightarrow O_3 + M$ where M is a third body to stabilize the nascent ozone

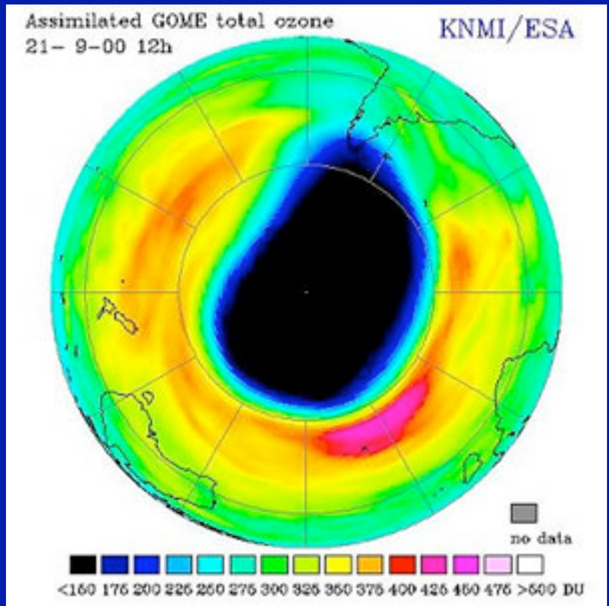
Electron Induced Processing

'Chapman reaction'

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

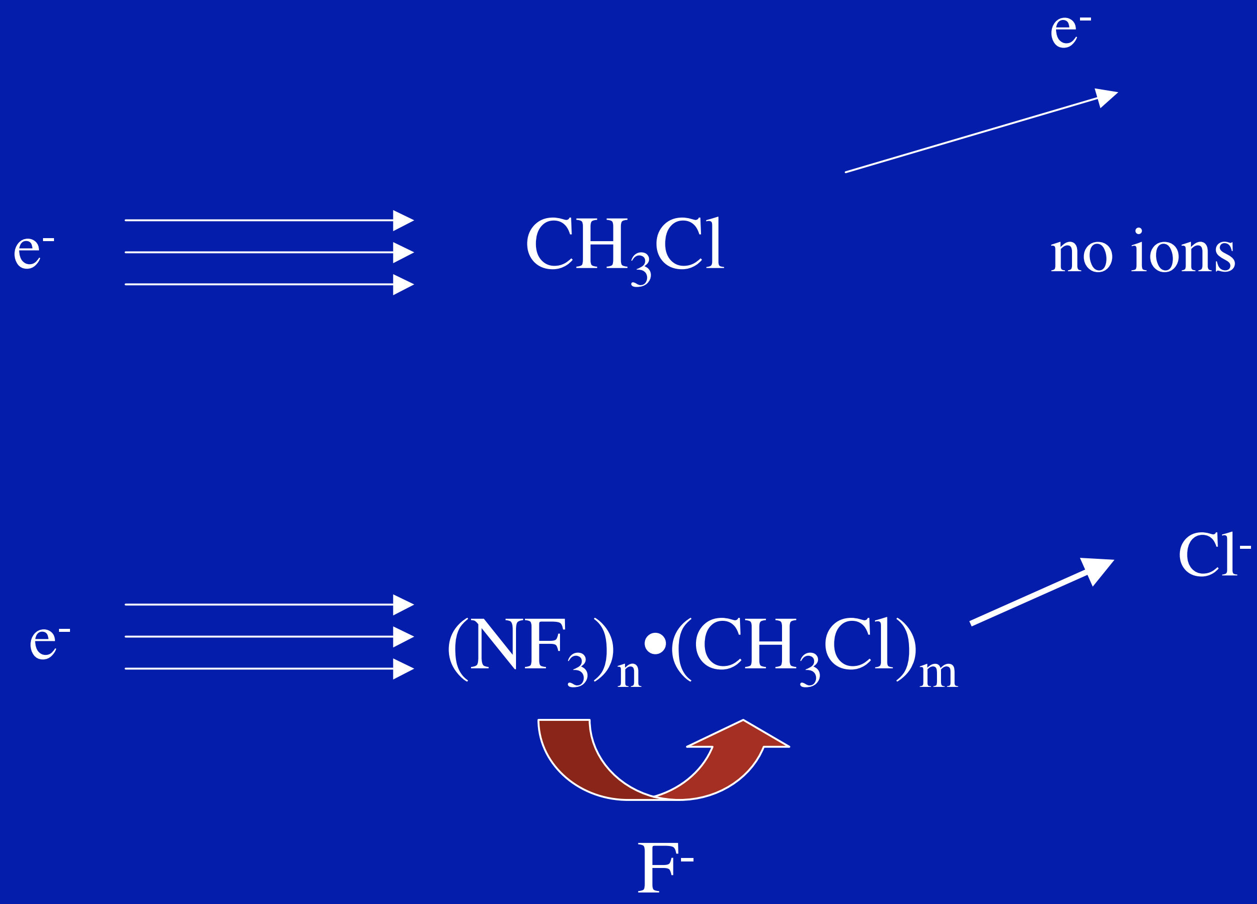
where M is a third body to stabilize the nascent ozone

As in Earth's stratopheric ozone formation (gas phase)



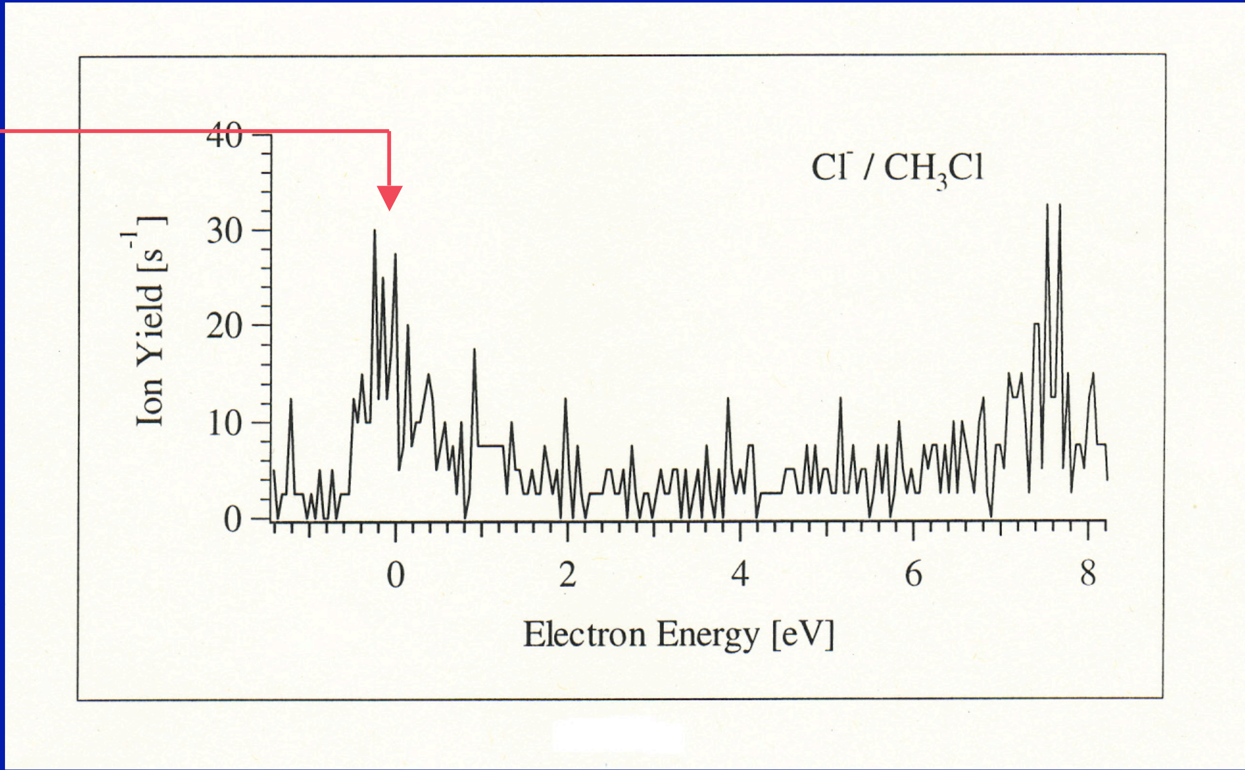
Nucleophilic Displacement (S_N2) Reaction

e.g. : $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$



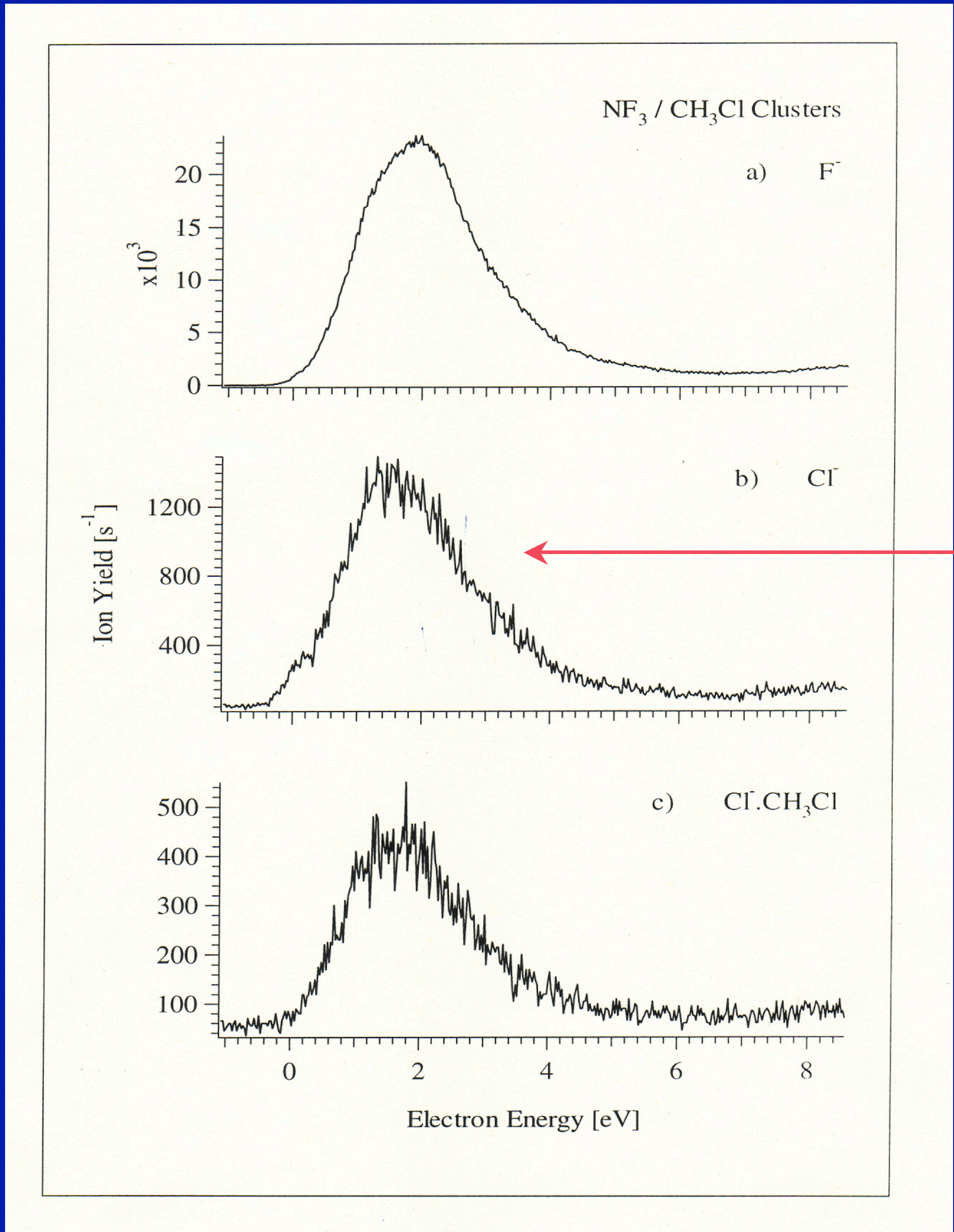
e-
CH3Cl
e-
no ions
e-
(NF3)n•(CH3Cl)m
Cl-
F-

