Low energy electron scattering from halogenated hydrocarbons

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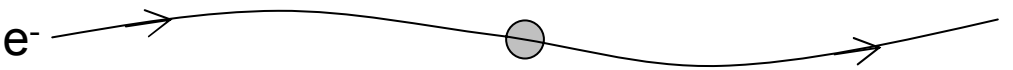
Plan of Talk

1. Introduction
   - Low energy electron-molecule collisions
   - Motivation
   - Some examples of data
2. How to study low energy electron-molecule collisions
   - Experimental requirements
   - Description of the experiment on the SGM2 undulator beamline at ASTRID
3. Results for several halogenated hydrocarbons
   - CCl_4, CF_4, CH_3Cl, CH_3Br, CH_3I, CF_3I, $CHCl_3$…

Low-Energy Electron-Molecule Collisions

- Define 'low energy'
  - Typically the lowest energy reached is 5-10 meV
- The de Broglie wavelength of a 10 meV electron is 12.2 nm
  - Compare this to molecule sizes which are typically a few tenths of nm



- Cold collisions occur at these low energies, where the wavelength of the electron is long compared to the size of the target
- You can no longer think of the interactions with molecules in a classical sense, instead we have to think in terms of waves with a specific angular momentum ℓ

Cross-Sections

- On interacting with a target, a partial wave will undergo a phase shift with the total cross-section for scattering $\sigma_{Integral}$ given by:

$$\sigma_{Integral} = \frac{4\pi}{k^2} \sum_{\ell} (2\ell + 1) \sin^2 \eta_\ell$$

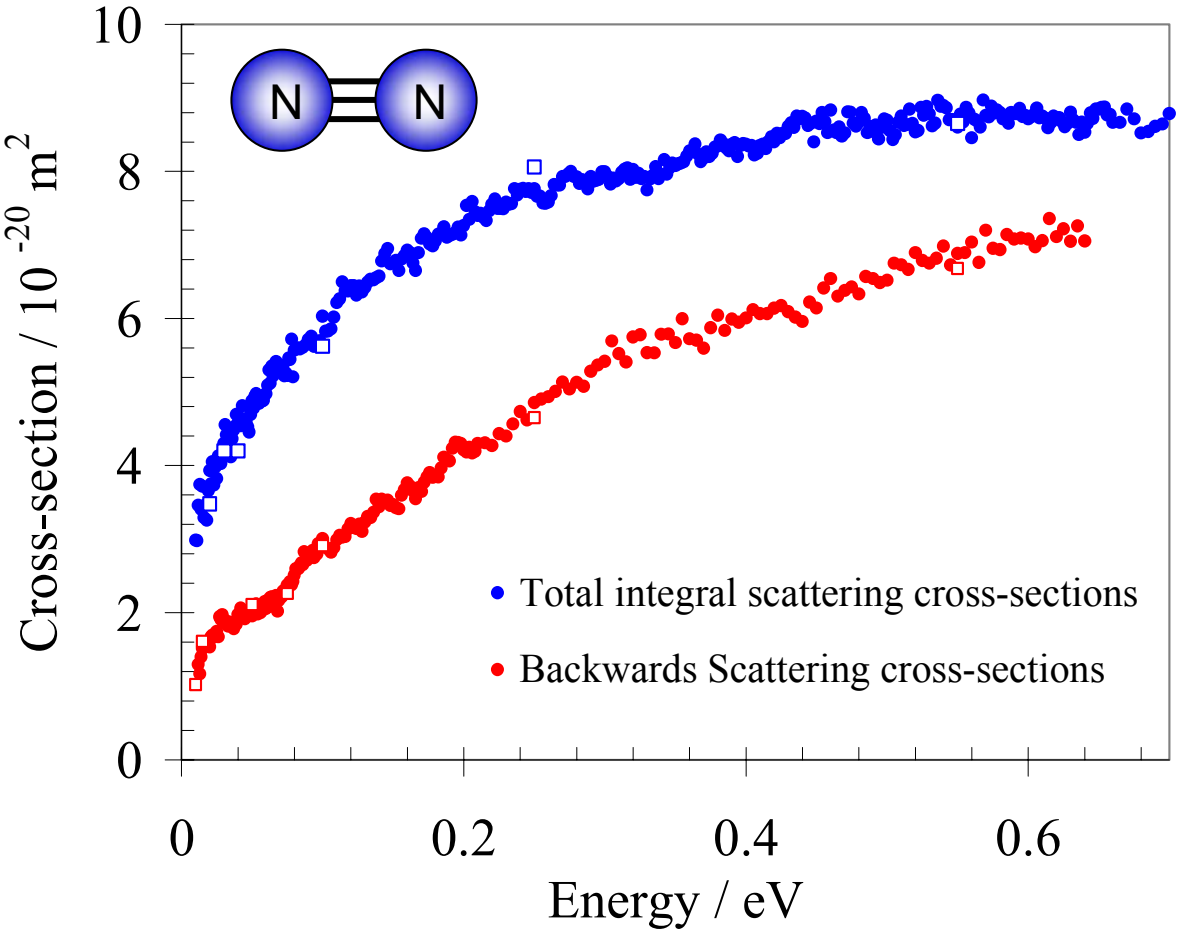
k is the wave vector k = √(2E)

- η_ℓ is the phase shift, which is a measure of the distortion of the incoming wave by the target
- s-wave (ℓ = 0) head on collision
- All knowledge of the nature of the scattering is contained in the phase shifts.

