Working Group 1 Meeting 2006

First experiments on the interaction of cold electrons with solids

and rotational scattering in water plus some thoughts about dipole bound states

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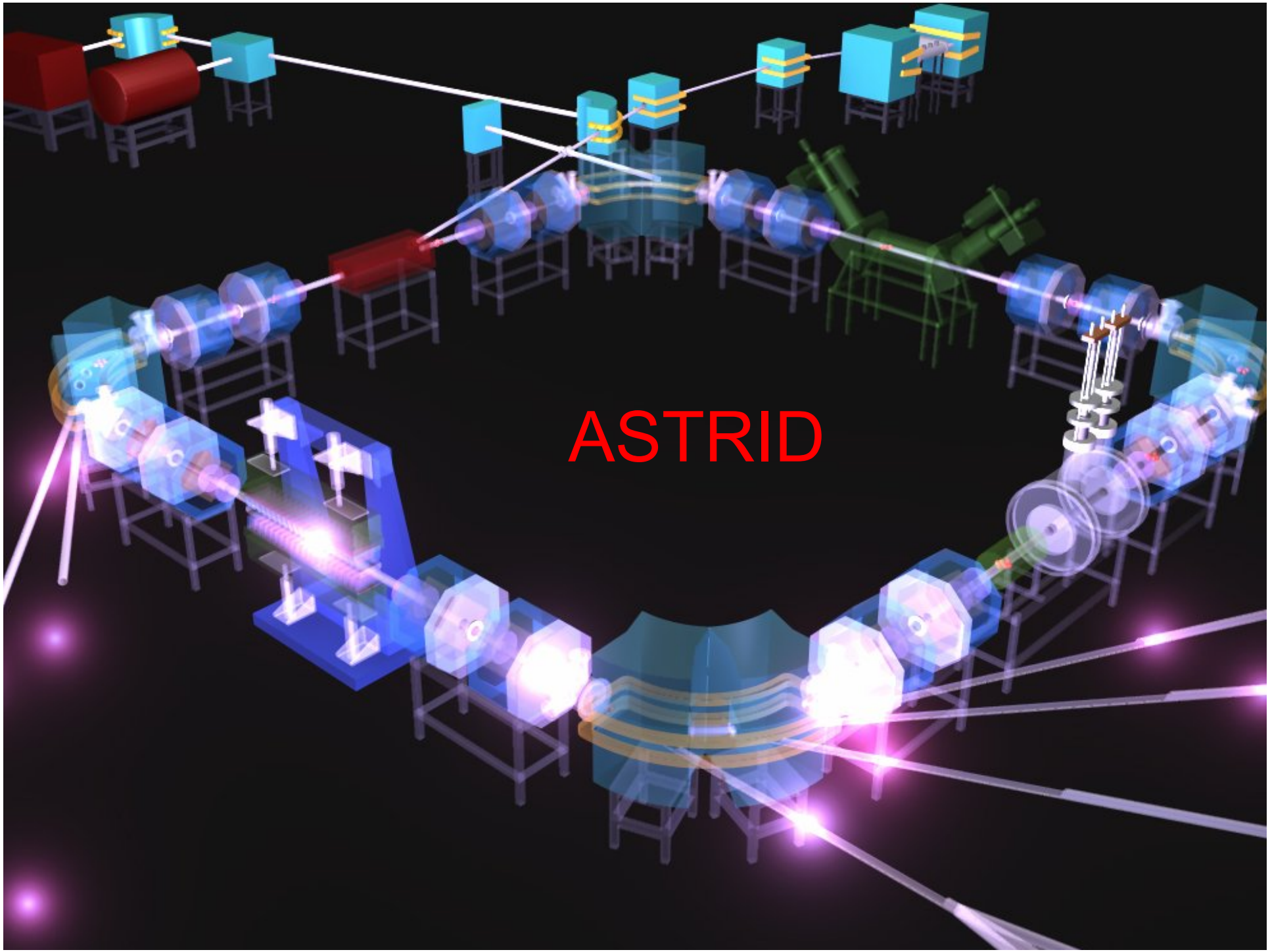
Cold electron experimental data

- We want to study collisions of electrons with gases and solids at energies between a few hundred meV and a few meV

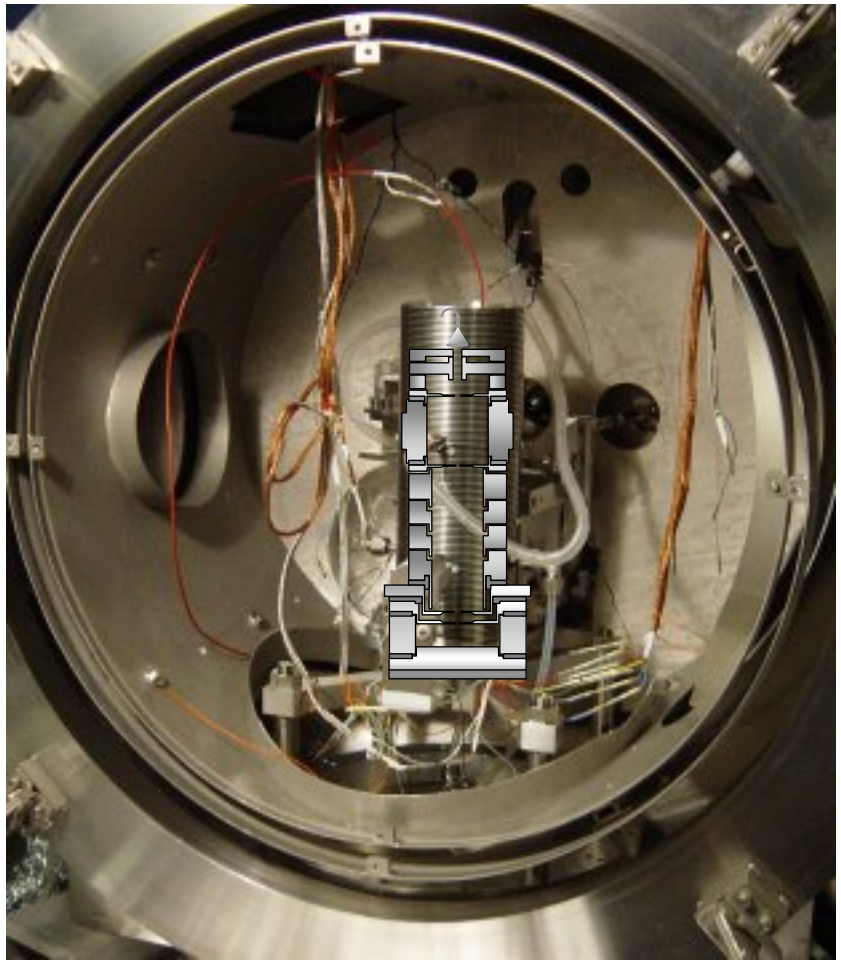
- We need to control electron beams down to these energies with a corresponding energy resolution of 1 meV (say)

- Electrons are formed by threshold photoionization of Argon at 15.75 eV using synchrotron radiation from the ASTRID storage ring at Aarhus University

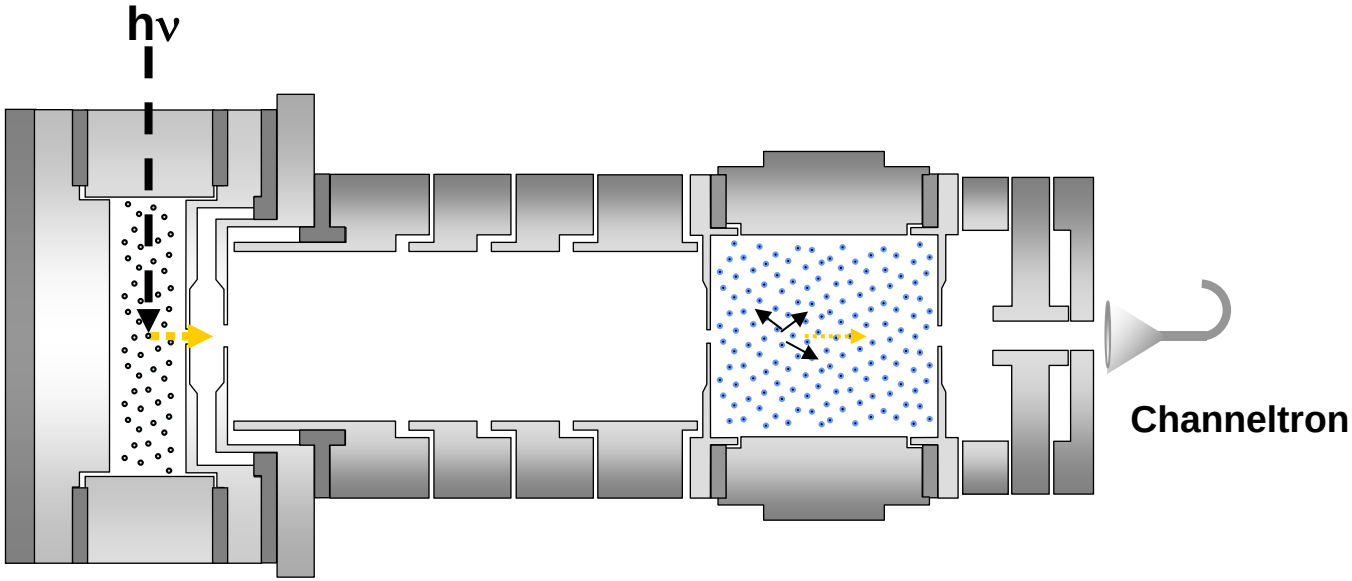
- Using this technique, the electron energy resolution = photon energy resolution and can be as good as ~0.7 meV FWHM