from
impurity



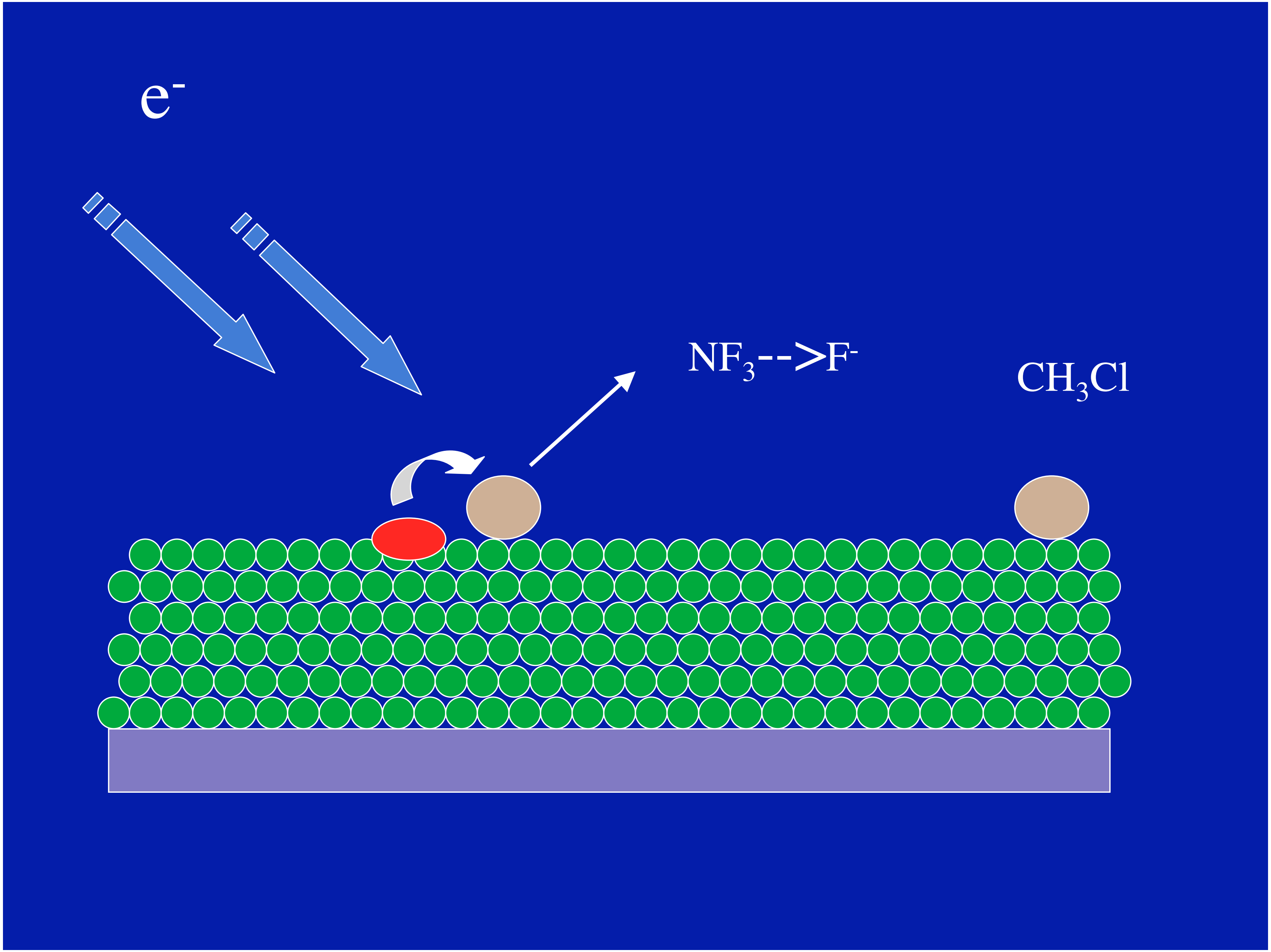
$e^- + CH_3Cl \rightarrow CH_3 + Cl^-$

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



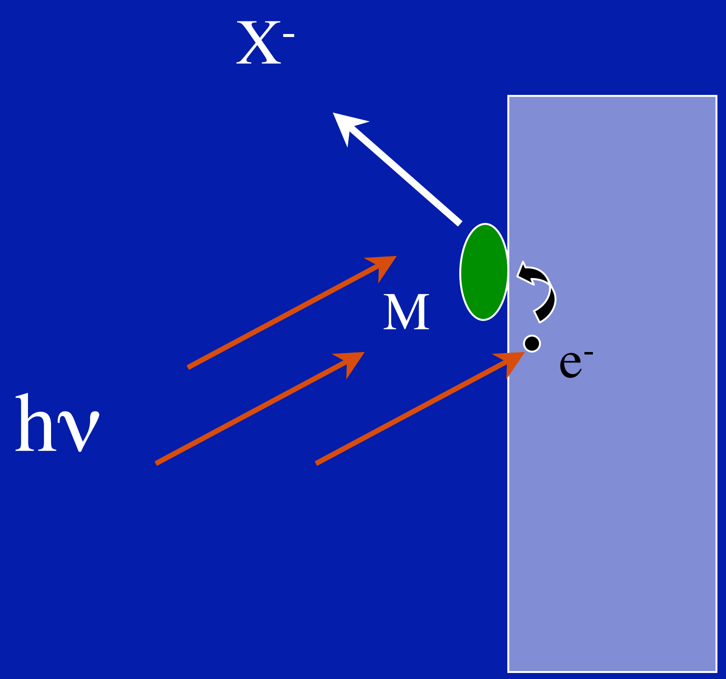
S_N2 Reaction

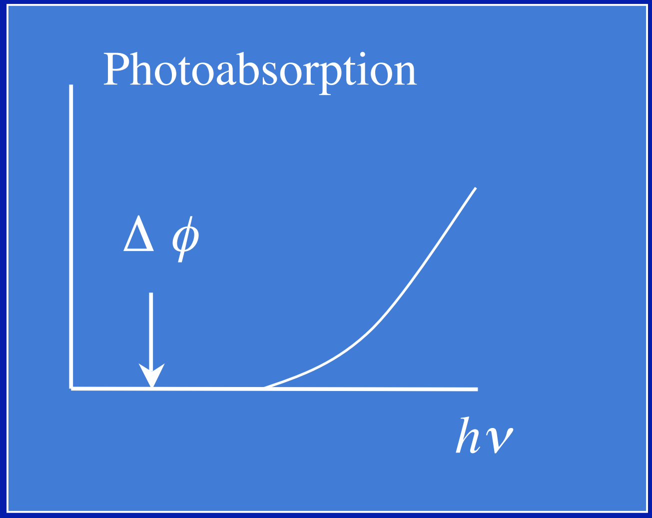
Illenberger et al Berlin



e^-
NF_3-->F^-
CH_3Cl

Substrate Induced Photochemistry





New Experiments now under way

- **Demonstrating the complete chemical transformation of a molecular film of 1,2-$C_2F_4Cl_2$ by low energy (< 3eV) electrons to form molecular chlorine and perfluorinated polymers. . OU/Berlin/Paris**

- **Revealing the formation of carbon dioxide in electron radiation of films of condensed formic acid . OU/Paris/Berlin**

ALL DEA Driven

In many molecules DEA leads to H atom loss

- This is most dominant process is in DEA to organic acids

- E.g. acectic, formic and …

DEA in propanoic acid

Dominant channel is H atom abstraction

$$e^- + CH_3CH_2COOH \rightarrow CH_3CH_2COO^- + H$$

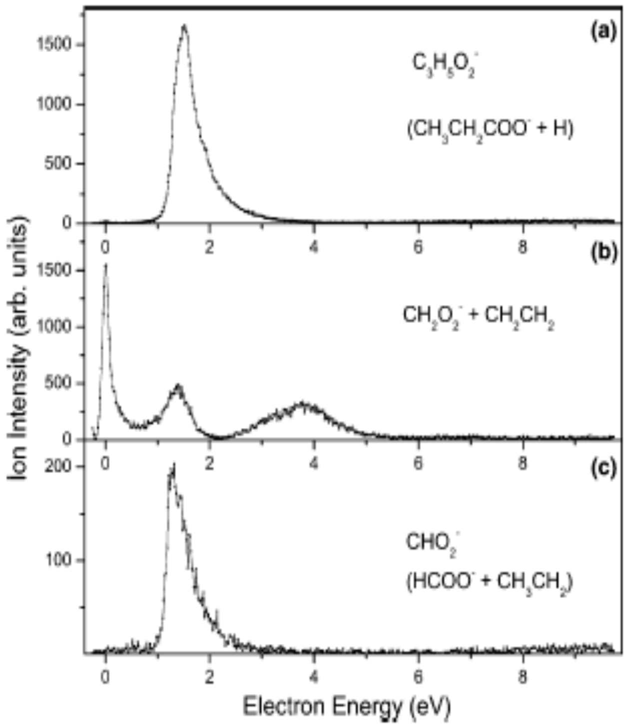


Fig. 1. Dominant fragment ions obtained from propanoic acid. The most intense channel ($C_3H_5O_2^-$) corresponds to hydrogen abstraction with a cross-section of $1.7 \times 10^{-20} m^2$ (see the text and Table 1).

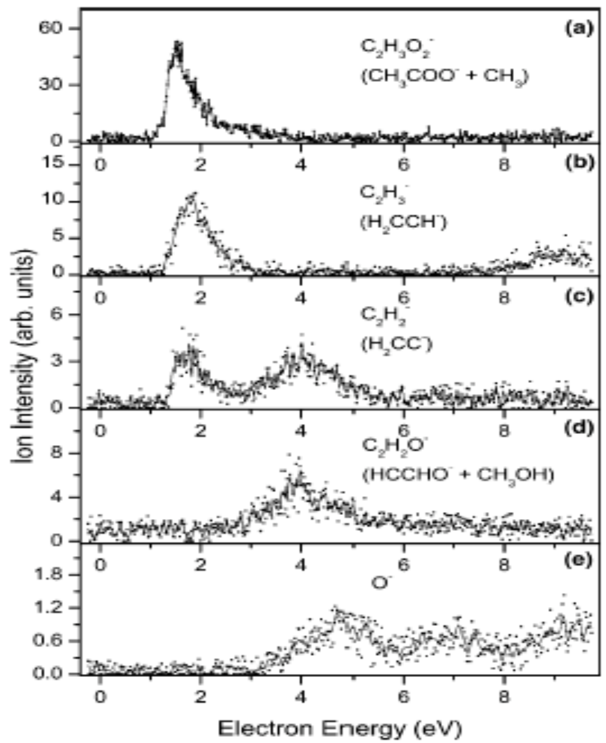


Fig. 2. Fragment ions observed from electron impact to propanoic acid.

DEA and biomolecules

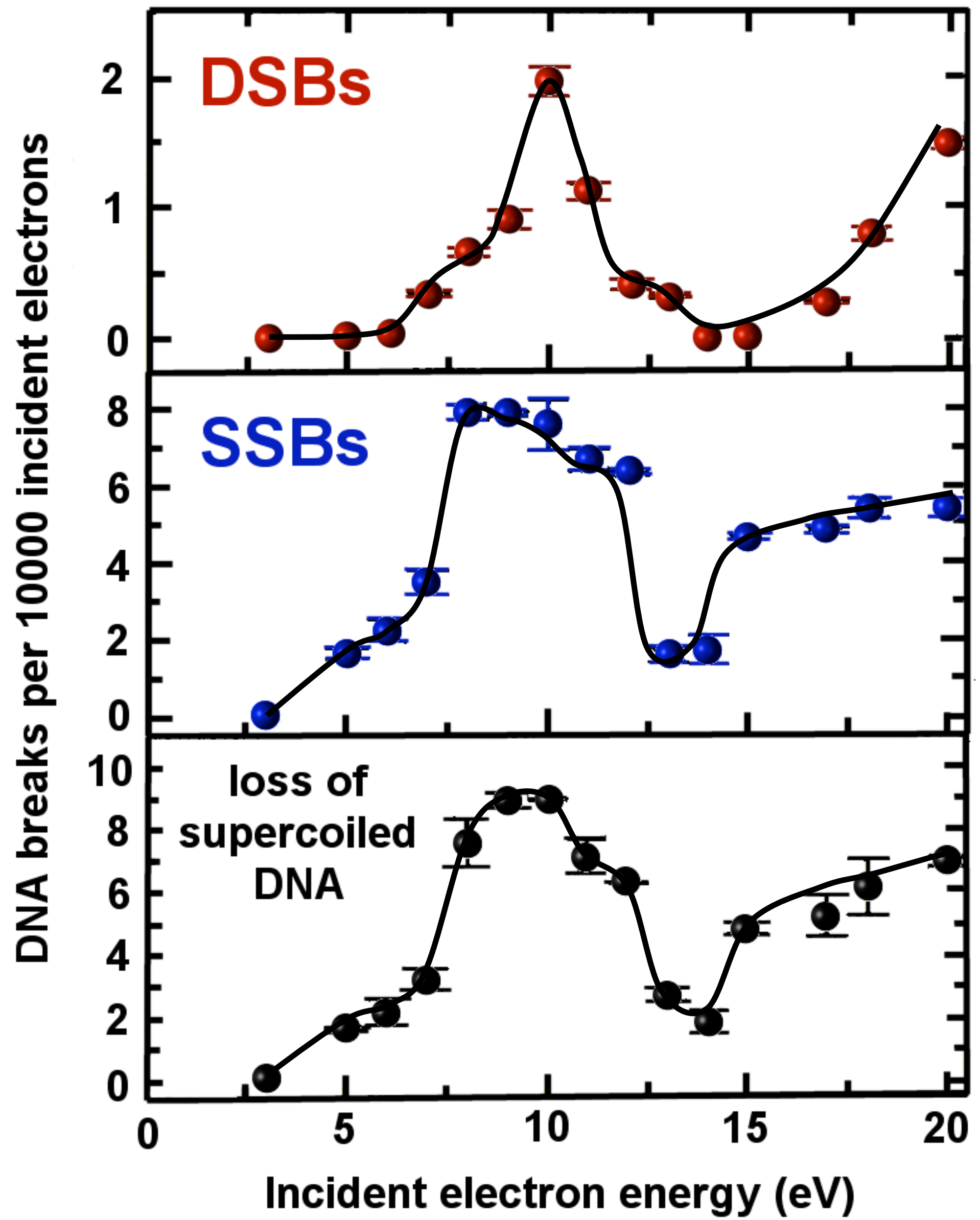
- DEA is a universal process
- So DEA will occur in biomolecules including those constituents of DNA
- So can DEA induced fragmentation lead to DNA damage ?