(Atomic units : ħ=e=m=1)

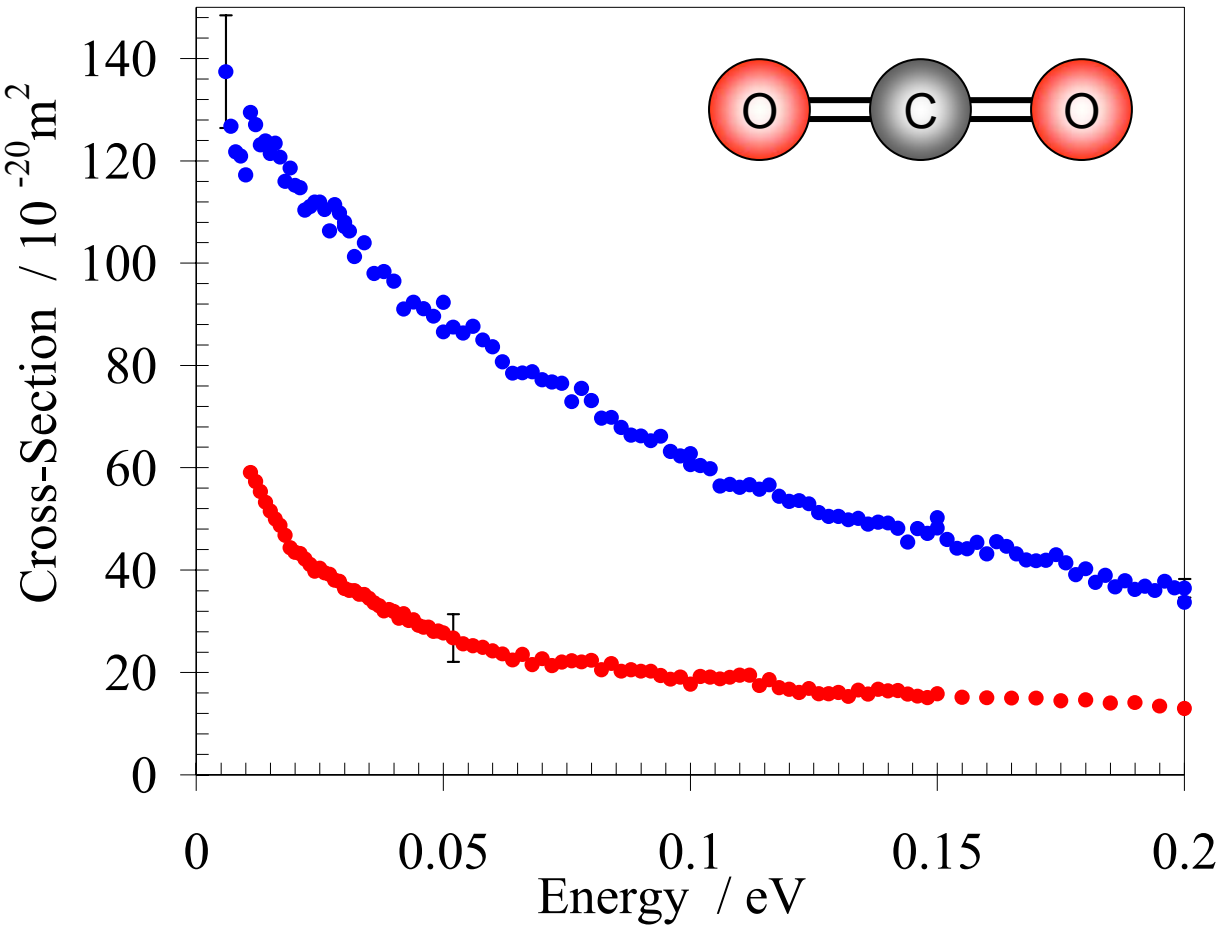
Examples of Data

- Electron scattering spectrum of nitrogen



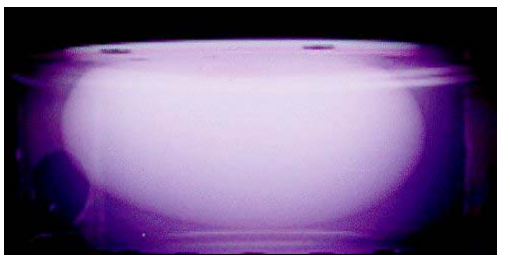
Examples of Data

- Carbon Dioxide Ref: Phys. Rev. A, 64, 022708 (2001)



Motivation – Why study cold collisions?

- Give physical insight into quantum-dominated collisions
- Collisions between electrons and molecules play a key role in the chemistry and physics of plasmas.
  - Cross-sections for electron-molecule collisions are important for modelling the chemistry of industrial plasmas.



- Low energy electrons are very efficient in causing molecules to become rotationally and vibrationally excited.
- There is a widespread occurrence in nature e.g. in the upper atmosphere and the interstellar medium.