ASTRID

Gas Phase Electron-Molecule Scattering



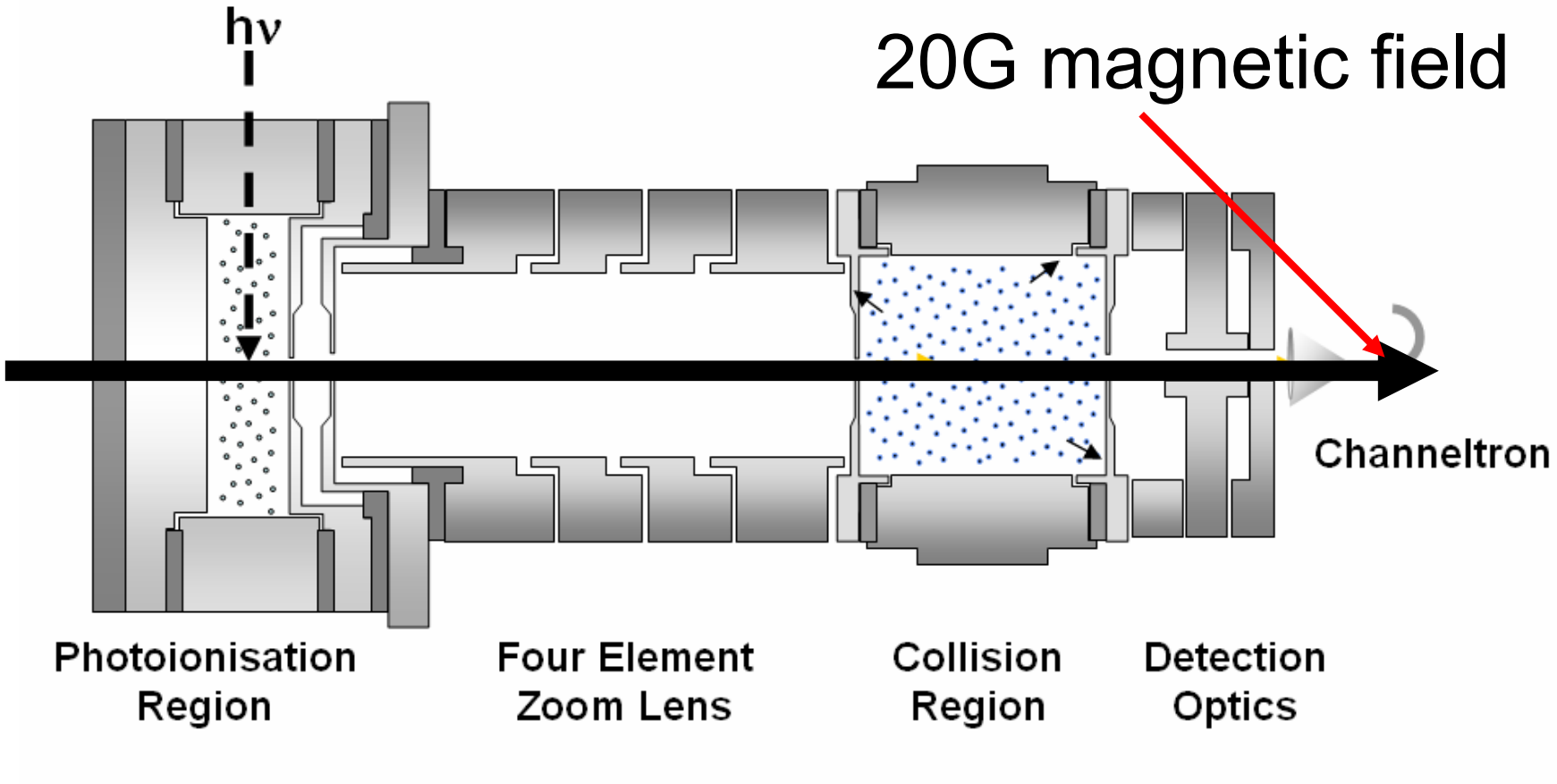
Gas Phase Electron-Molecule Scattering



$$I_t = I_o e^{-\sigma N \ell}$$

σ : the scattering cross-section

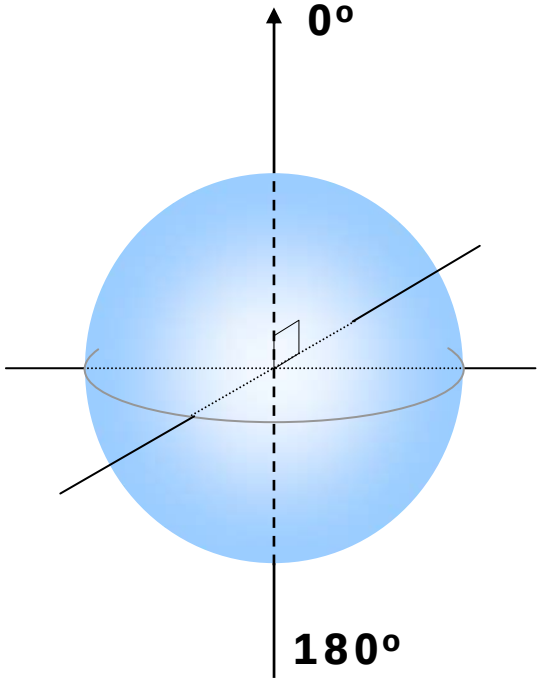
Apparatus with axial magnetic field



Cross-sections: without the magnetic field

- The experiment measures “total integral” cross-sections as a function of electron kinetic energy.

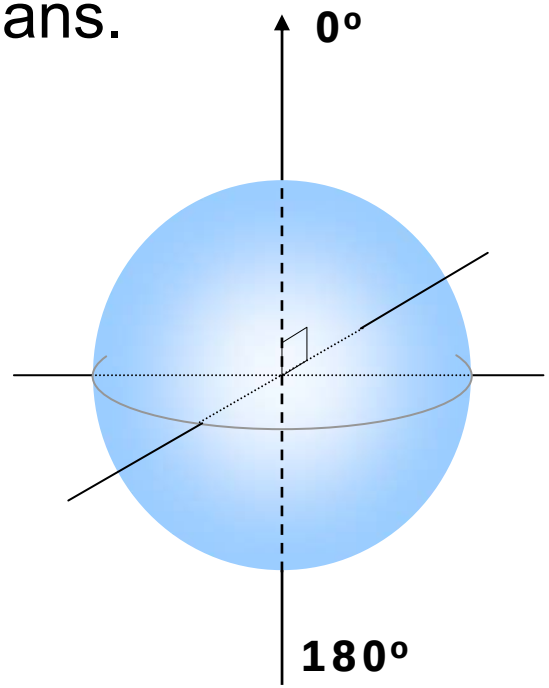
- "Total" refers to the measurement of all elastic and inelastic events and "integral" to integration over the full 4π steradians.



Cross-sections

The experiment measures “total integral” cross-sections as a function of electron kinetic energy.

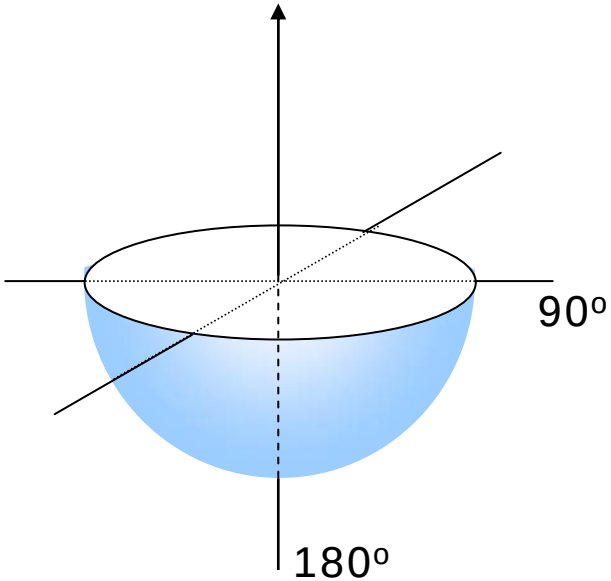
- "Total" refers to the measurement of all elastic, inelastic and reaction events and "integral" to integration over the full 4π steradians.



NB Since there is strong forward scattering for polar molecules, we underestimate the integral cross-section