Mechanisms for ssb and dsb induction at low-energies

- Boudaiffa et al. (Leon Sanche, Sherbrooke Canada) demonstrated that there apperas tpo be a corrrelation between patterns of ssb and dsb induced in DNA and **DEA of constituent molecules**

Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20eV) Electrons. Science **287**, *1658-1660* (2000). B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels et L. Sanche.

DNA-strand breaks



Sanche a.c. Science, 287 (2000) 1659

Mechanisms for ssb and dsb induction at low-energies

“This finding presents a fundamental challenge to the traditional notion that genotoxic damage by secondary electrons can only occur at energies above the onset of ionization…”

DEA to Uracil (Innsbruck)

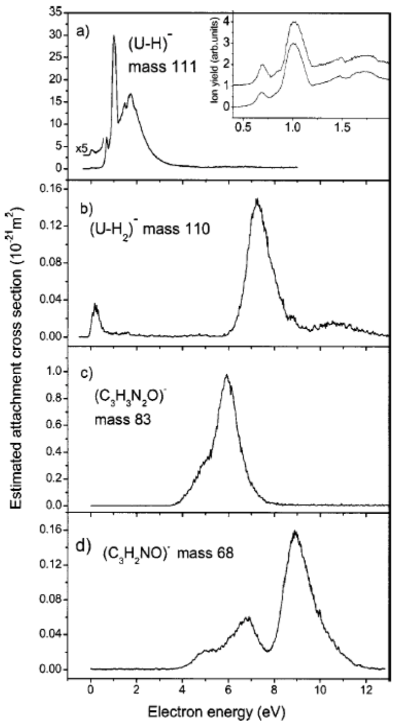


FIG. 3. Ion yield of $(U\text{-}H)^-$, $(U\text{-}H_2)^-$, $(C_3H_3N_2O)^-$, and $(C_3H_2NO)^-$ for dissociative electron attachment to uracil as a function of electron energy. These ion yields were measured without any presence of a calibration gas. The partial cross section scale was determined relative to the Cl^-/CCl_4 ion yield and has an accuracy within one order of magnitude. The inset in (a) shows the ion yield of $(U\text{-}H)^-$ measured at an electron energy resolution of 60 meV (upper curve) and 90 meV (lower curve), respectively.

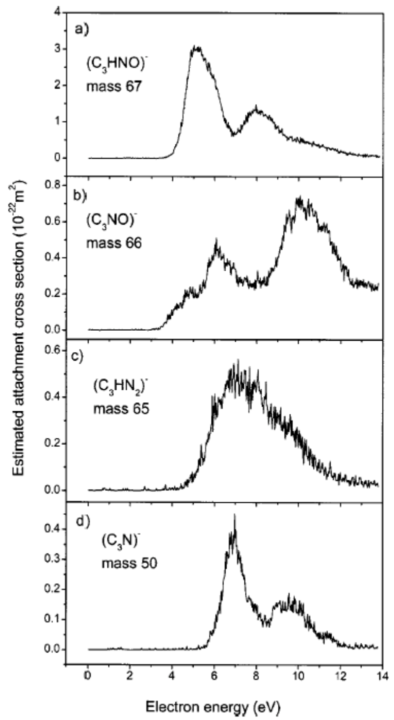
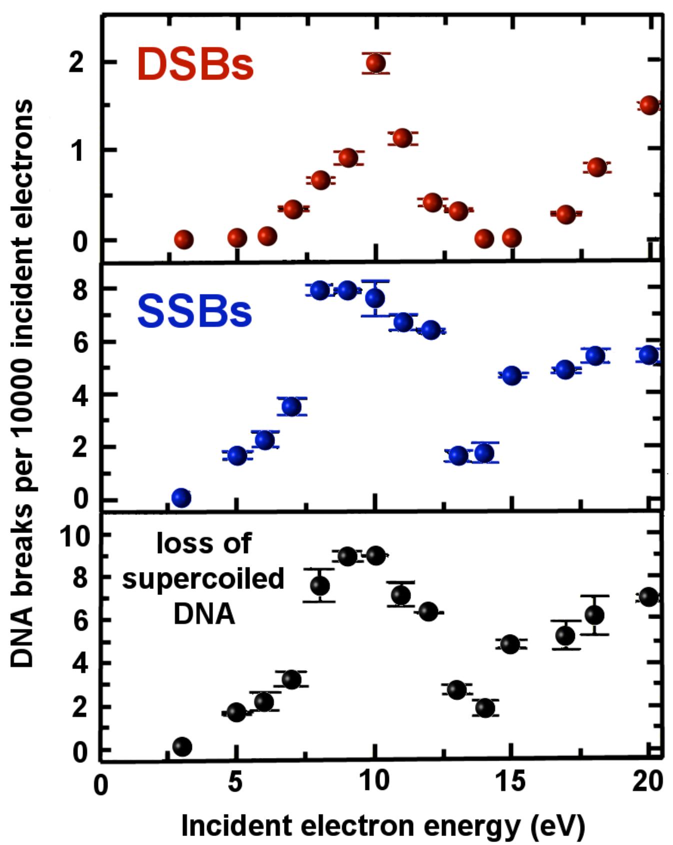
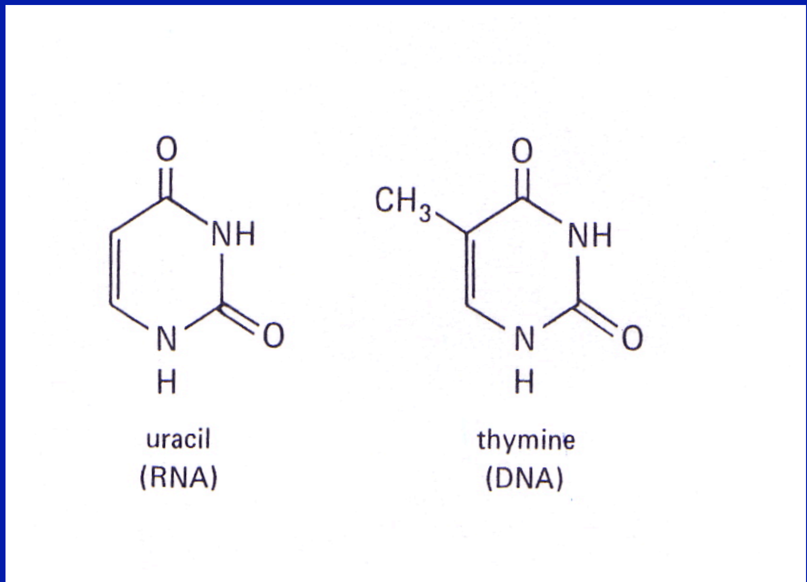


FIG. 4. Ion yield of $(C_3HNO)^-$, $(C_3NO)^-$, $(C_3HN_2)^-$, and $(C_3N)^-$ for dissociative electron attachment to uracil as a function of electron energy from about 0 to 14 eV. The partial cross section scale was determined relative to the Cl^-/CCl_4 ion yield and has an accuracy within one order of magnitude.



Does DEA explain effectiveness of some radiosensitizers ?

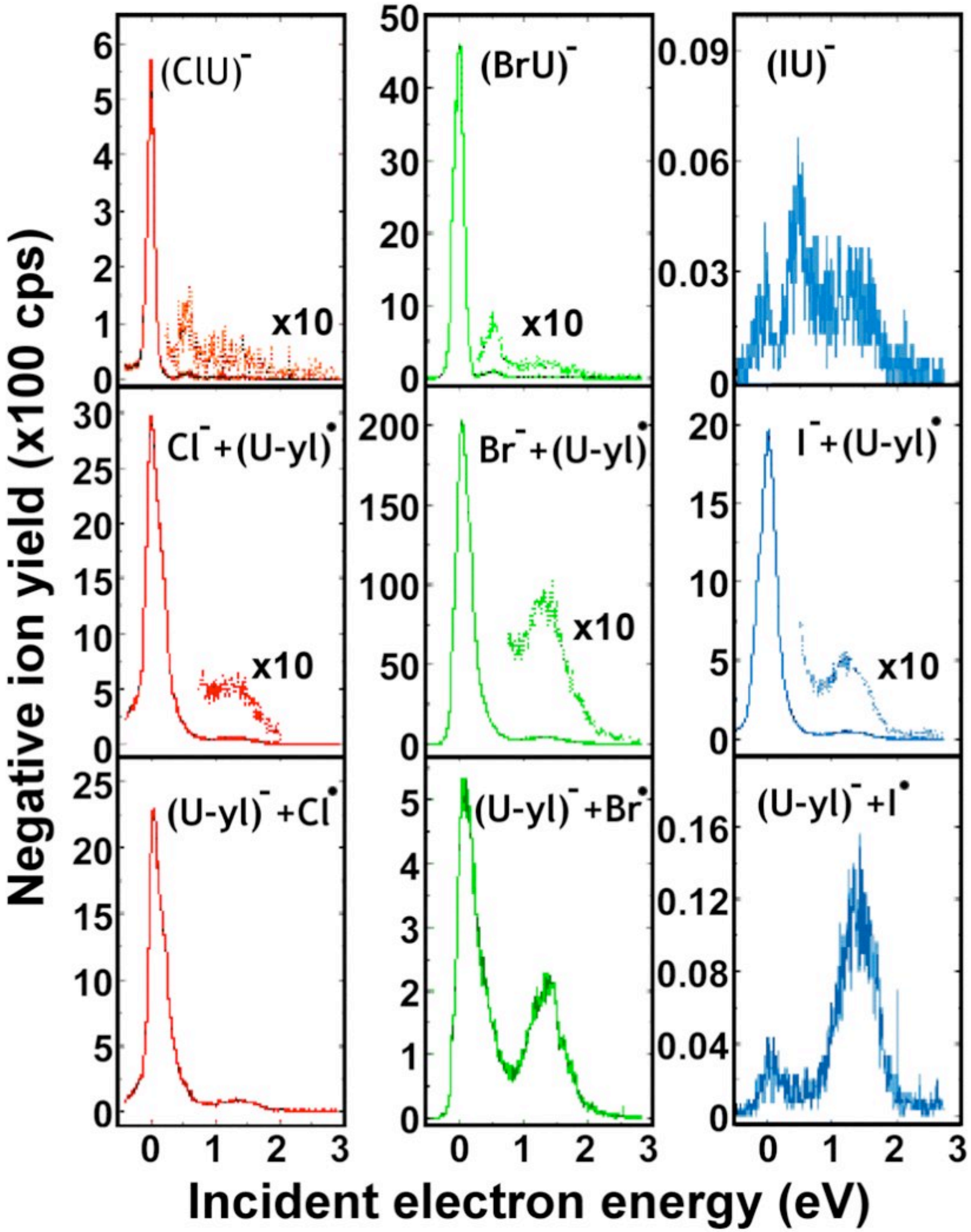
- Observation of correlation between carcinogens and DEA rates ?
- Effectiveness of halogenated compounds as radiosensitizers