How to Study Electron-Molecule Collisions

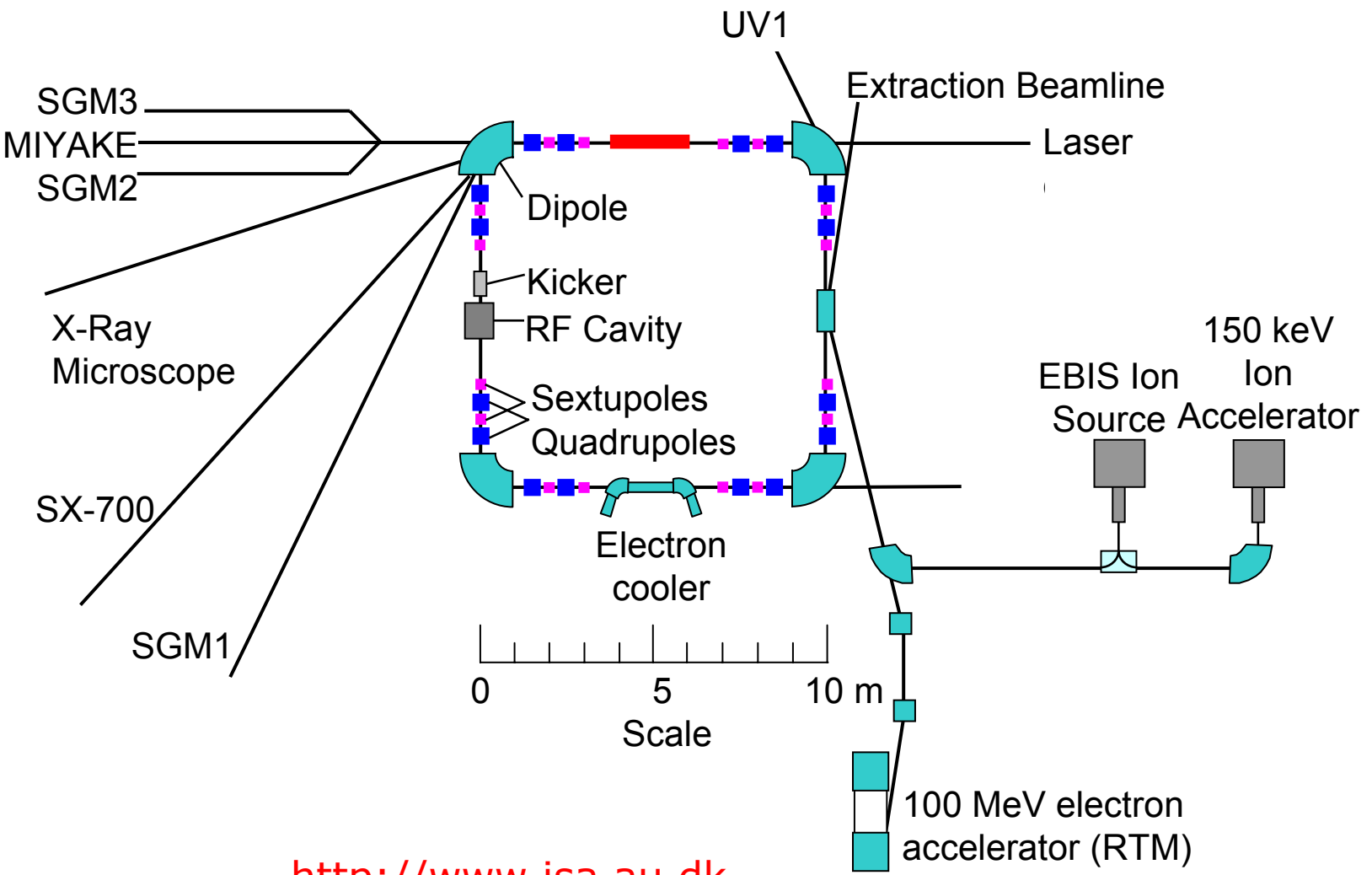
- Experimental requirements
  - We want to obtain high resolution data in the energy range of a few meV to a few eV.
- In order to do this we require:
  - A beam of electrons with tuneable kinetic energy between a few meV and several electron volts, with as high as possible energy resolution (a few meV or better).

Experiment Outline

- Synchrotron radiation from the ASTRID storage ring is used to photoionise Argon
- Photoelectrons are formed 2 or 3 meV above the ionisation threshold at 78.67 nm
- The resulting photoelectrons are formed into a beam and used in scattering experiments
- The energy resolution of electrons = energy resolution of photons

[Ref: Hoffmann et al. Rev. Sci. Instrum. (2002) 73, 4157]