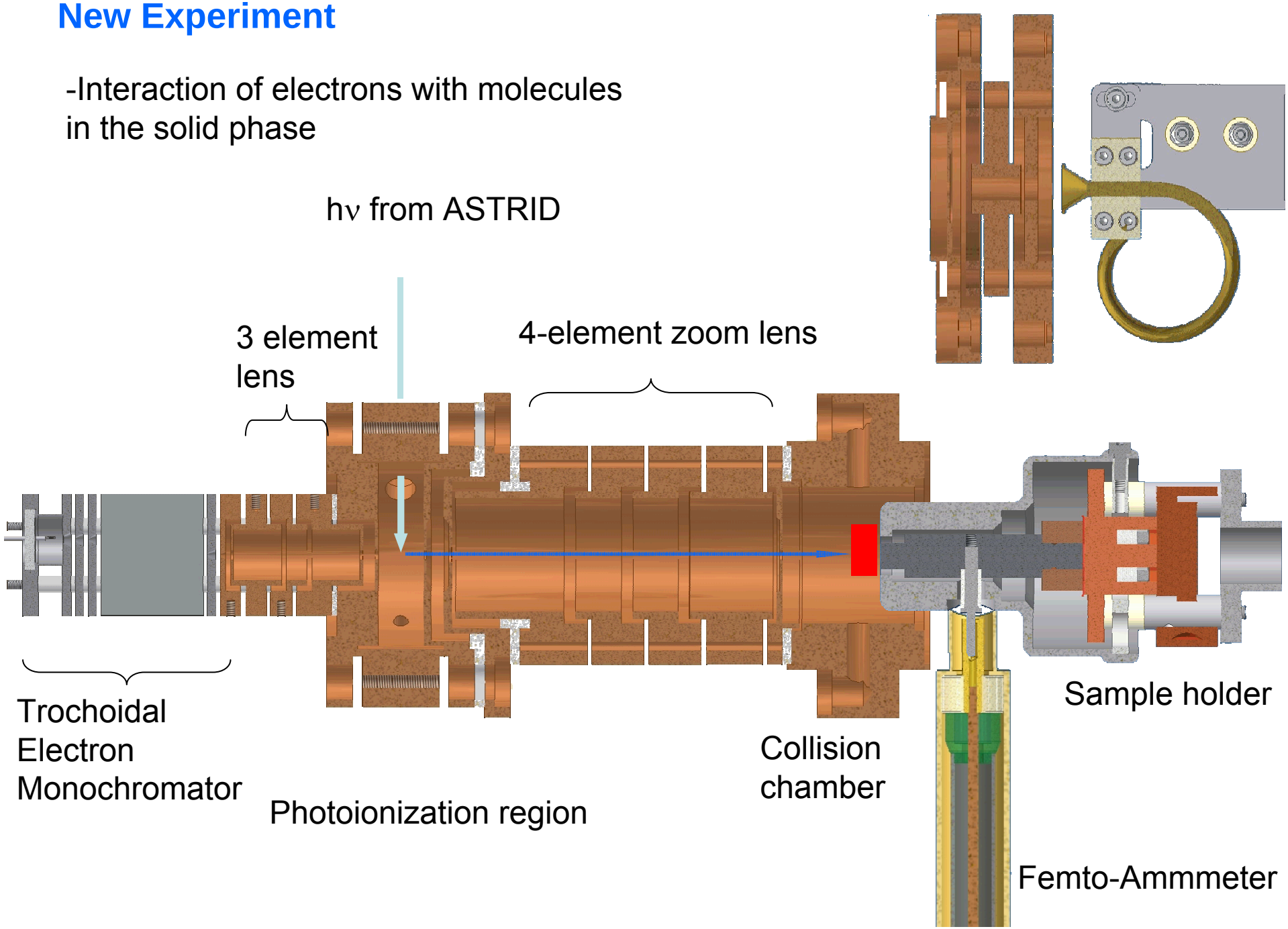
Cross-sections with a magnetic field

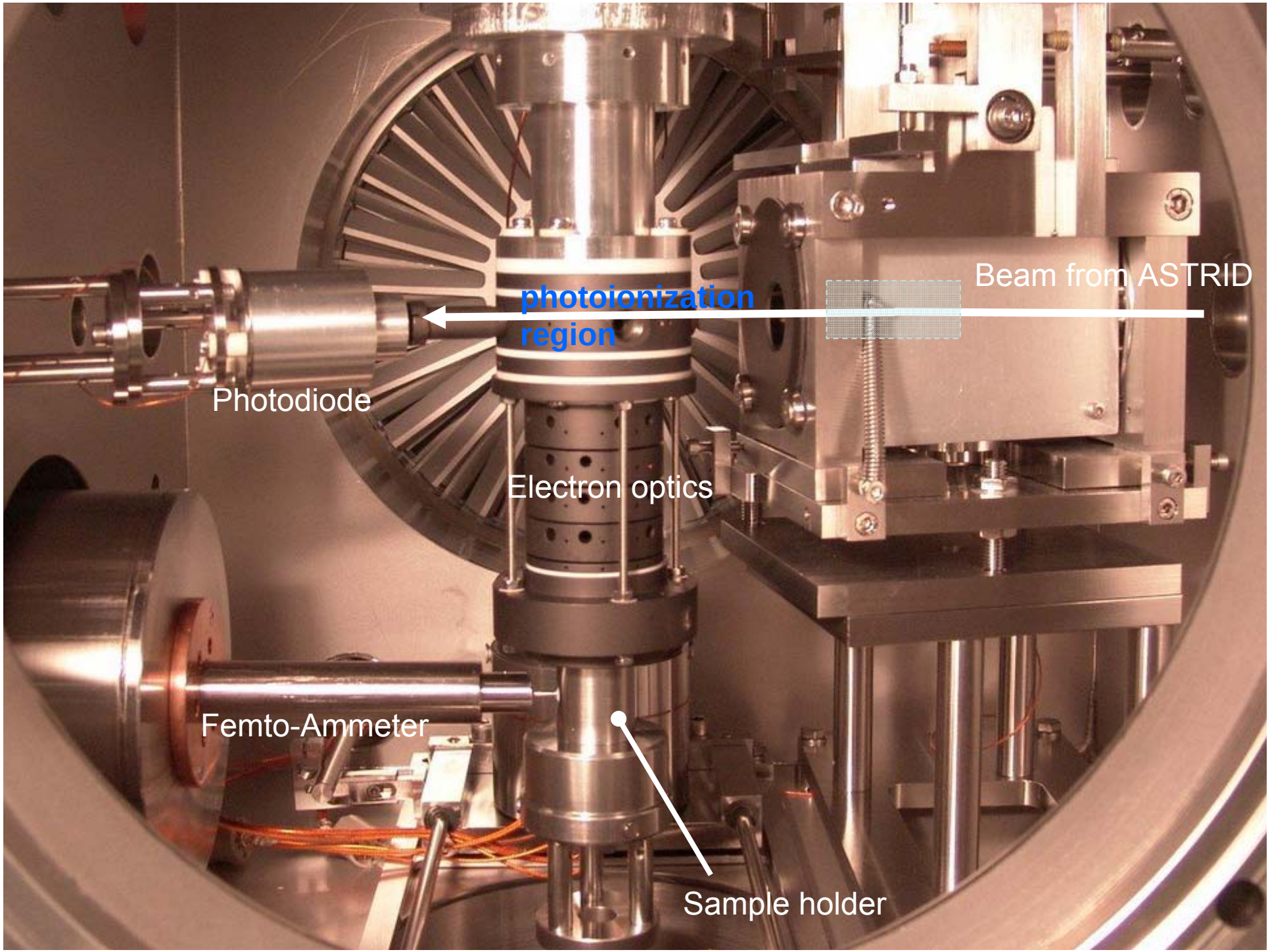
- In separate experiments, in the presence of an axial 20G magnetic field, the experiment measures the variation of the ***backward scattering*** cross-section as a function of electron kinetic energy, i.e. for scattering into the backward 2π steradians.



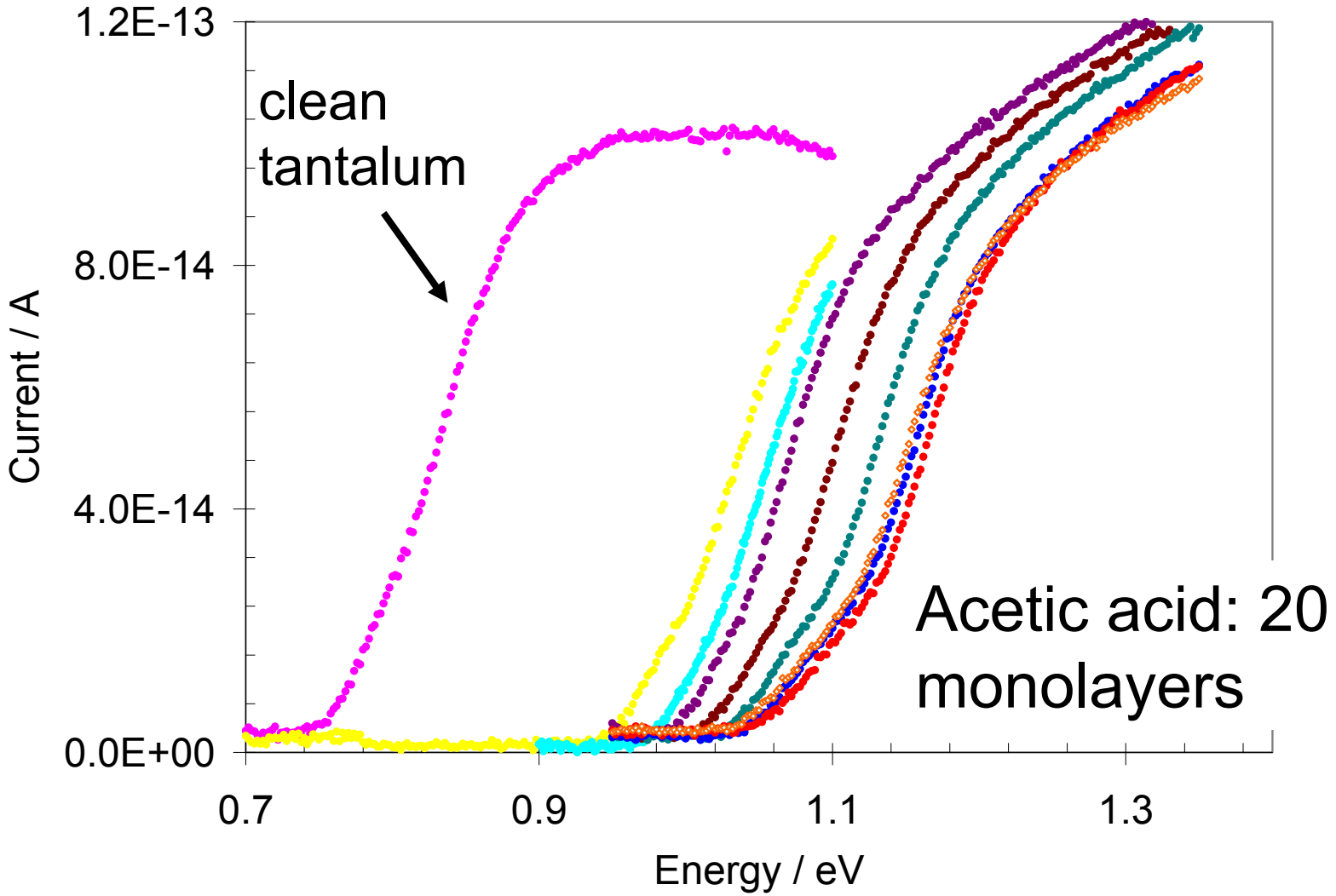
New Experiment

-Interaction of electrons with molecules in the solid phase




photoionization region
Beam from ASTRID
Photodiode
Electron optics
Femto-Ammeter
Sample holder