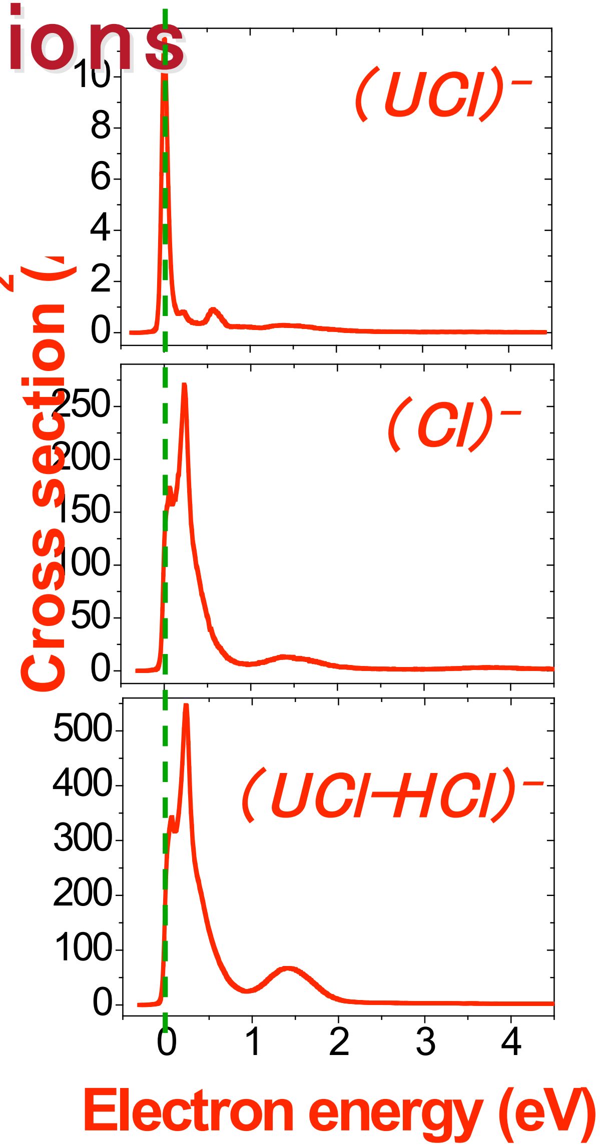


Uracil Thymine Bromouracil (Radiosensitizer)

Halo-uracils measured by Illenberger et al Berlin.

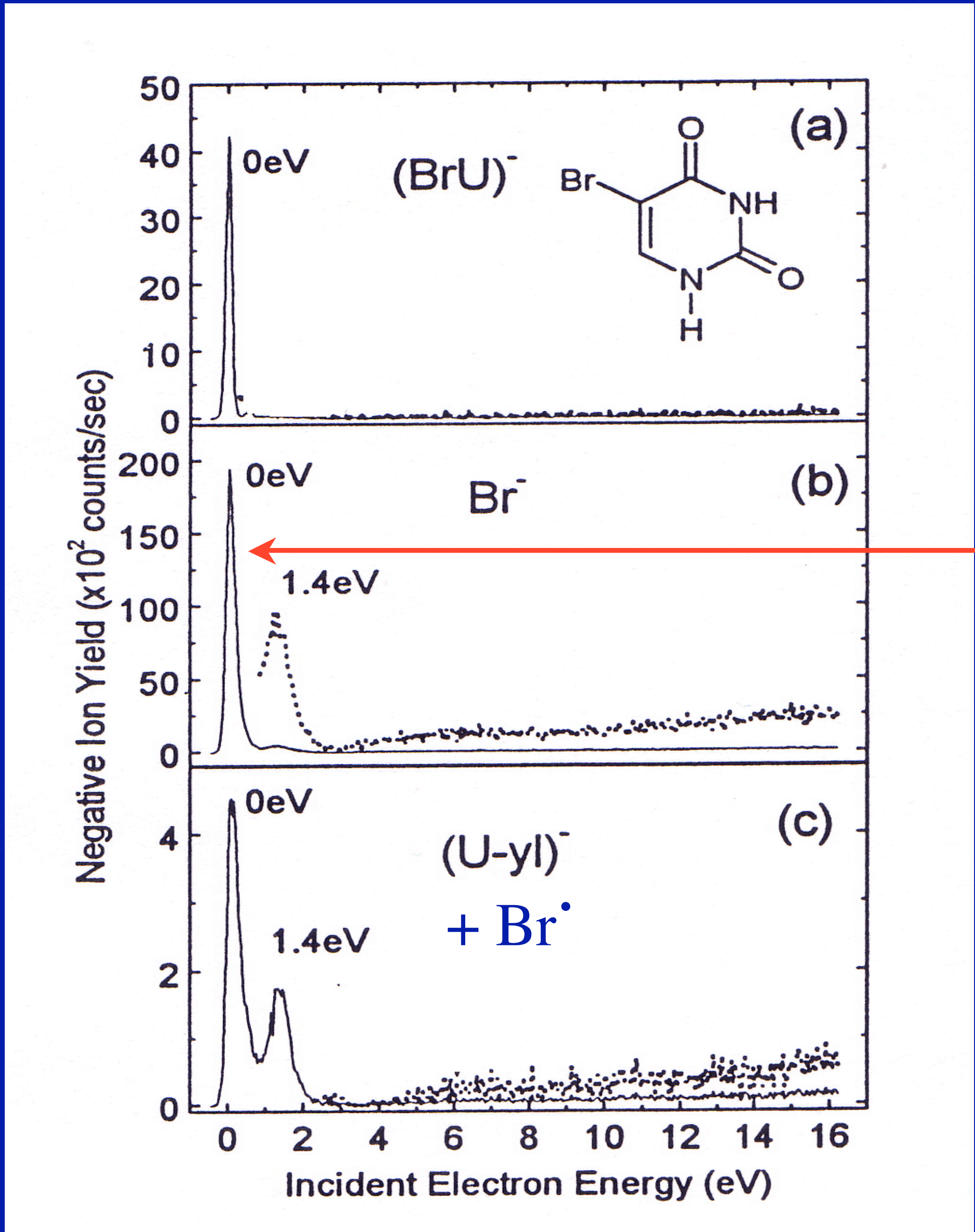
UCl + e⁻ → anions





Ratios: $X^-/(U\text{-}yl)^-$ = 1.3, 40, 490 (X=Cl,Br,I)

Present: $Cl^-/($



Freie University Berlin

$\sigma \approx 600$ Å^2

Hypothesis for Mechanism of SSB and DSB?

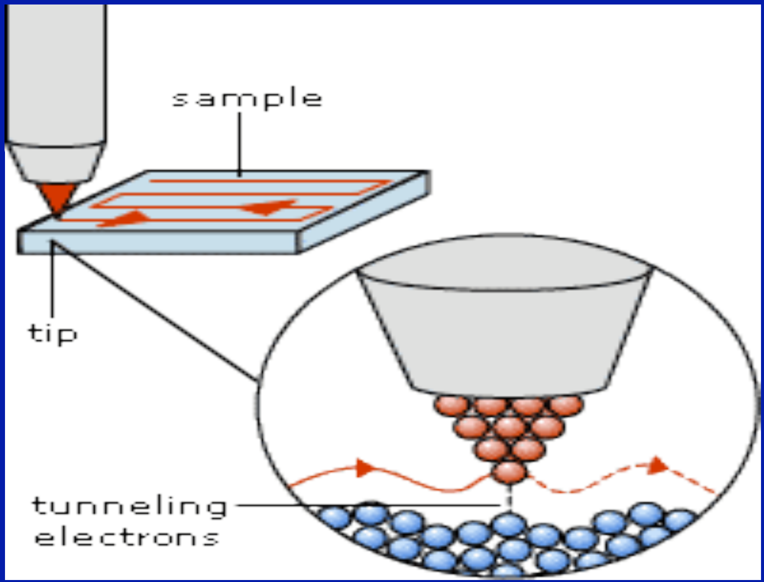
- Electron attachment liberates H atoms
    - This can induce an SSB
- DSB induction occurs when fragmentation components react with the opposite strand

Electron Induced Processing

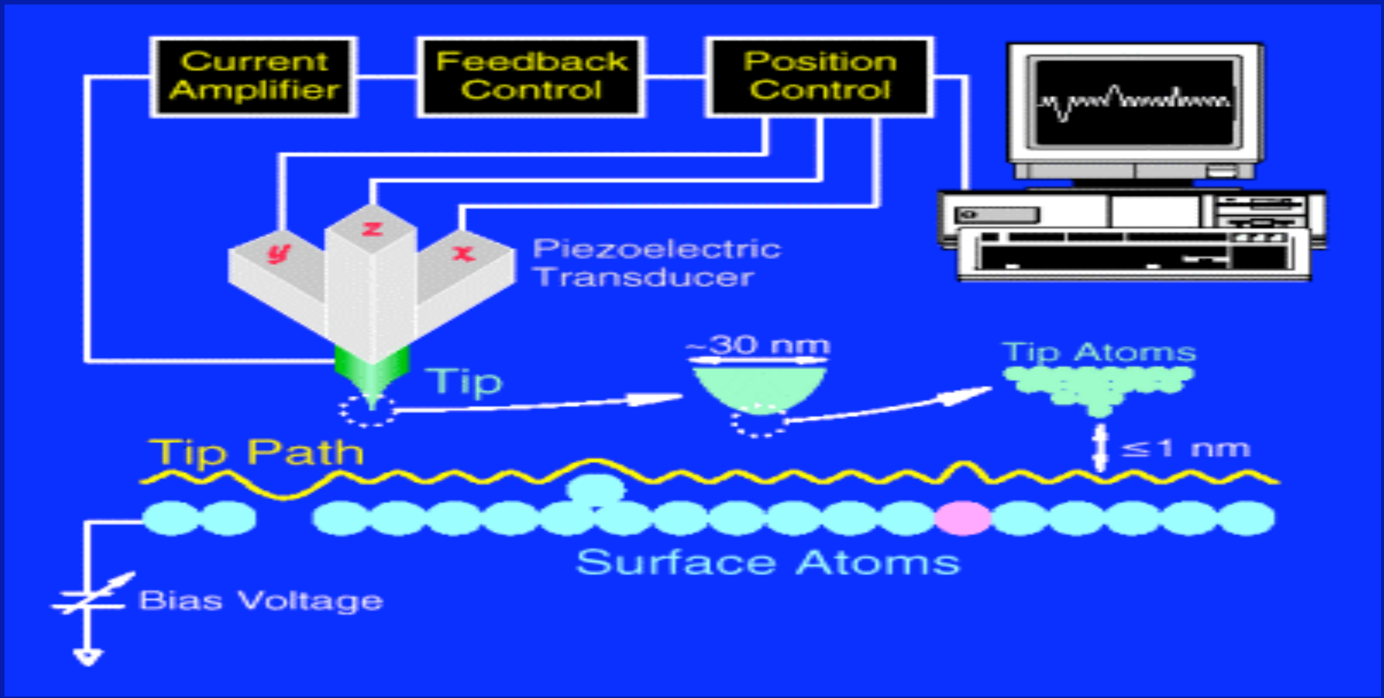
New techniques for electron scattering!