Aarhus STorage Ring In Denmark



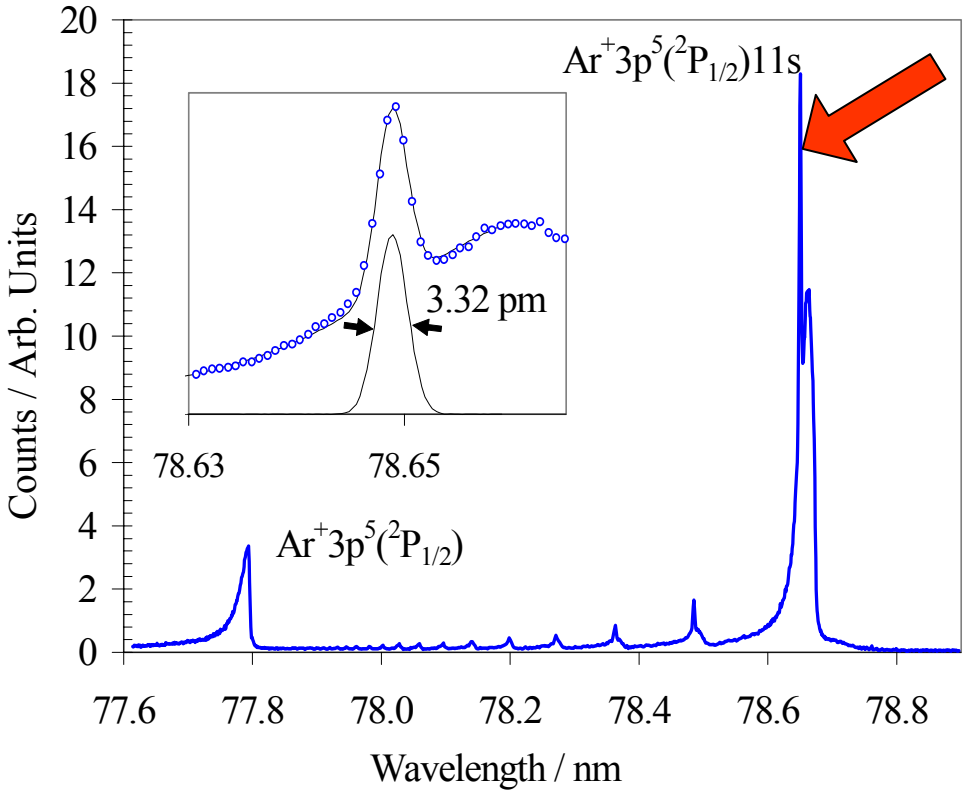
http://www.isa.au.dk

Aarhus STorage Ring In Denmark

View From Corner 2

http://www.isa.au.dk

Photoionisation of Argon

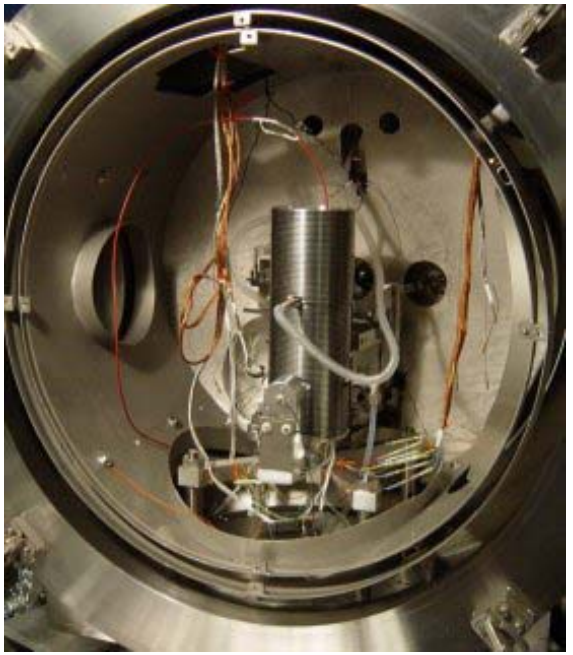


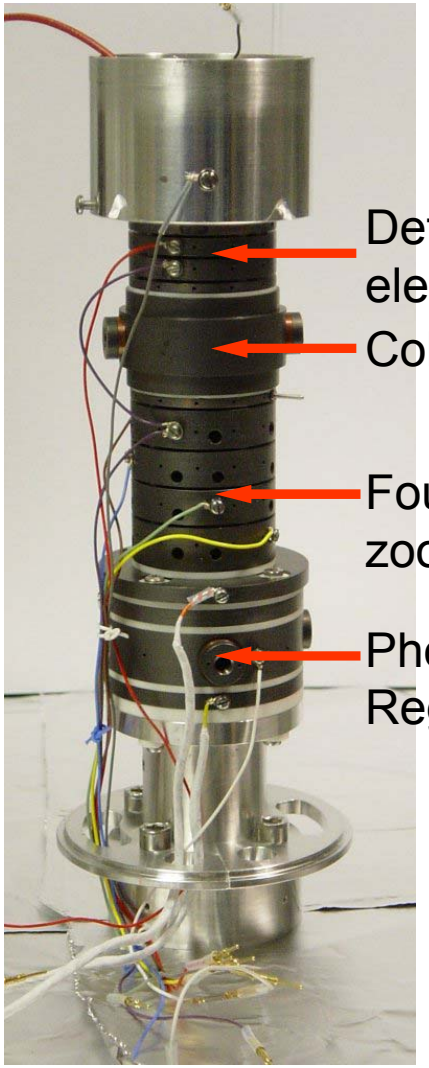
Entrance and Exit Slit Widths /μm	Resolution of photoelectrons (FWHM) / meV
10	0.67
20	0.9
30	1.3
40	1.6

[Ref: Hoffmann et al. Rev. Sci. Instrum. (2002) 73, 4157]

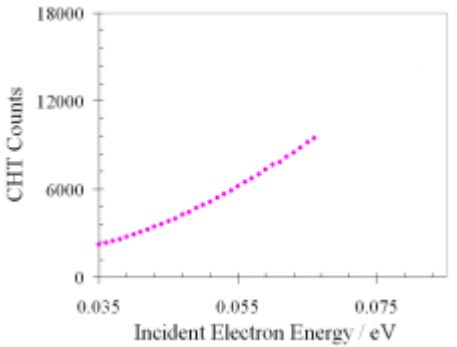
Electron Scattering Apparatus

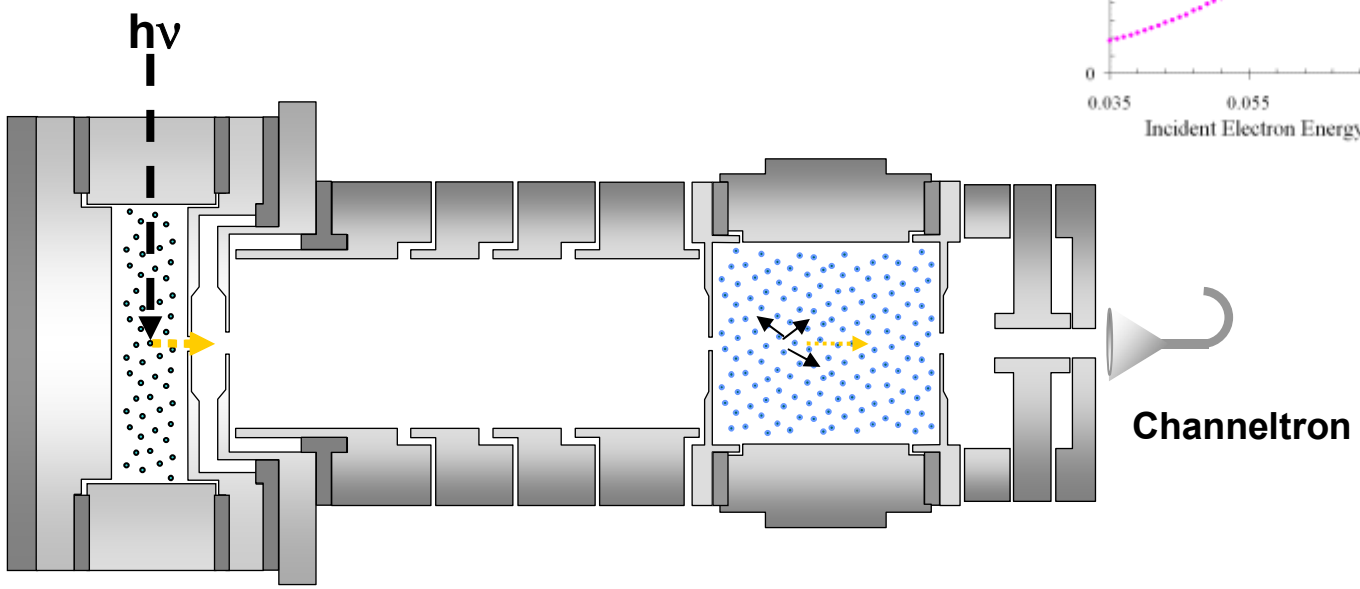
- The photoelectrons produced have to be controlled and focused into a beam in order to be used for scattering investigations.
- Optional 20 G axial field





Electron optics for transmission experiment





Transmission Experiment

- The beam of electrons produced are passed through a cell containing the target gas at room temperature. The cross-section (σ) can then be determined using the Beer-Lambert Law:

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

where I_t = transmitted current, I_o = incident current,

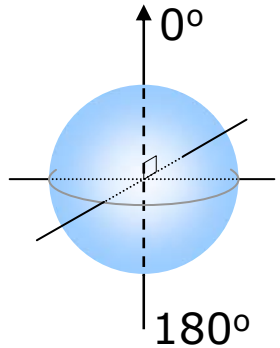
N = Number density

ℓ = path length of electrons through the target gas

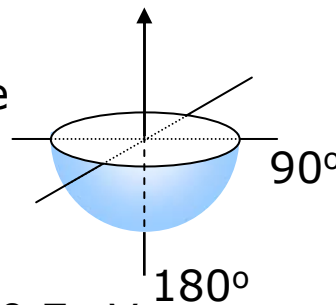
Transmission Experiment

- There are two modes in which this experiment is run

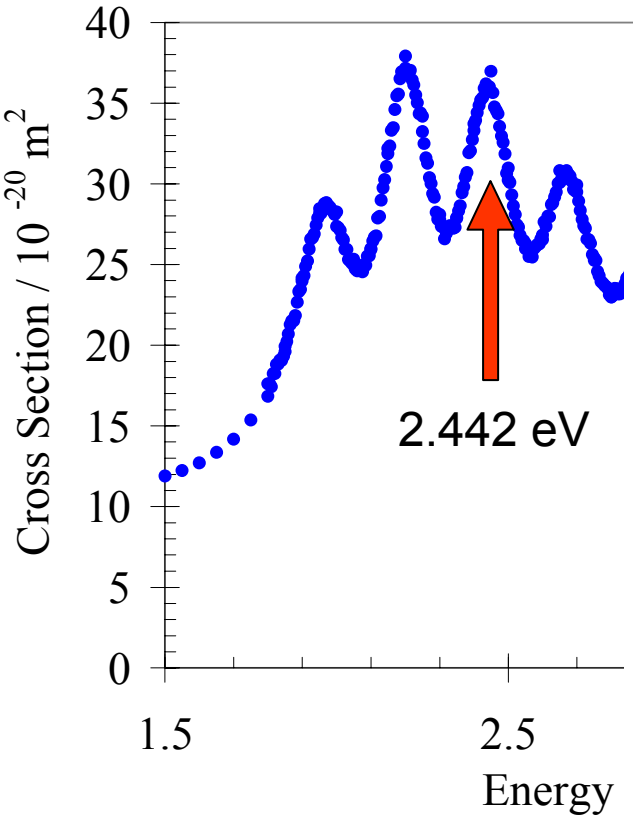
  - Without a magnetic field
    - Measures total integral cross-sections as a function of electron kinetic energy.
    - "Total" refers to the measurement of all elastic and inelastic events and "integral" to integration over the full 4π steradians.
    - Data are taken over the range of a few meV up to 10 eV

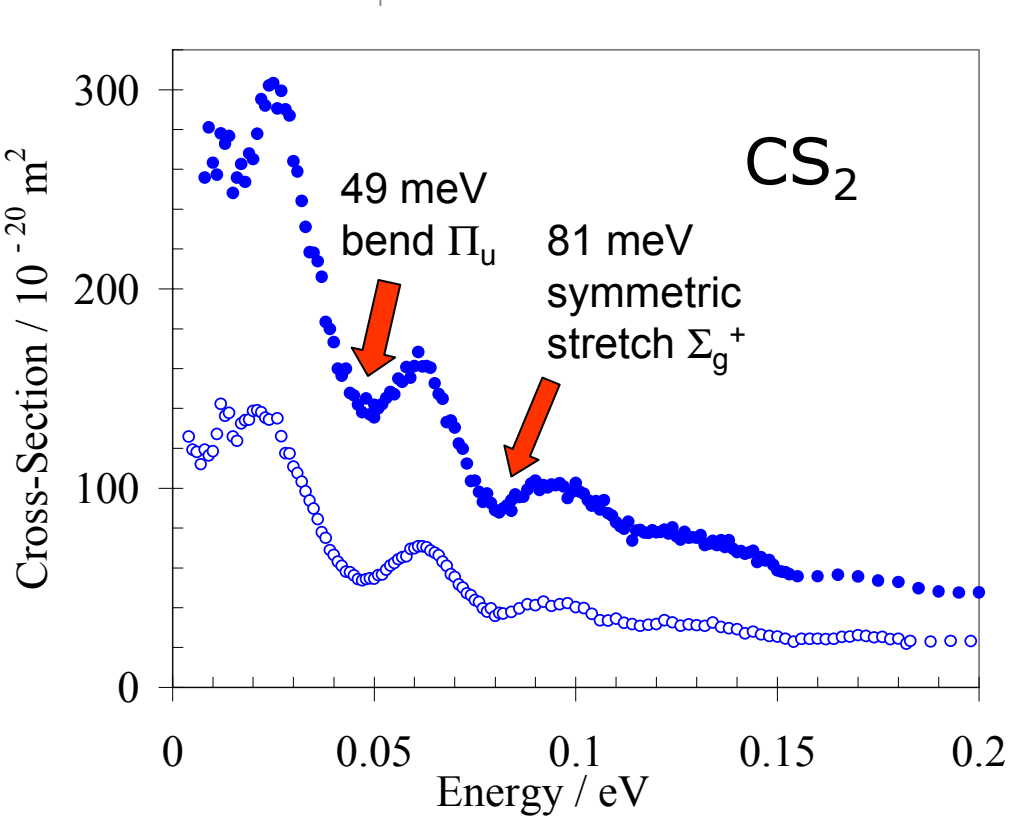


  - With a 20 G axial magnetic field
    - All electrons scattered into the forward hemisphere are detected by the channeltron
    - Electrons scattered into the backward hemisphere are lost to the system and not detected
    - Data are taken over the range of a few meV up to 0.7 eV



Calibration of electron beam energy





CS_2 ref: Phys. Rev. Lett. 89 (9), 093201 (2002)

Electron-Molecule Collisions

- What can happen when an electron collides with a molecule?
  - Elastic scattering $AB + e^-_E \rightarrow AB + e^-_E$
  - Inelastic scattering $AB + e^-_E \rightarrow AB + e^-_{E-\Delta E}$
    Which includes the processes of rotational, vibrational (and electronic) excitation
  - Attachment $AB + e^-_E \rightarrow AB^{*-}$
    e.g. SF_6
  - Dissociative attachment $AB + e^-_E \rightarrow A^- + B$
    e.g. CCl_4