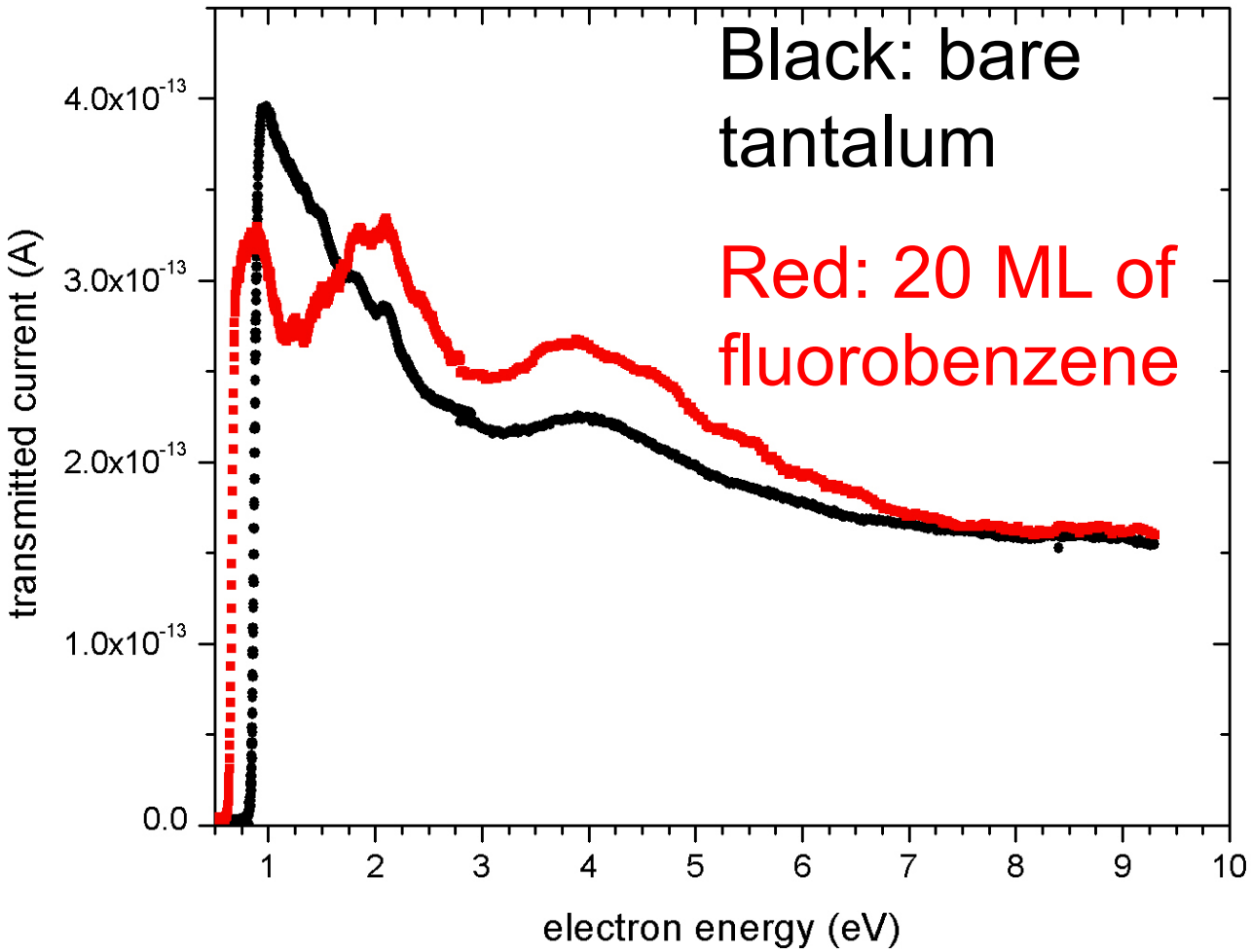
current of electrons with energies between zero and a few hundred meV interacting with solid acetic acid at 110K



electrons and solid acetic acid

- Highly efficient electron capture at the surface and/or within the acetic acid
- The first evidence that very low energy electrons may be highly reactive in solid material?
- An efficient route to chemical change with very low energy electrons?

electron transmission through solid fluorobenzene at 120K



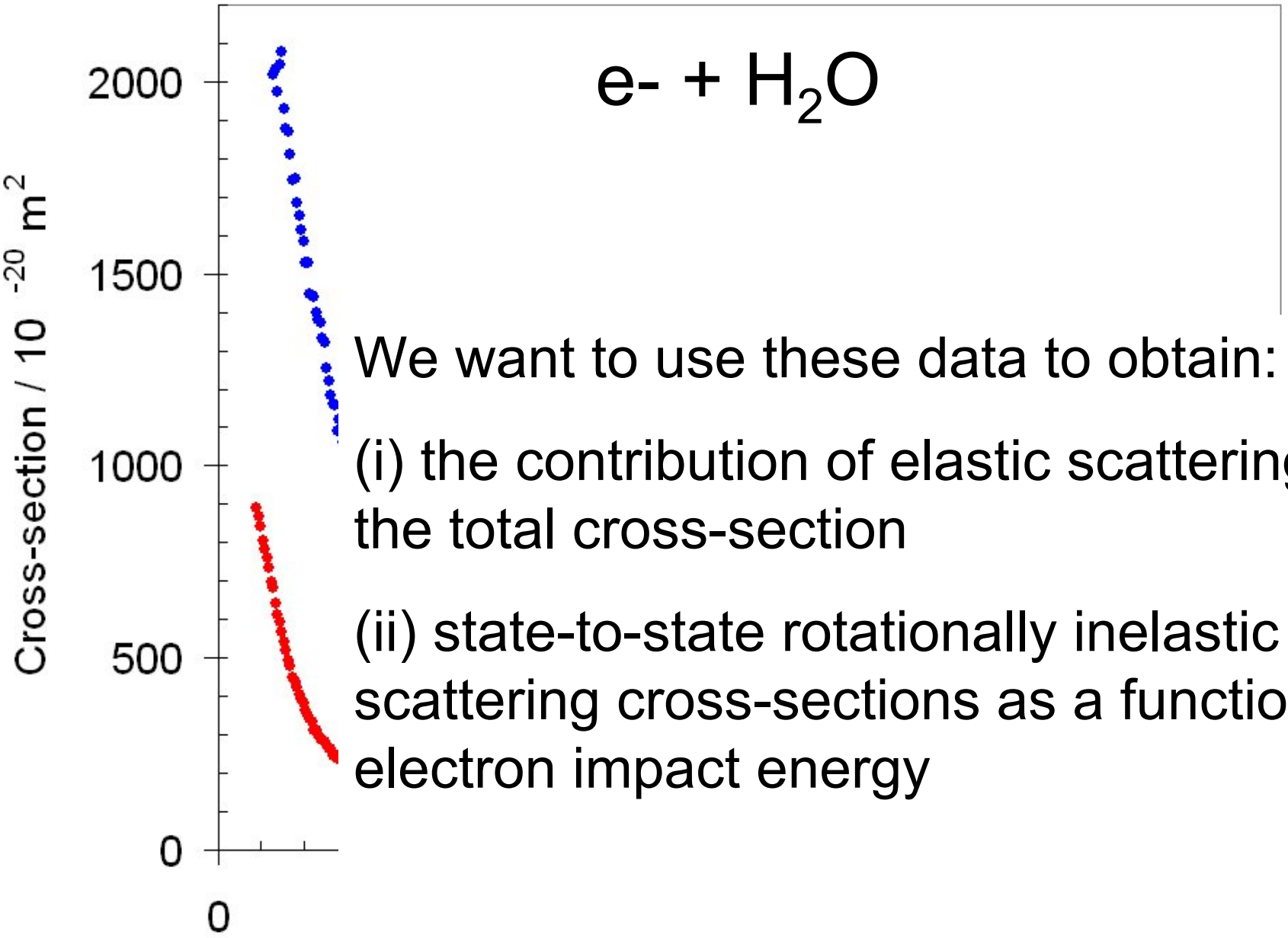
GAS PHASE EXPERIMENTS
elastic and rotationally inelastic scattering cross-sections

We measure the cross-section for all scattering events = elastic scattering + rotationally inelastic scattering

$e^- + H_2O\ (J''K_a''K_c'') \rightarrow e^- + H_2O\ (J''K_a''K_c'')$ (elastic)

and

$e^- + H_2O\ (J''K_a''K_c'') \rightarrow e^- + H_2O\ (J'K_a'K_c')$ (inelastic)



We want to use these data to obtain:

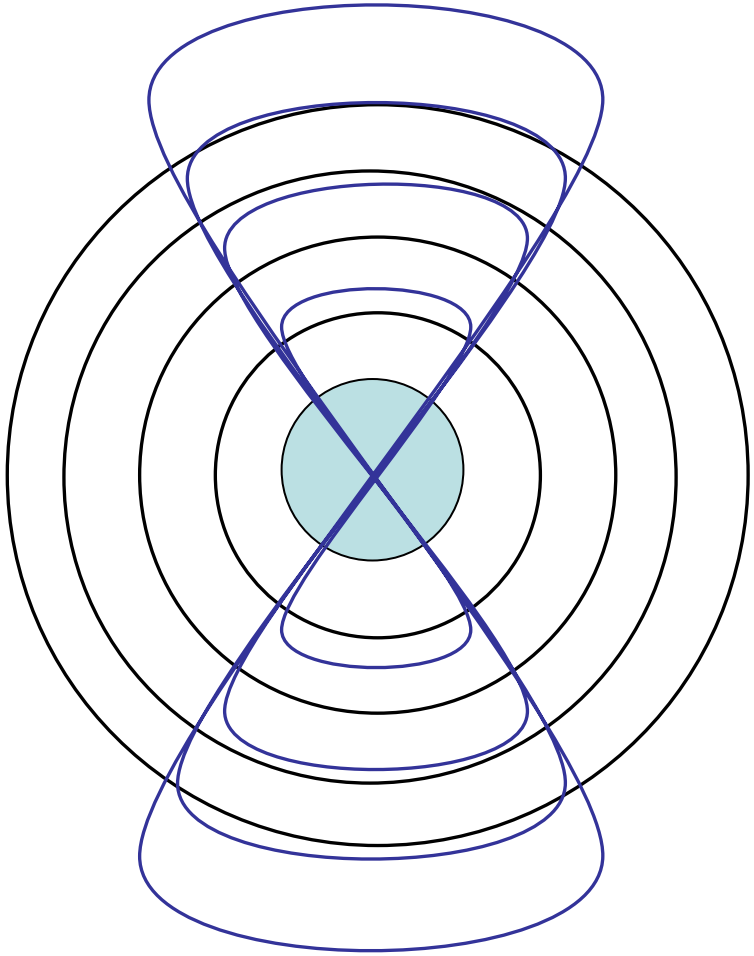
(i) the contribution of elastic scattering to the total cross-section

(ii) state-to-state rotationally inelastic scattering cross-sections as a function of electron impact energy

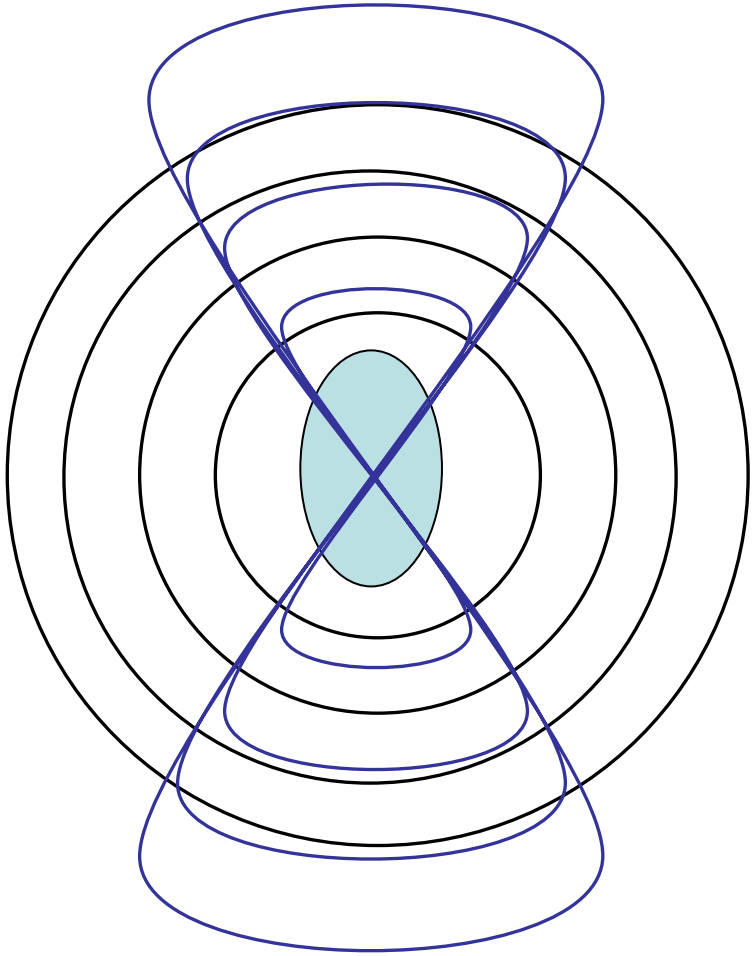
some theoretical concepts

- Partial waves and mixing of partial waves
- Phase shifts of partial waves induced by scattering
- Electron-molecule interaction potentials
- The critical dipole

Partial waves scattered by a spherical potential:
first s-waves (zero AM), then p-waves (1 unit of AM)

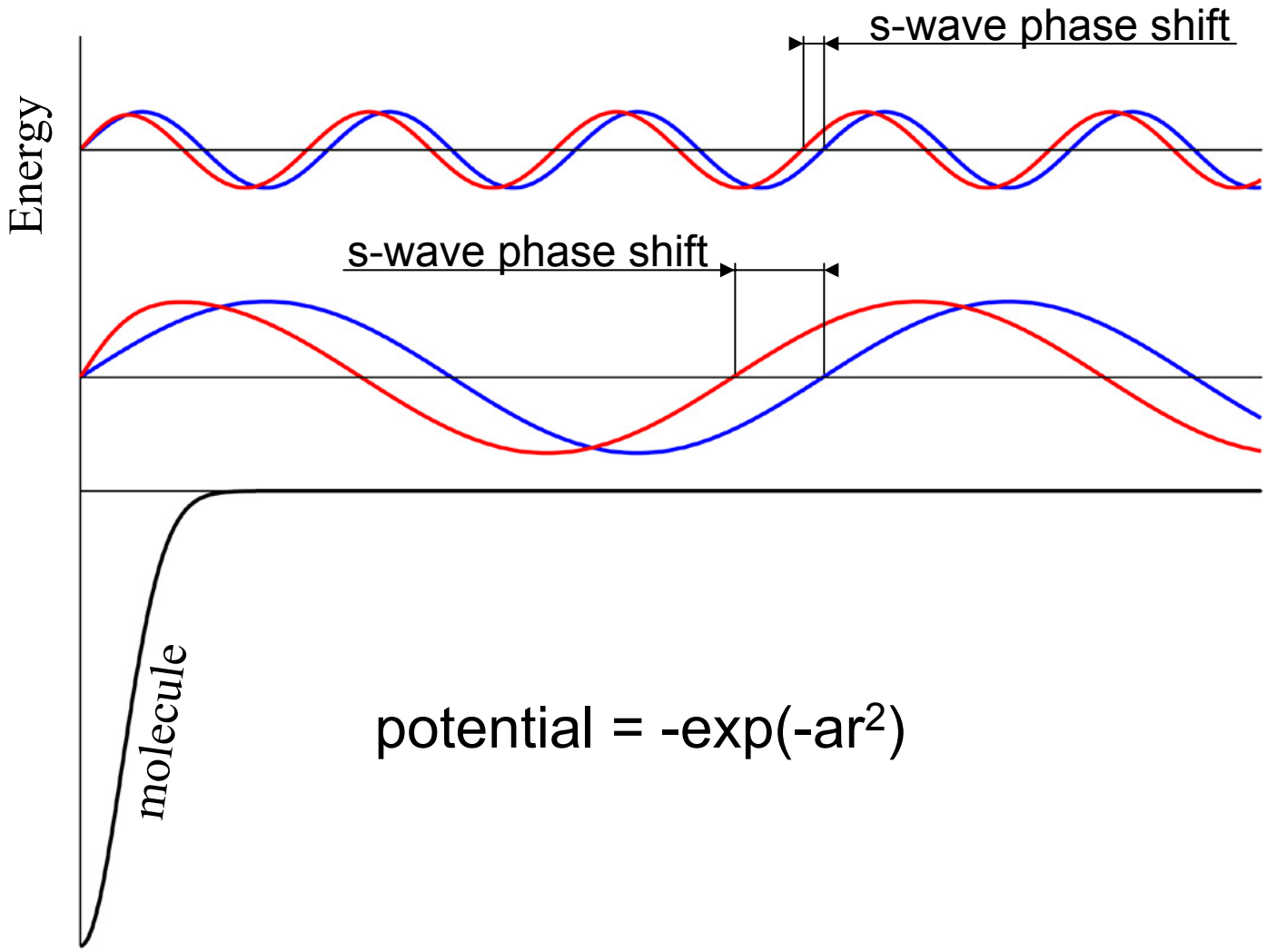


Partial waves scattered by a non-spherical potential: the s-wave is scattered as a superposition of s- and p-waves



molecules with permanent dipole moments mix s,p,d … waves

s-wave phase shifts



- in a short range potential at low electron energy (<100 meV or <1000K), very few partial waves are involved

- typically just s- with a bit of p-

- but when the target has a permanent dipole, you always get all partial waves involved, at all energies, because the potential is $-1/r^2$

“dipole harmonics”

- we start with plane waves composed of the standard superposition of spherical harmonics

- solve the scattering problem analytically in a $-1/r^2$ dipole potential and we generate “dipole harmonics”

- these are waves which are linear combinations of spherical harmonics (s-, p-, d- etc.)

- a superposition of these dipole harmonic waves now encounter the true molecular potential and the component dipole harmonics are scattered

electron collisions with dipolar molecules

- spherical harmonics are converted into dipole harmonics by the $-1/r^2$ potential
- $L^2|\ell m\rangle = \ell(\ell+1)|\ell m\rangle$, the standard case, whose solutions are spherical harmonics, becomes
- $L^2+D\cos\theta|\lambda m\rangle = \lambda(\lambda+1)|\lambda m\rangle$, whose solutions are “dipole harmonics”
- the dipole potential couples all angular momenta together, so λ contains all ℓ.