The Method of Scanning Tunnel Microscopy

Electron current from fine metal tip interacts with (metal) substrate



Electron Induced Processing

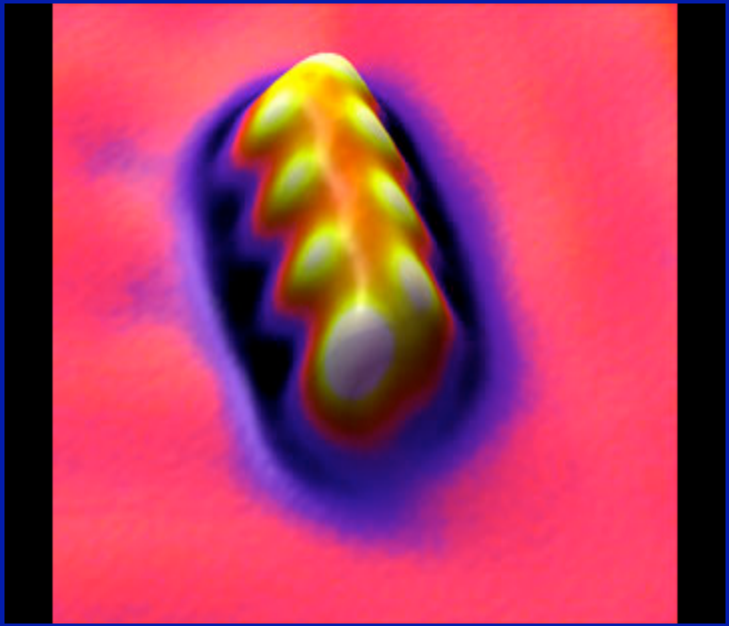


www.eng.yale.edu/.../ spm/stm-operation.gif

Electron Induced Processing

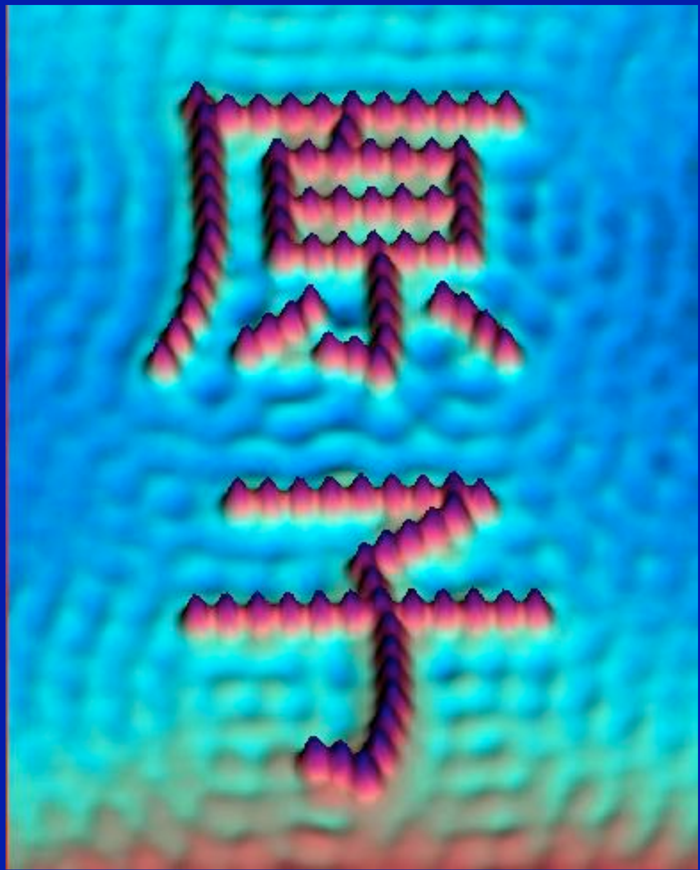
- You can then 'see molecules'
- Here Caesium and Iodine atoms

!

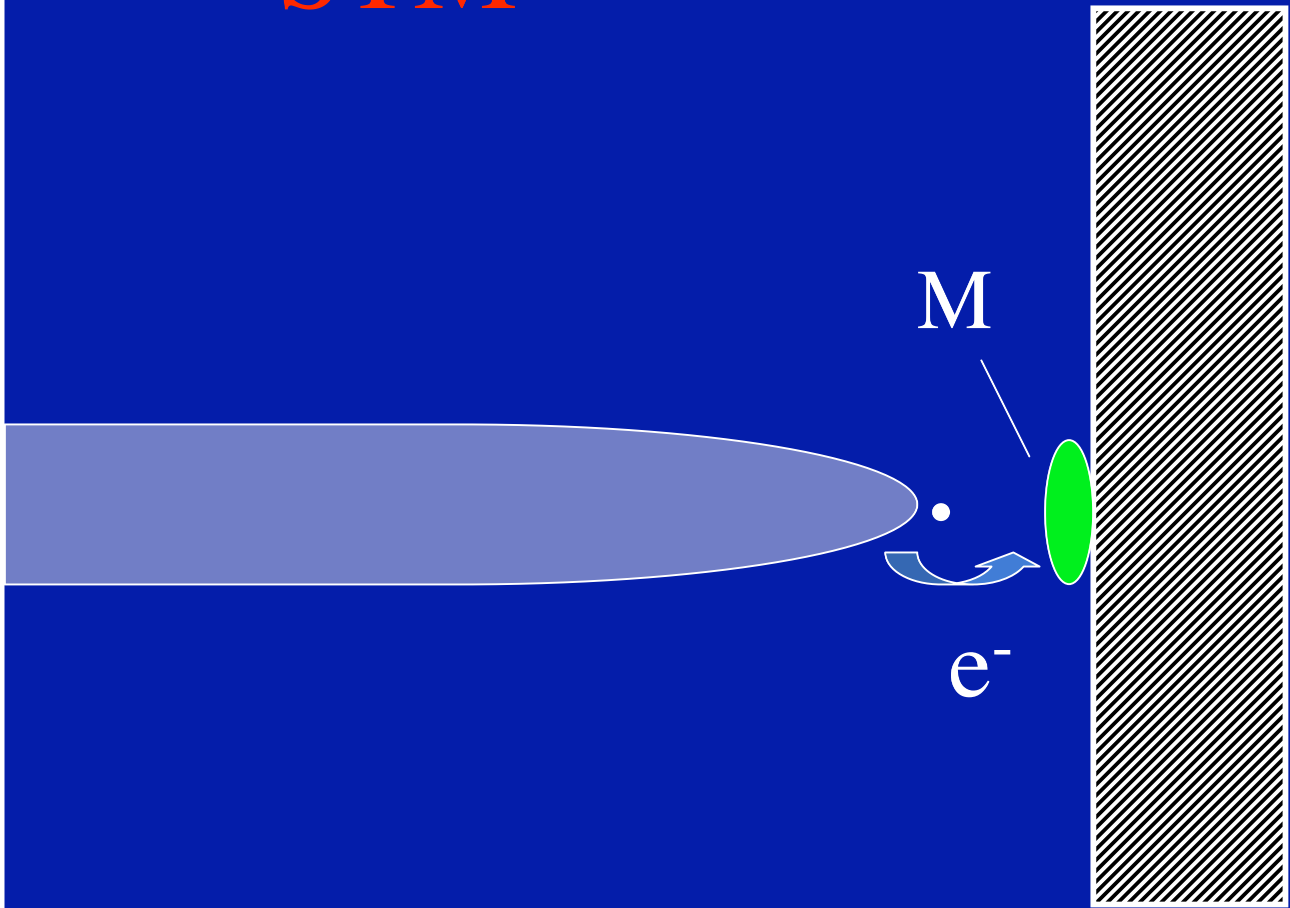


Electron Induced Processing

- With the STM you can move the atoms and molecules
- And arrange them !
- Here Iron atoms on copper



STM



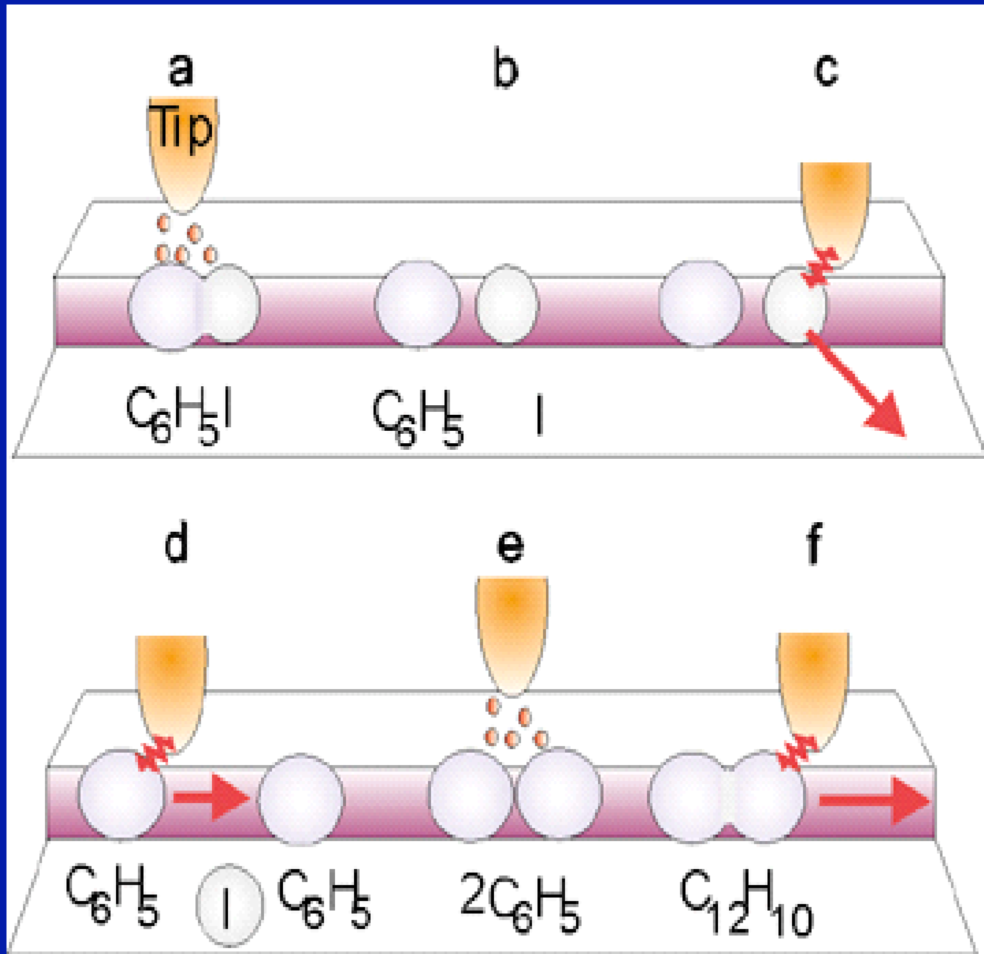
Single Molecule Engineering

Electron Induced Processing

Making new molecules

Hla et al (Berlin)

$C_{12}H_{10}$



Electron Induced Processing
Chemical Control at the Molecular Level

Sloan and Palmer ***Nature*** **434**, 367-371

Two-electron dissociation of single molecules by atomic manipulation at room temperature

Electron Induced Processing

Electron excitation and dissociation of individual oriented chlorobenzene molecules on a Si(111)-7 7 surface at room temperature by a two-electron mechanism that couples vibrational excitation and *dissociative electron attachment* steps.

The first electron interacts with the chlorobenzene molecule; ***the*** *molecule is left vibrationally excited (specifically, the C—Cl wag mode is excited); the second electron interacts with the molecule before the C—Cl wag mode has fully relaxed, leading to dissociation of the C—Cl bond by DEA;*

Electron Induced Processing

So What Next ?????

- Plan for 2006-9 (in Europe)

1. Negative ions in plasmas programme Europe with Japan.
2. Tune fragmentation pathways in semiconductor plasmas.

Electron Induced Processing

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(with Australia ??).

Electron Induced Processing

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Electron Induced Processing
Plan for 2006-9 (in Europe)

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3. Electron damage of biomolecules and DNA (electron transport in DNA nanowires) EU Programme.

4. Astrochemistry; low temperature electron processing of ices to probe molecular formation in space; origins of life

So what to do with all this data ?

How to assemble data and knowledge ?

Commissioned set of books reviewing

Basic science;

Latest methods

Data compilations

So what to do with all this data ?

Commissioned set of books - Springer Verlag

2007 Radiation damage/modelling

2008 Electron induced processing

2009 Astrochemistry (tbc)

2010 ??

So what to do with all this data ?

Commissioned set of books

Photoabsorption cross sections

- rewrite and update of ROBIN (1970-1980)

- Update of ‘Christophorou’ electron/molecule
- In discussion

So what to do with all this data ?

But need for more

- Online submission of data – much still is not published
- Weblog- open discussion of data submitted
- Validation and recommendation
- Online access to computation eg BE for ionisation data and QUANTAMOL (UK)

So what to do with all this data ?