A Selection of Molecules Investigated

- Elastic scattering
  - CF_4
- Rotational excitation + elastic scattering
  - CH_3Cl, $CHCl_3$, CH_3Br
- Rotational excitation, attachment + elastic scattering
  - CH_3I, CF_3I, SF_5CF_3
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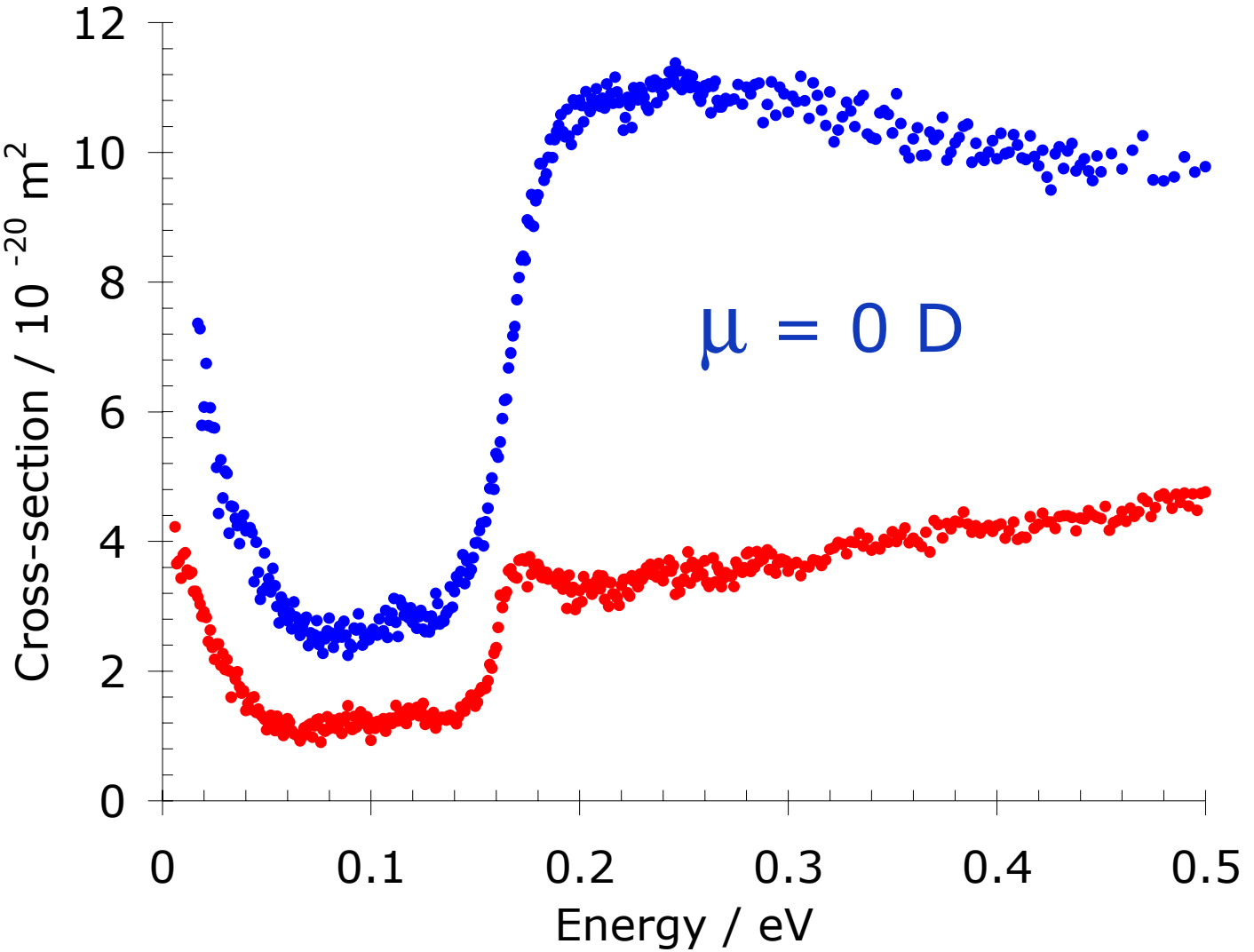
Vibrationally inelastic scattering is also observed, but cross-sections tend to be only a few $Å^2$

Carbon tetrafluoride – CF_4



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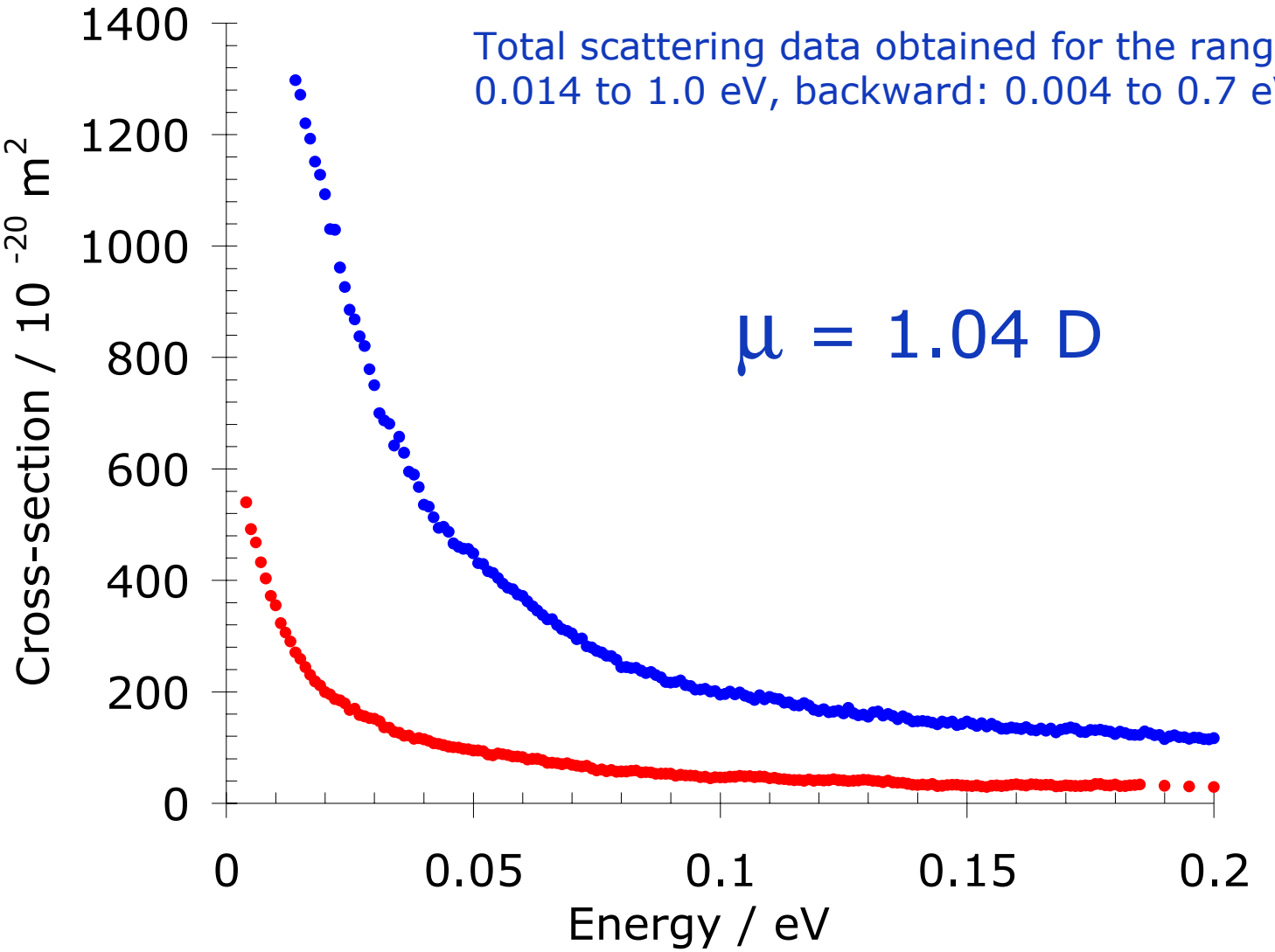
Rotational Inelastic Scattering