Dipole Harmonics

Eigenfunctions of the operator $L^2 + D \cos\theta$

dipole harmonics are weighted linear combinations of spherical harmonics.

the weighting depends on the dipole moment of the target molecule

D=0.729 a.u. =1.853D for H_2O

σ-,π-, δ-…dipole harmonic waves

obtaining cross-sections for rotational state-to-state transitions in H_2O: fitting parameters

- at energies of 30-40 meV, only the σ- wave needs to be included: there is one parameter to vary, the phase shift of the σ- wave – and two values of cross-section, integral and backward
- >40 meV, there are two parameters, one for the σ- wave and one for the π-wave, and two sets of data
- important message: at 250 meV energy, fitting begins to need δ- dipole harmonics

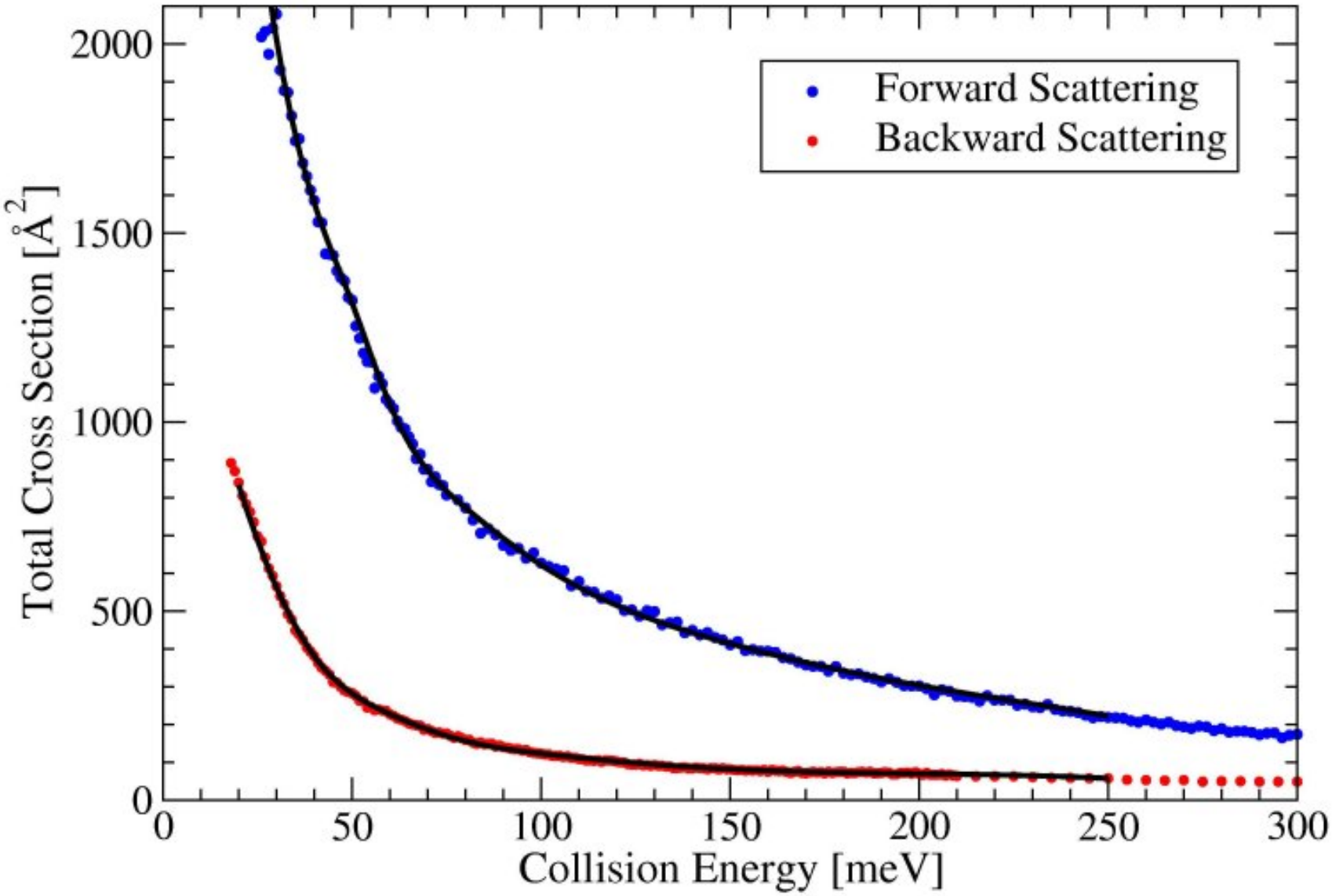
fitting to the experimental data

- the target gas is at room temperature: >98% of the target populations are in rotational states up to J=8

- include all possible inelastic and elastic processes

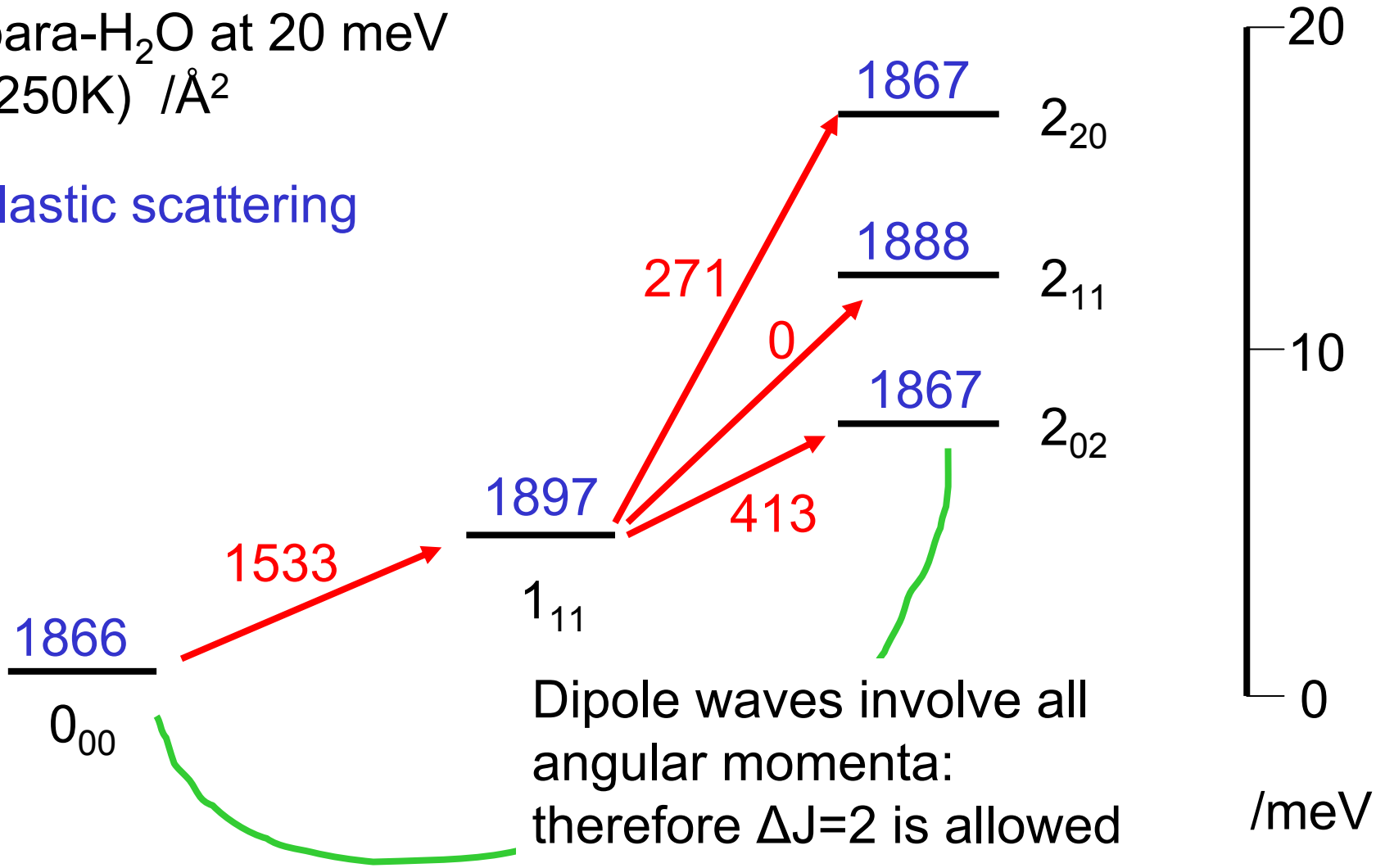
- attempt to reproduce the experimental data by varying the σ- and π-phase shifts and summing over all processes weighted by the respective target populations