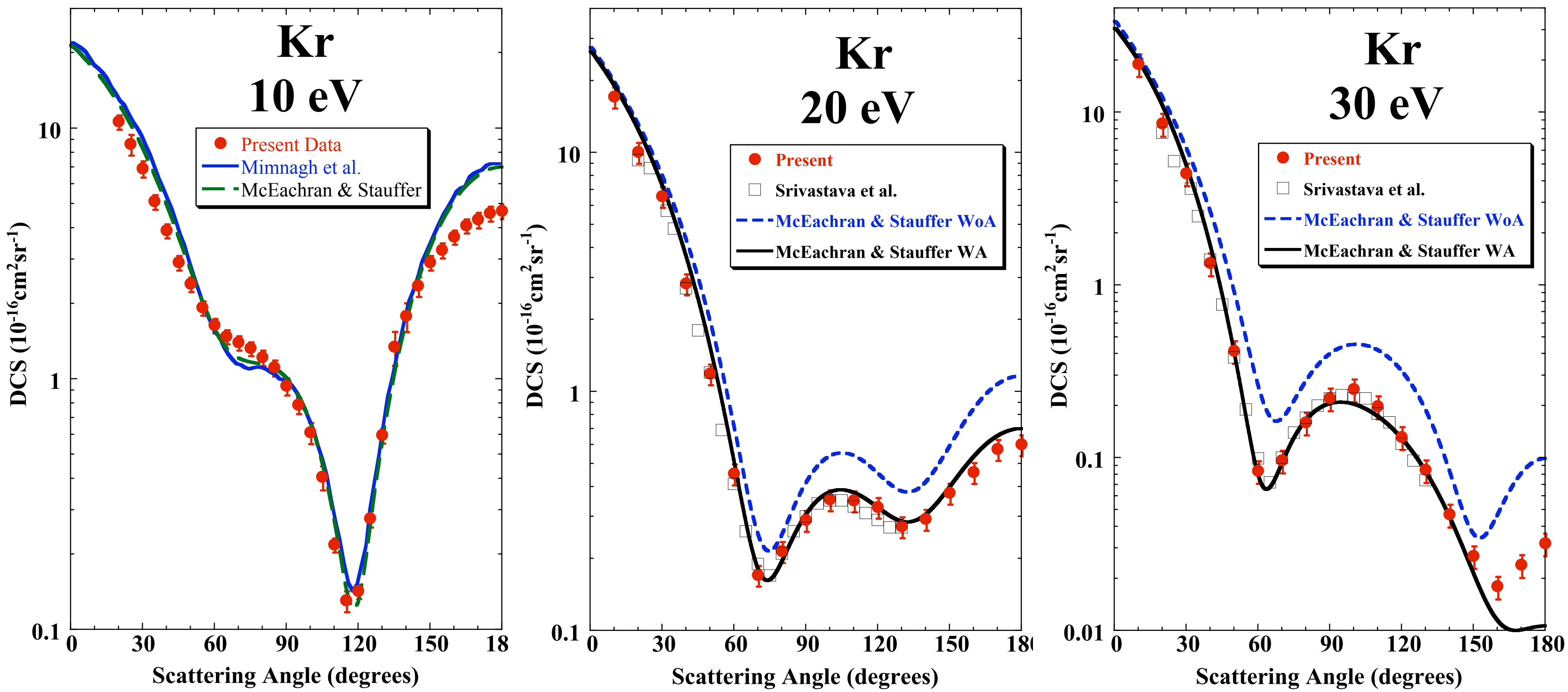
- Difficulties

- Newest is not always best.
- Yours is not always best.
- Need to compare with standards /search for systematic errors.
- Theory vs experiment

So where are we now in electron studies ?

- Electron – atom scattering K Bartschat
- Really quite good now at least for light atoms
- Elastic, excitation (including resonances)
- Ionisation

Elastic Scattering - rare gases



Cho, McEachran, Tanaka, Buckman
JPB **37** 4639 (2004)

So where are we now in electron studies ?

- Electron –molecule interactions

- Very VERY poor c.f. atoms
- Difficulty is complexity of target
- New processes – dissociation – drives chemistry

So where are we now in electron studies ?

Electron –molecule interactions

Total cross sections;

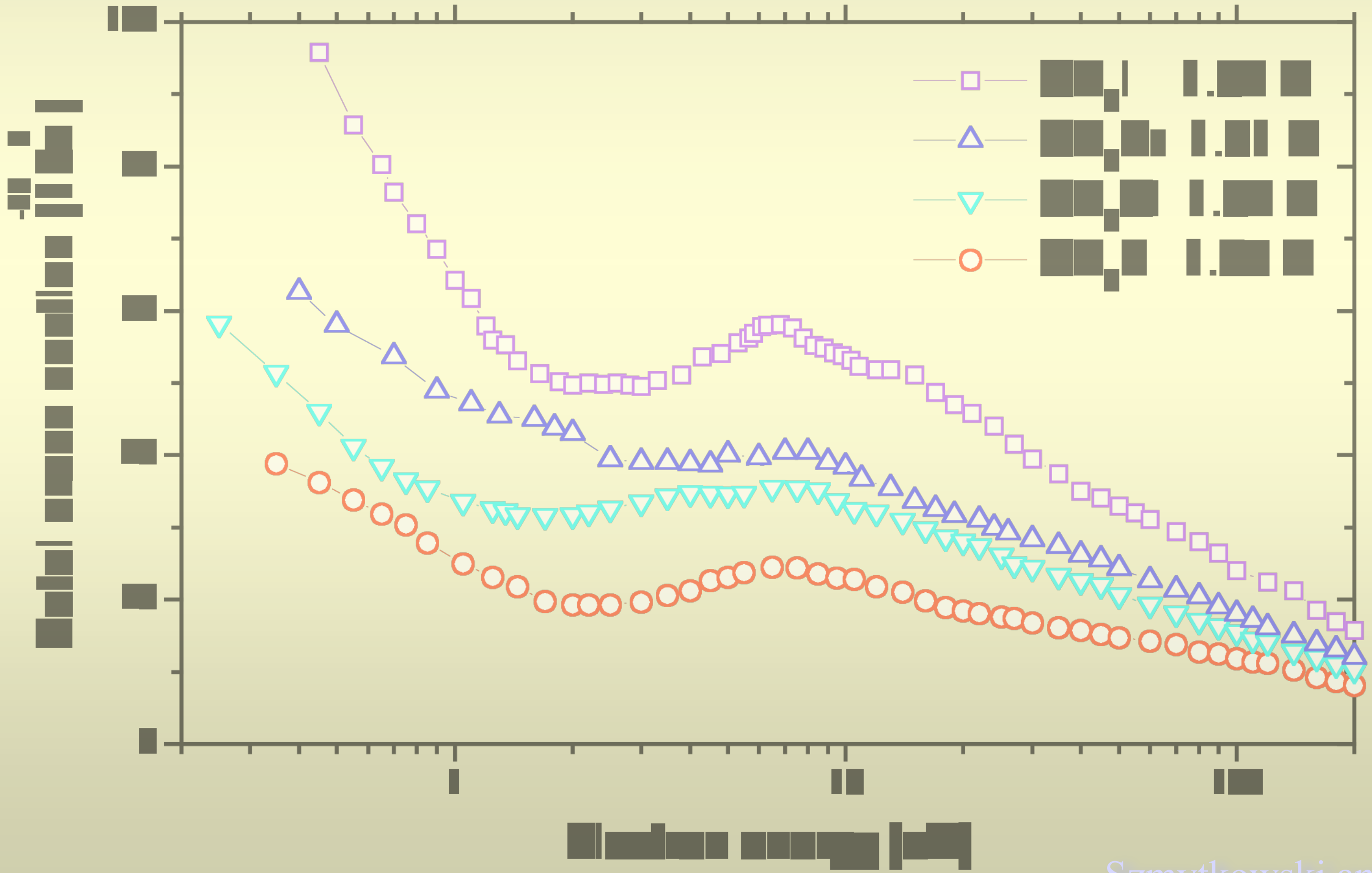
Accurate to some 5%

(allow for forward scattering)

Lowest energies few meV ! Hotop and Field

Total cross sections for electron scattering

$$I = I_0 \exp(-\sigma n l)$$



Szmytkowski and collaborators

So where are we now in electron studies ?

Electron –molecule interactions

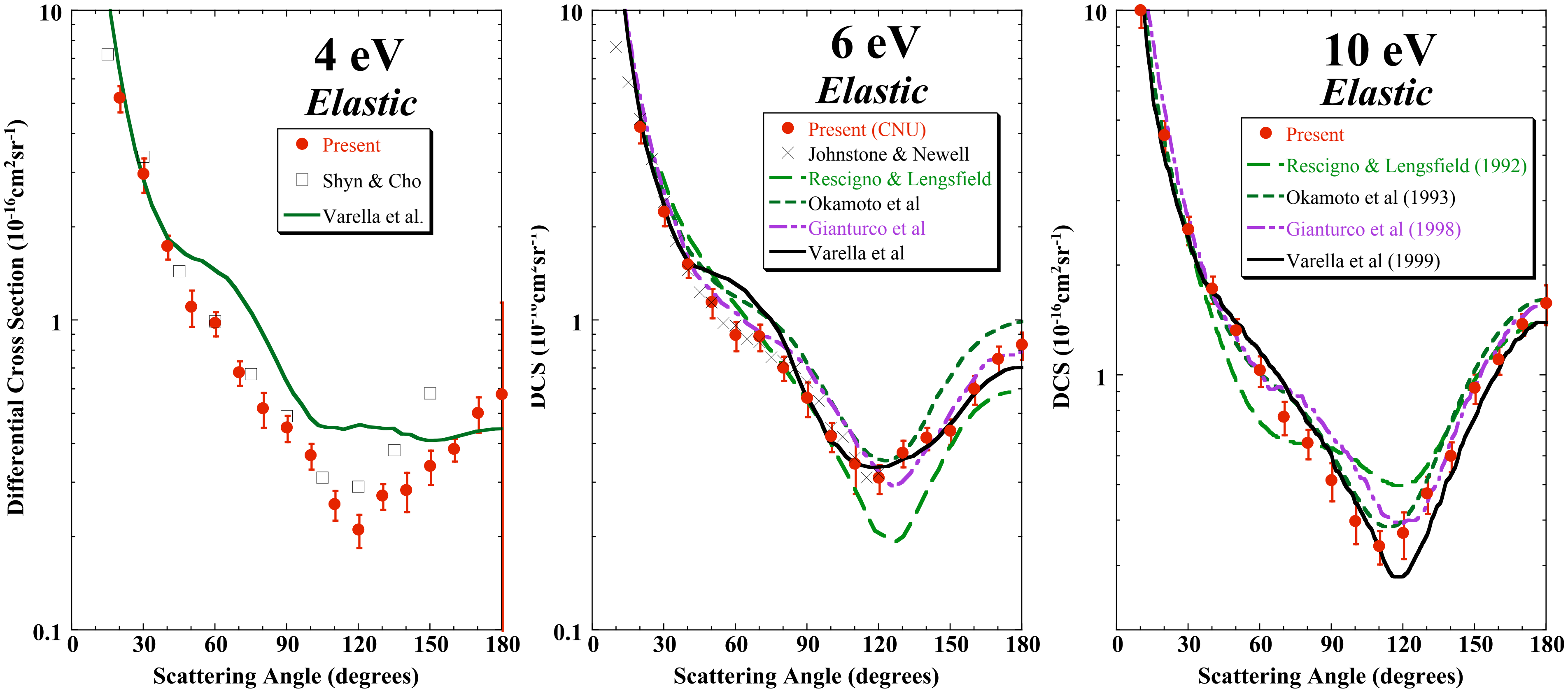
Elastic cross sections;

Accurate to some 10% - good standards

e.g. ANU data

Angular range – Magnetic angle changer 0 to 180

Elastic scattering - H_2O



Cho, Park, Tanaka, Buckman
JPB **37** 625 (2004)

So where are we now in electron studies ?