- For molecules which have a permanent dipole moment rotational excitation occurs

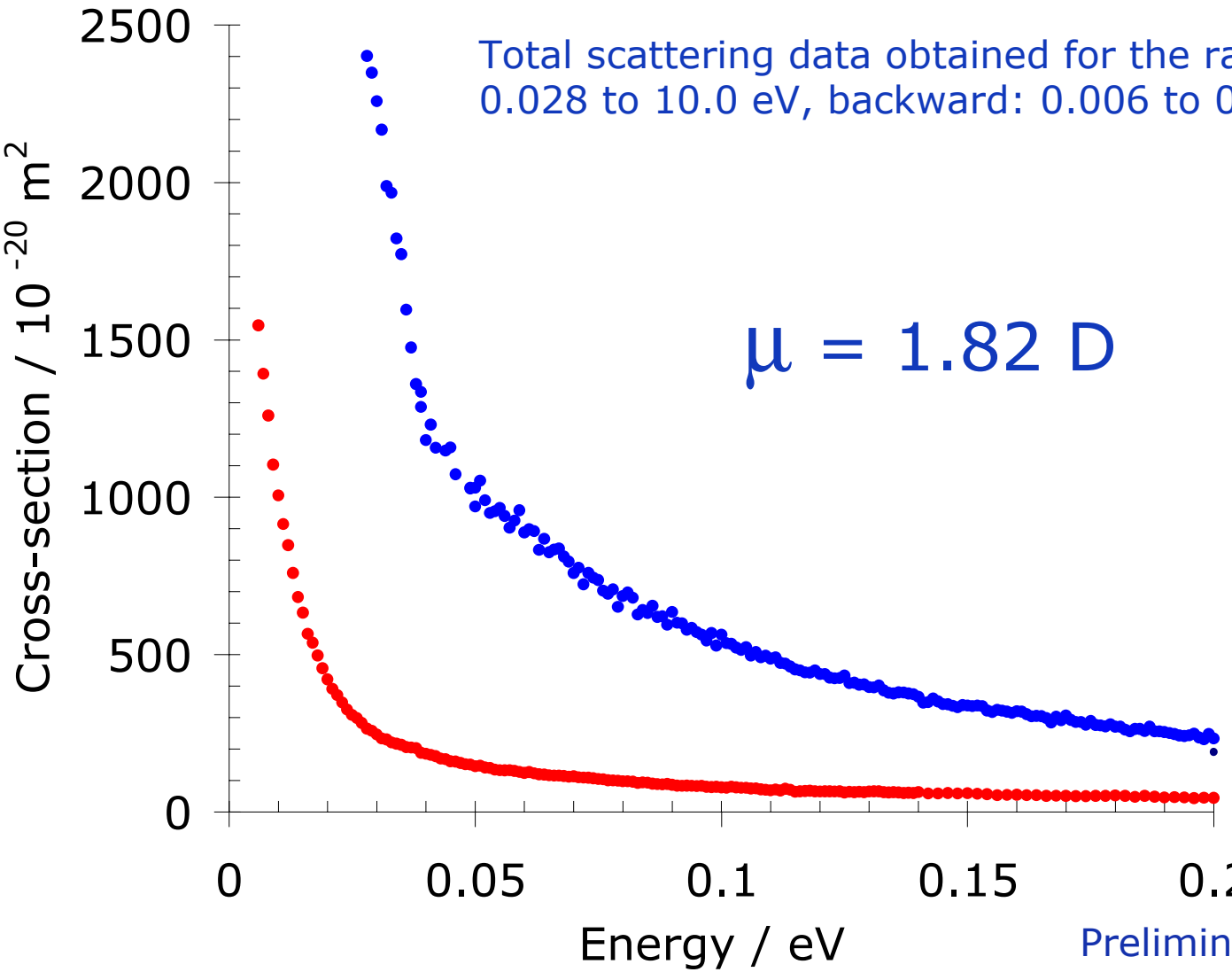
Chloroform	μ = 1.04 D
Bromomethane	μ = 1.82 D
Chloromethane	μ = 1.89 D

  - Rotational and vibrationally inelastic events and elastic scattering occurring for these molecules.