Inelastic scattering data for H_2O



cross-sections for
rotational excitation of
para-H_2O at 20 meV
(250K) /Å^2

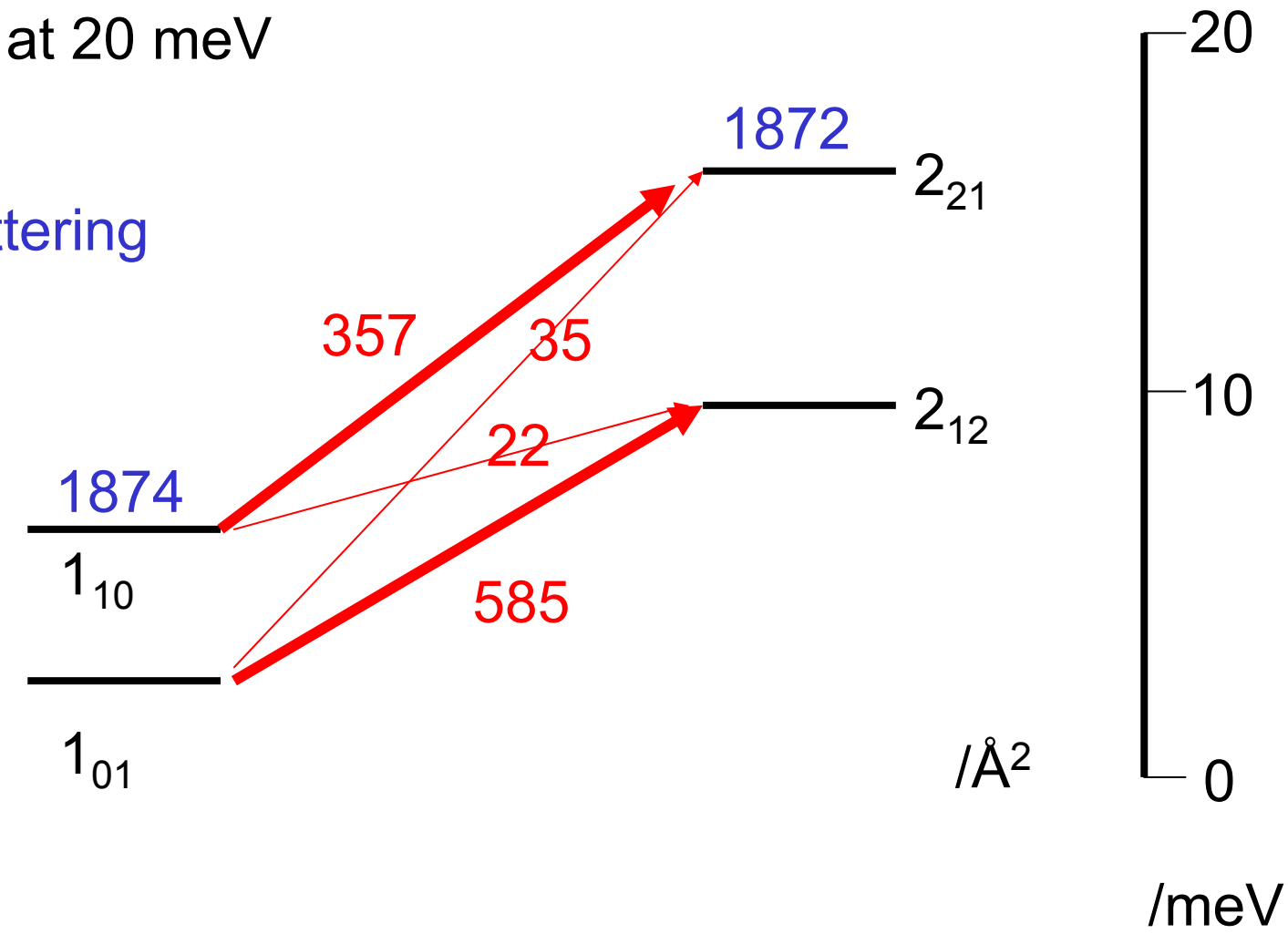
Elastic scattering



Dipole waves involve all
angular momenta:
therefore ΔJ=2 is allowed

cross-sections for
rotational excitation of
ortho-H_2O at 20 meV
(250K)

elastic scattering



The critical dipole

- If the dipole moment of the target is too large, something horrible happens to the electron waves very close to the molecule
- in theory, the waves begin to oscillate with infinite amplitude and frequency as range tends to zero
- the dipole moment for which this occurs is called the “critical dipole”
- of course the potential is not $1/r^2$ all the way to r=0 – but it is a very good approximation at long range

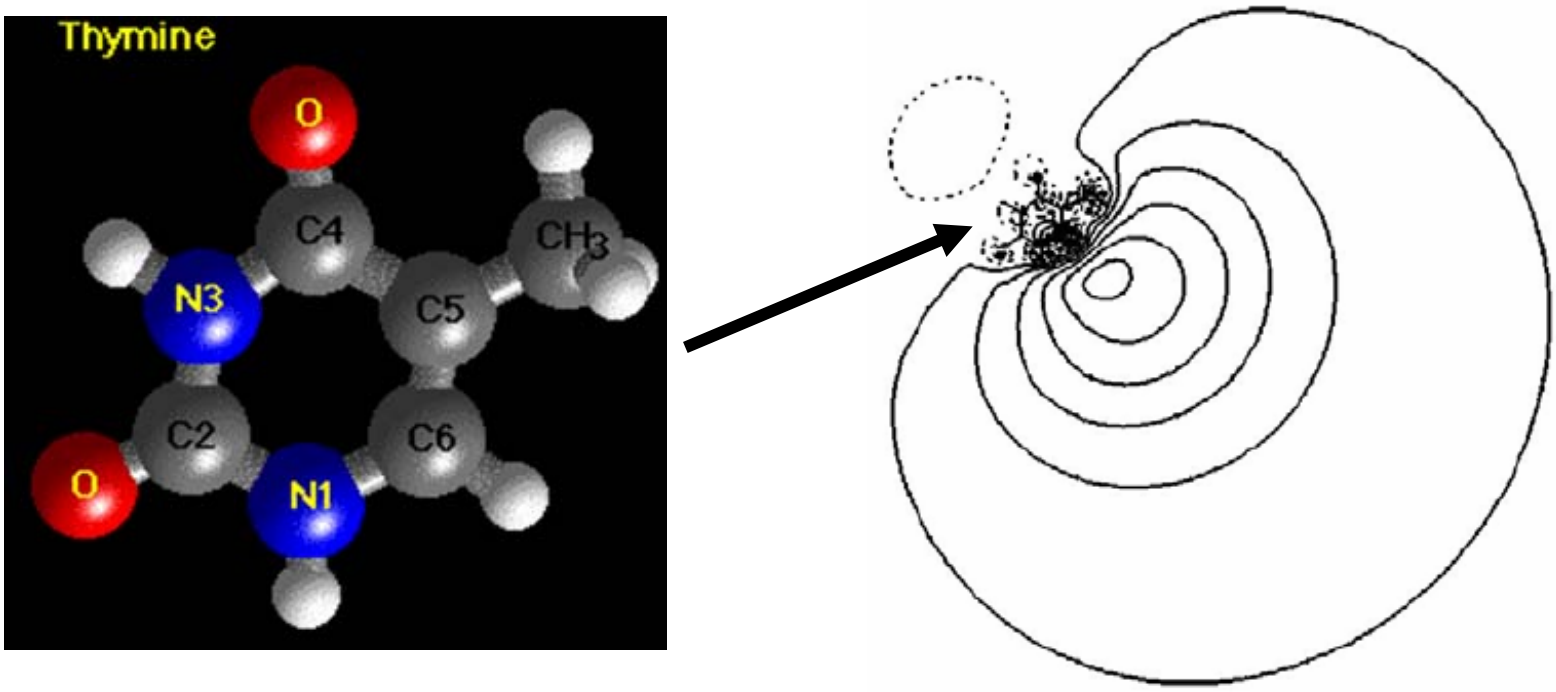
The critical dipole

- it is often stated that the electron is “captured” if the dipole moment is > 1.625D
- this statement is misleading on two counts
- first, the electron is in the continuum, and can only be captured by the molecule if electron kinetic energy is given up to internal nuclear motion

The critical dipole

- Second, it is a very incomplete statement to say that the critical dipole is 1.625D
- This point is important for the interpretation of electron scattering data by biomolecules (including dissociative attachment)
- Biomolecules tend to have large dipole moments of several Debyes

The dipole bound state in thymine (Burrow et al. JCP *to appear – Innsbruck and Nebraska)*