Electron –molecule interactions

Inelastic cross sections;

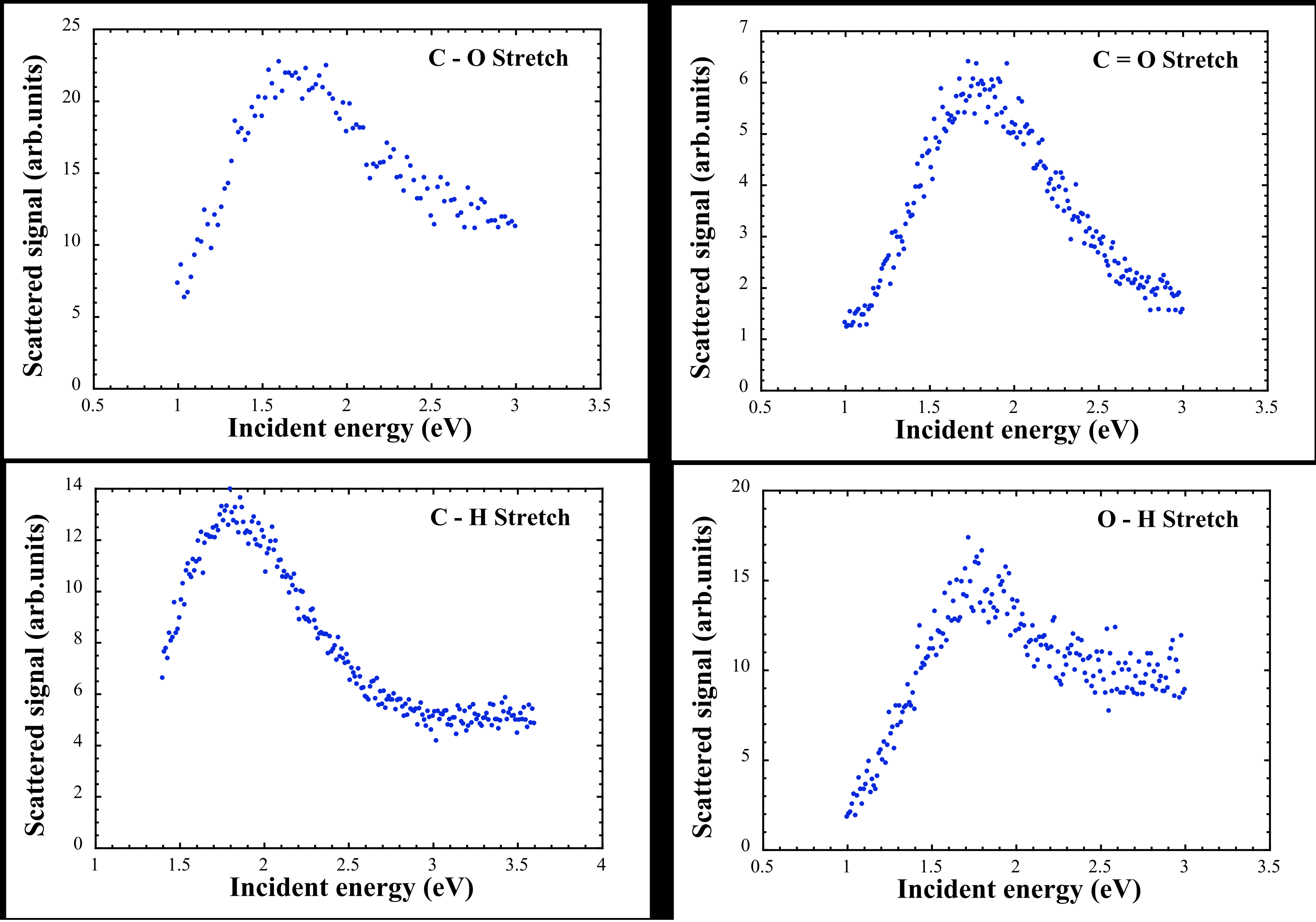
Vibrational (but resolution and deconvolution)

Excitation – hopeless despite importance

Transmission effects

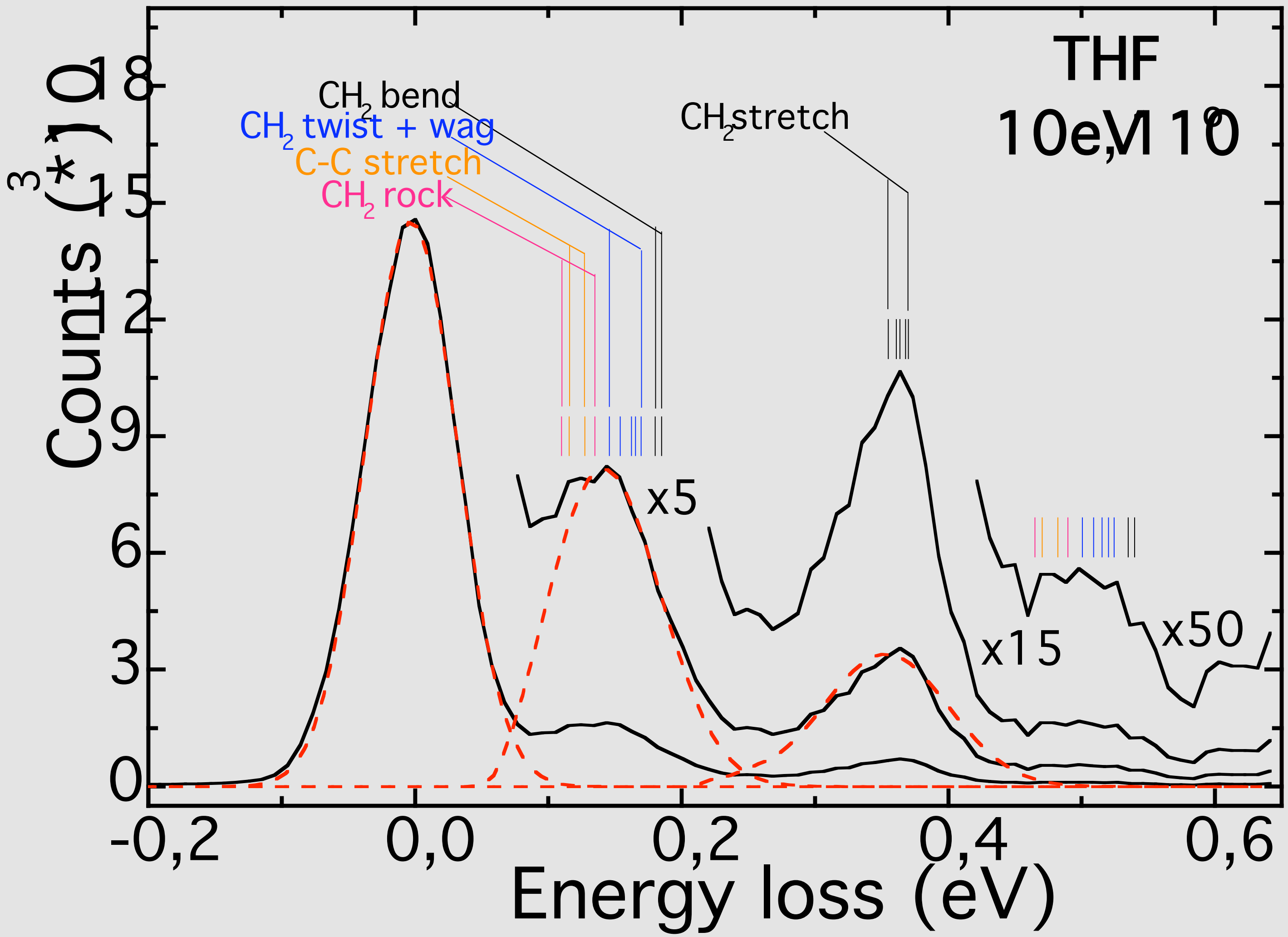
Rotational excitation…

Vibrational excitation - HCOOH



Vibrational excitation

Energy loss spectra



So where are we now in electron studies ?

Electron –molecule interactions

Ionisation;

Better data sets

(cf Theory – Kim (BE) and Deutsch Maerk)

But Kinetic effects in products

So where are we now in electron studies ?

Electron –molecule interactions

Ionisation; DEA

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 ?

Electron –molecule interactions

Dissociation to neutrals

Ground state products – in its infancy

Still testing methodologies

No standard

Kinetic effects in products

So where are we now in electron studies ?

Electron –molecule interactions

Dissociation to excited states

Fluorescence– lots of data but

Detector calibrations

Role of cascade

Kinetic energy – Doppler broadening

So where are we now in electron studies ?

Electron –molecule interactions

The REAL TEST

Summation of independent cross sections to
get total cross section

No data set really does this !!!!!

What do we need in electron molecule studies ?

- Electronic excitation – new methods and a standard needed to check these
- Dissociation – particularly neutrals
- Role of internal energy (metastable states)

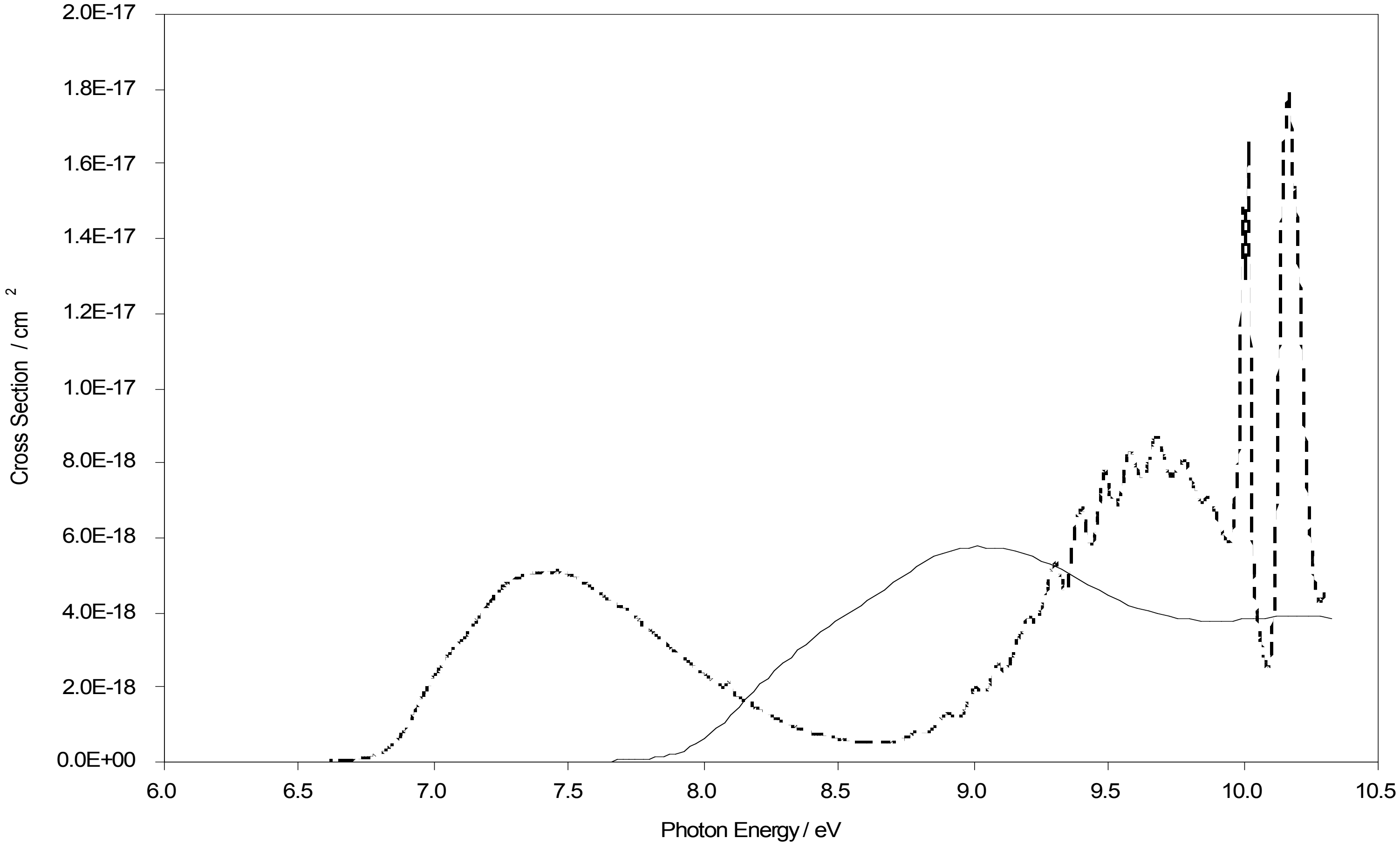
What do we need in electron molecule studies ?

Surface studies

- How to define a cross section on a surface
- Role of molecular orientation
- Role of morphology
- Shift in energy levels and electronic states !