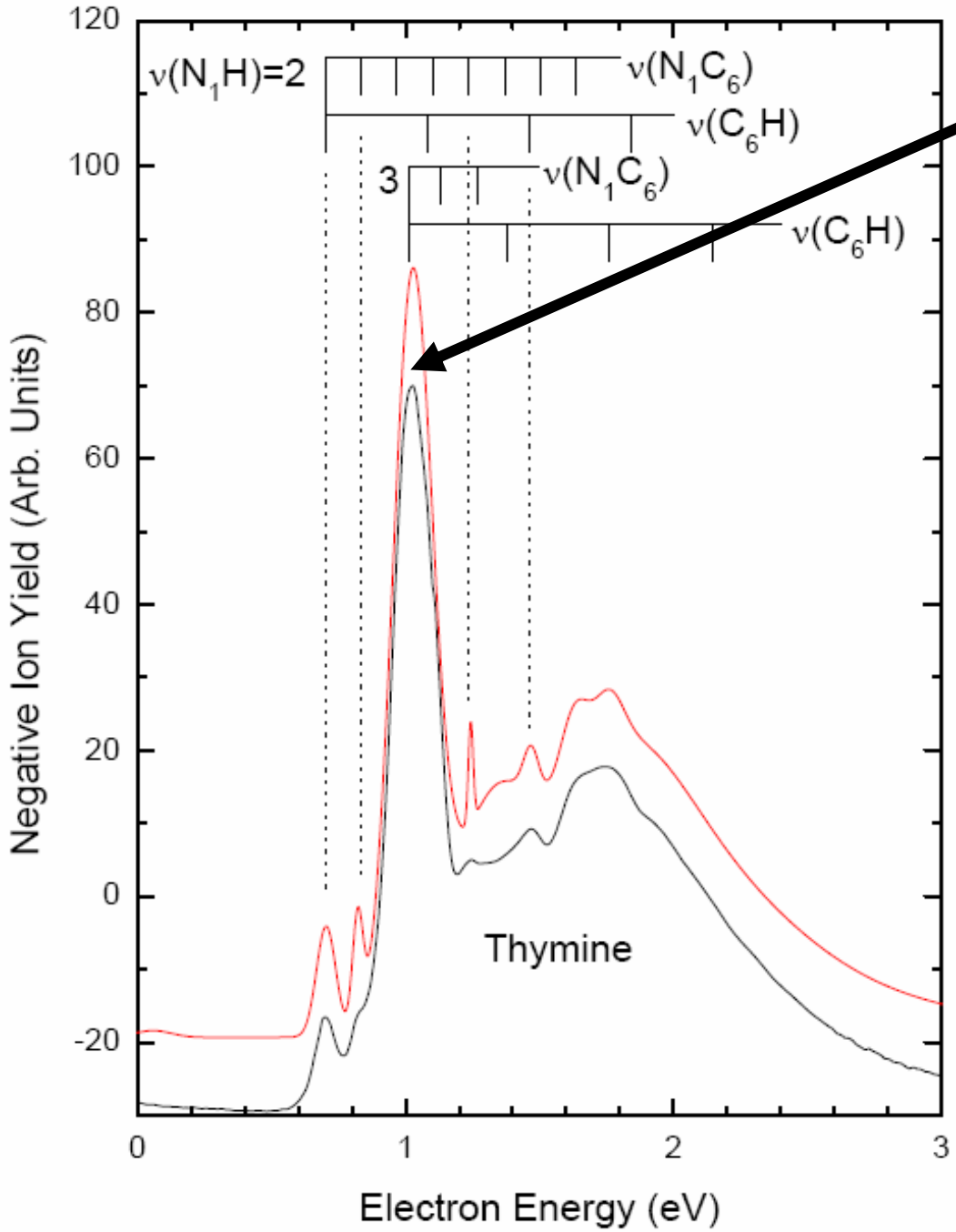
Thymine dipole moment ~4.6D

The critical dipole

- we know from H_2O that the interaction at energies >250 meV requires σ-,π-, δ- dipole harmonic waves

- in a more polarizable molecule such as thymine, higher dipole harmonics will be necessary (even at 250 meV)

- if we look at the 1eV resonance for dissociative attachment in thymine:



Dipole bound state?

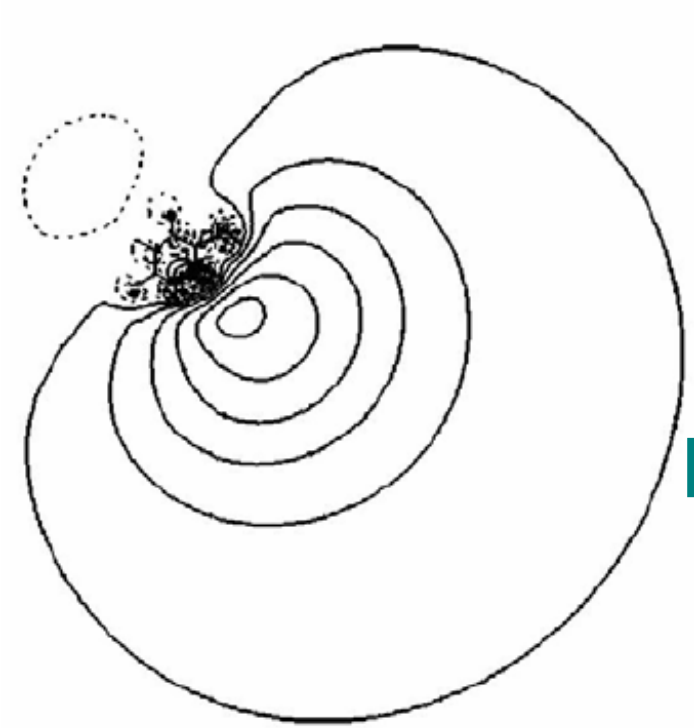
thymine dissociative attachment (Burrow et al. JCP *to appear*)

thymine dissociative attachment at 1eV: dipole bound state?

- at an energy of 1eV, several dipole harmonic waves are necessary to describe the scattering
- the critical dipole to bind an electron σ-wave is 1.625D
- the critical dipole to bind an electron $\pi_{x,y}$- wave is 9.683D
- the critical dipole to bind an electron π_z- wave is 19.195D

The critical dipole

- only the σ-wave can bind to thymine, with a dipole moment of ~4.6D



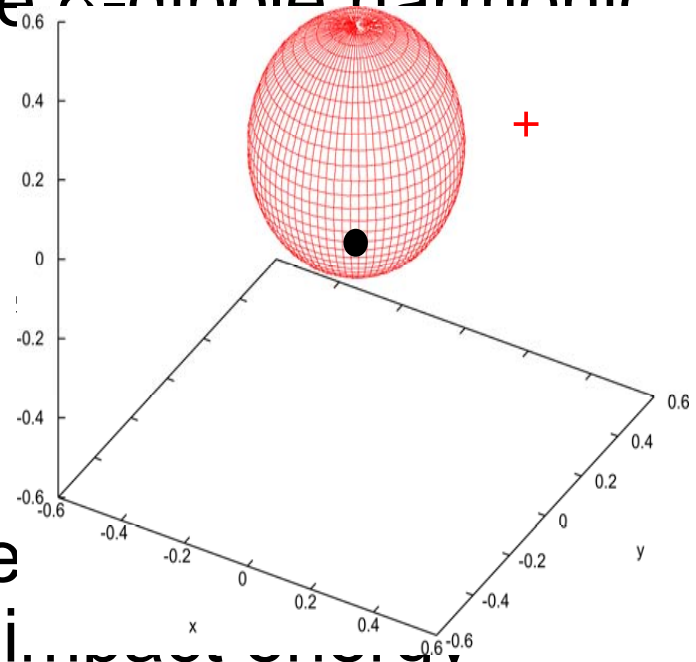
σ-wave

ther like the σ-dipole harmonic

-wave is 1

ution is like

proportion of the total at 1eV i…pact energy

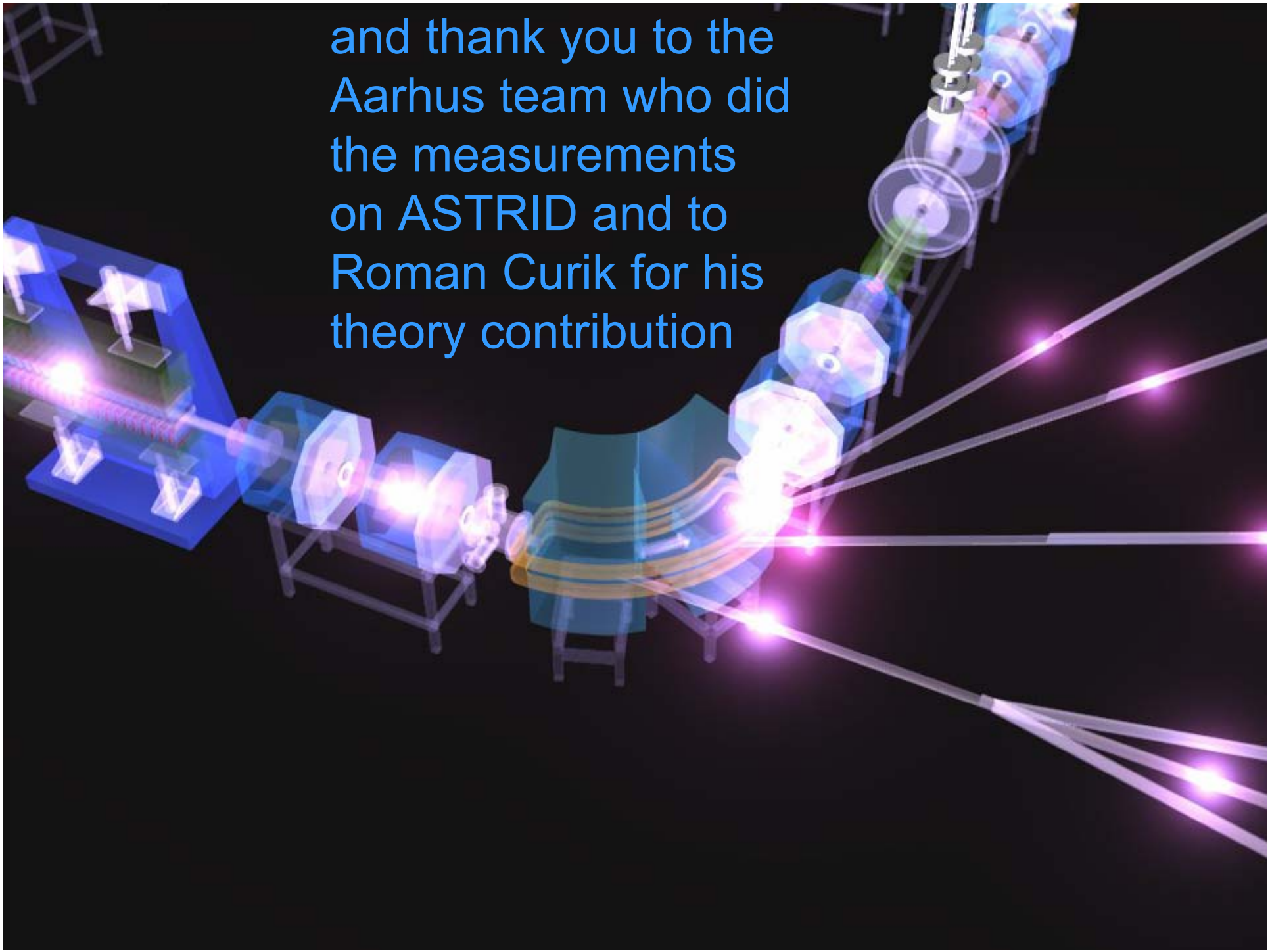


The critical dipole

- pause for thought before invoking dipole bound states as a significant mechanism in electron scattering at higher energies

- dipole bound states will certainly form very readily at “zero” energy (below a few tens of meV) for molecules with >1.625D

- at “zero” energy scattering is dominated by the σ-wave


and thank you to the
Aarhus team who did
the measurements
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Roman Curik for his
theory contribution