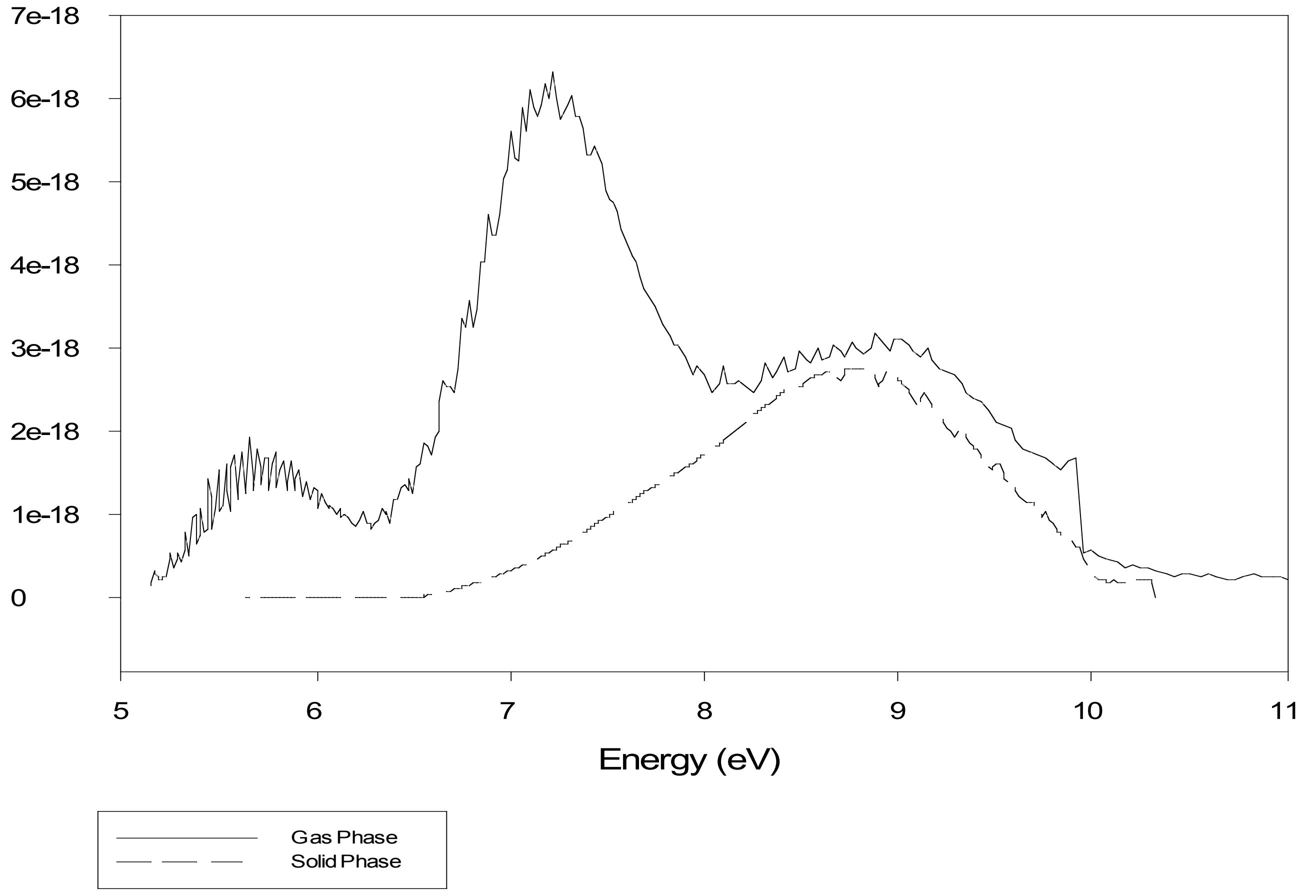
Water ice

Note : Blue shift in the solid phase



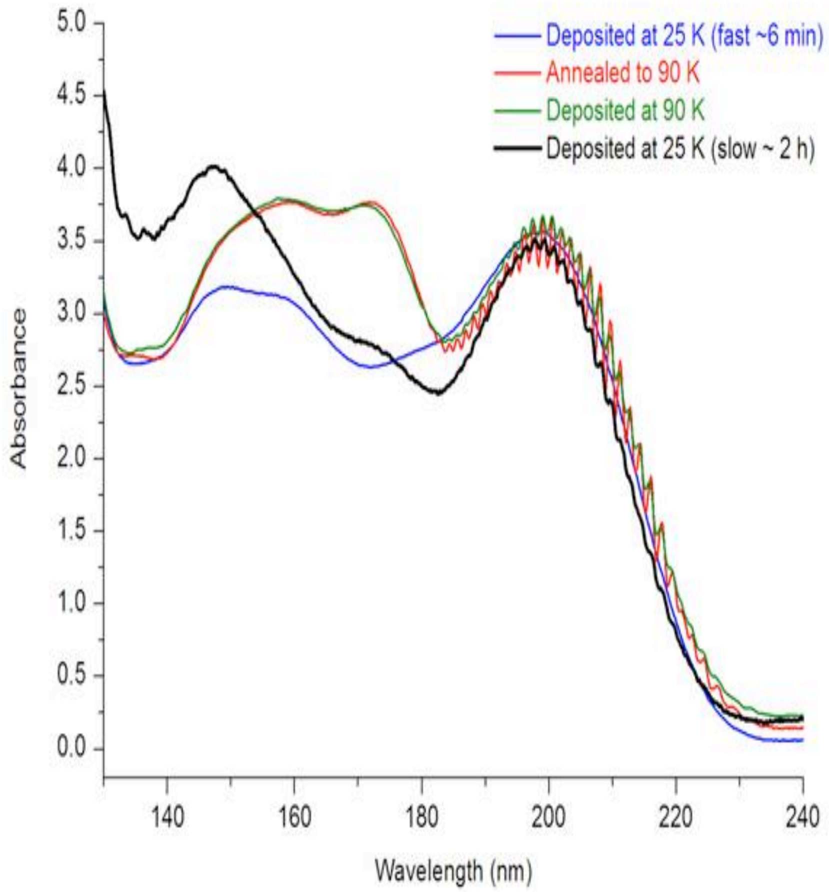
Comparison of gas and solid phase Methylamine

Note absence of low lying bands in solid phase



SO_2

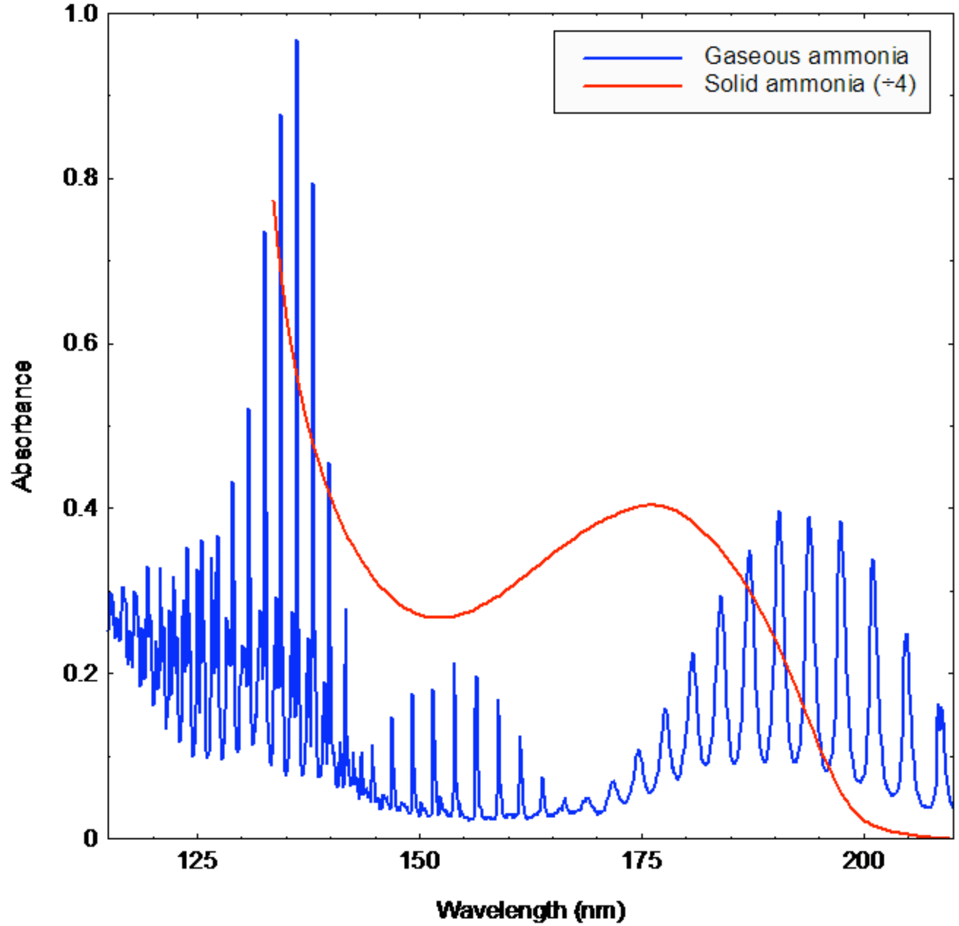
- 'Fast' deposition at 25 K
  No vibrational structure → Amorphous ice
- Annealed to/deposited at 90 K
  vibrational structure & evidence of Davydov splitting → Crystalline ice
- Slow' deposition at 25 K
  Weak vibrational structure → evidence of some degree of crystallinity!



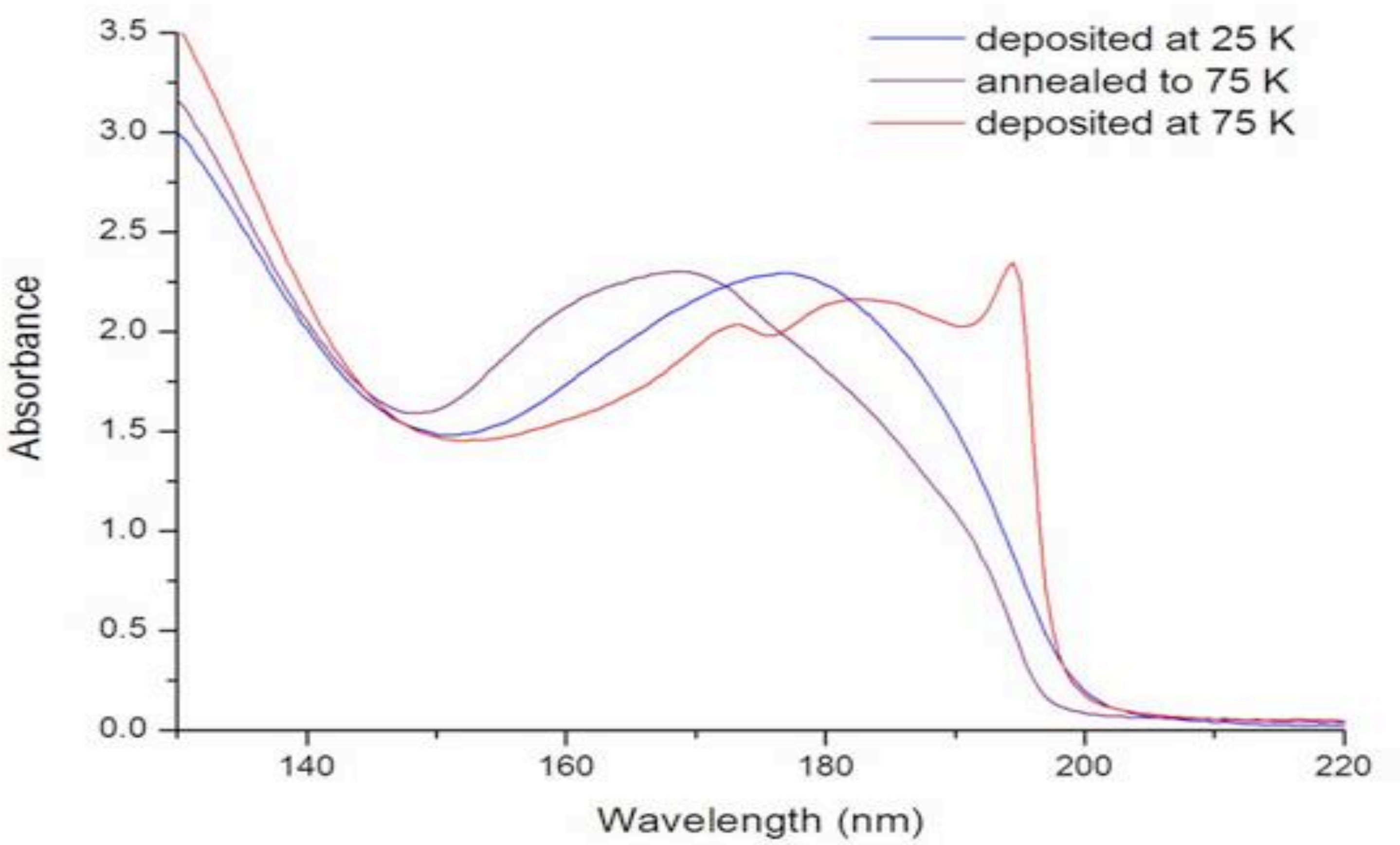
SO_2

- Rate of deposition is important in determining ice morphology.
- May form mixed amorphous/crystalline ice

Ammonia gas vs solid (25K)



Ammonia Different T



NH_3

- Formation of crystalites
- New excitations in the ice (excitons)

And finally

- Theory vs experiment

- Two worlds same language but different spellings
- Modeling vs modelling

And finally

- Theory vs experiment

- Theory needs an ‘error analysis’
- What is a good fit ?
- What are flexible parameters ?
- What are limitations – very hard for users to understand !

The team – with thanks

UCL and OU

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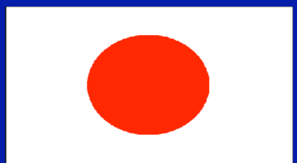

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