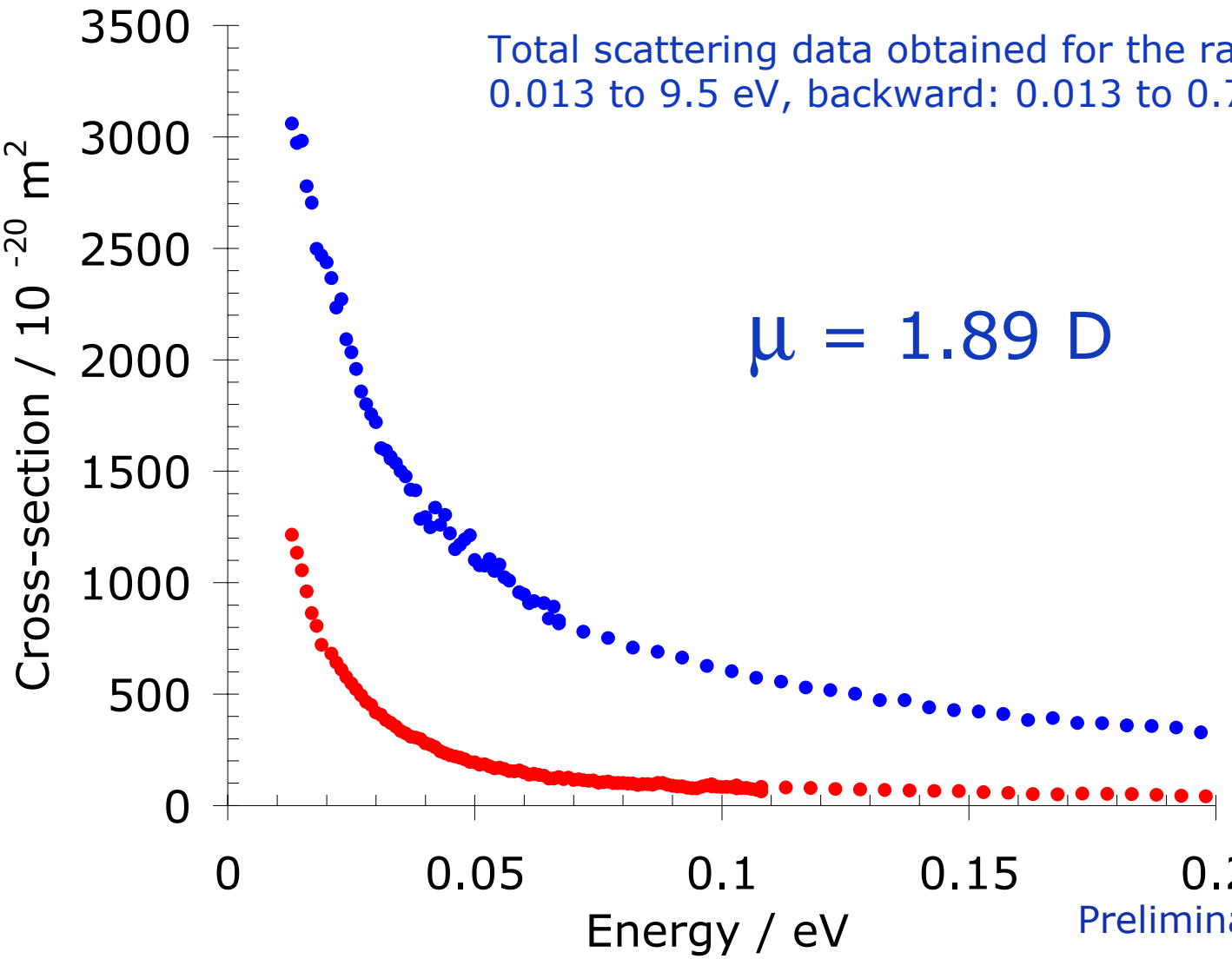
Chloroform – $CHCl_3$



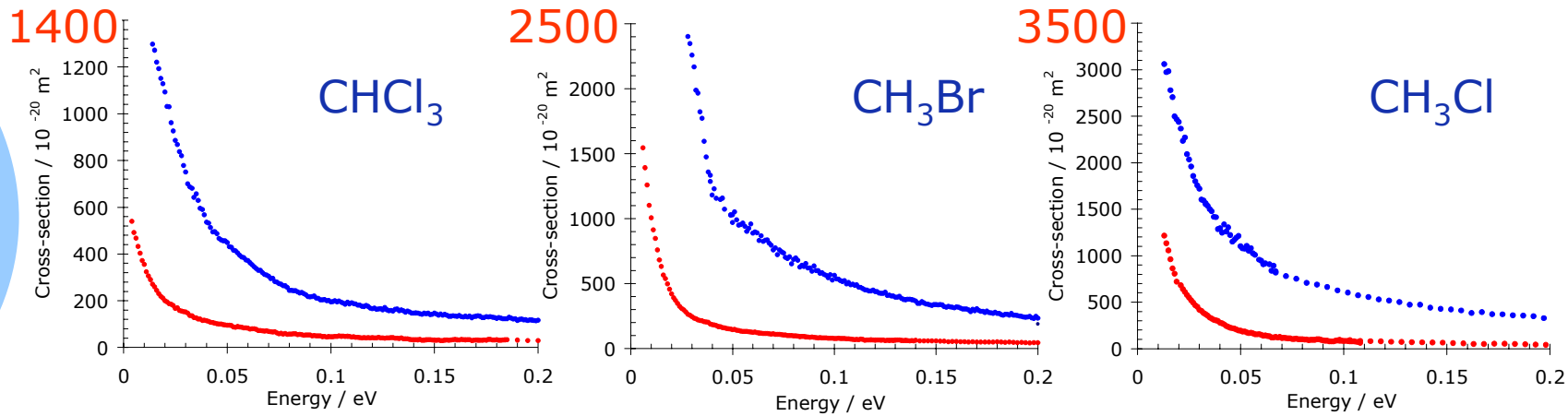
Methyl Bromide – CH_3Br



Chloromethane – CH_3Cl



CH_3Cl, CH_3Br, $CHCl_3$ Data



- Very high cross-sections at low energies
- Strong forward scattering
  - Ratio σ_B/σ_T for $CHCl_3$ at 15 meV is 0.2, rising to 0.25 at 200 meV
- A portion of forward scattering is missed. This is less important at the lowest energies, but could be as much as a factor of two or more at higher energies.
- No portion of the backward scattering cross-sections is missed. Useful as a test for theoretical models

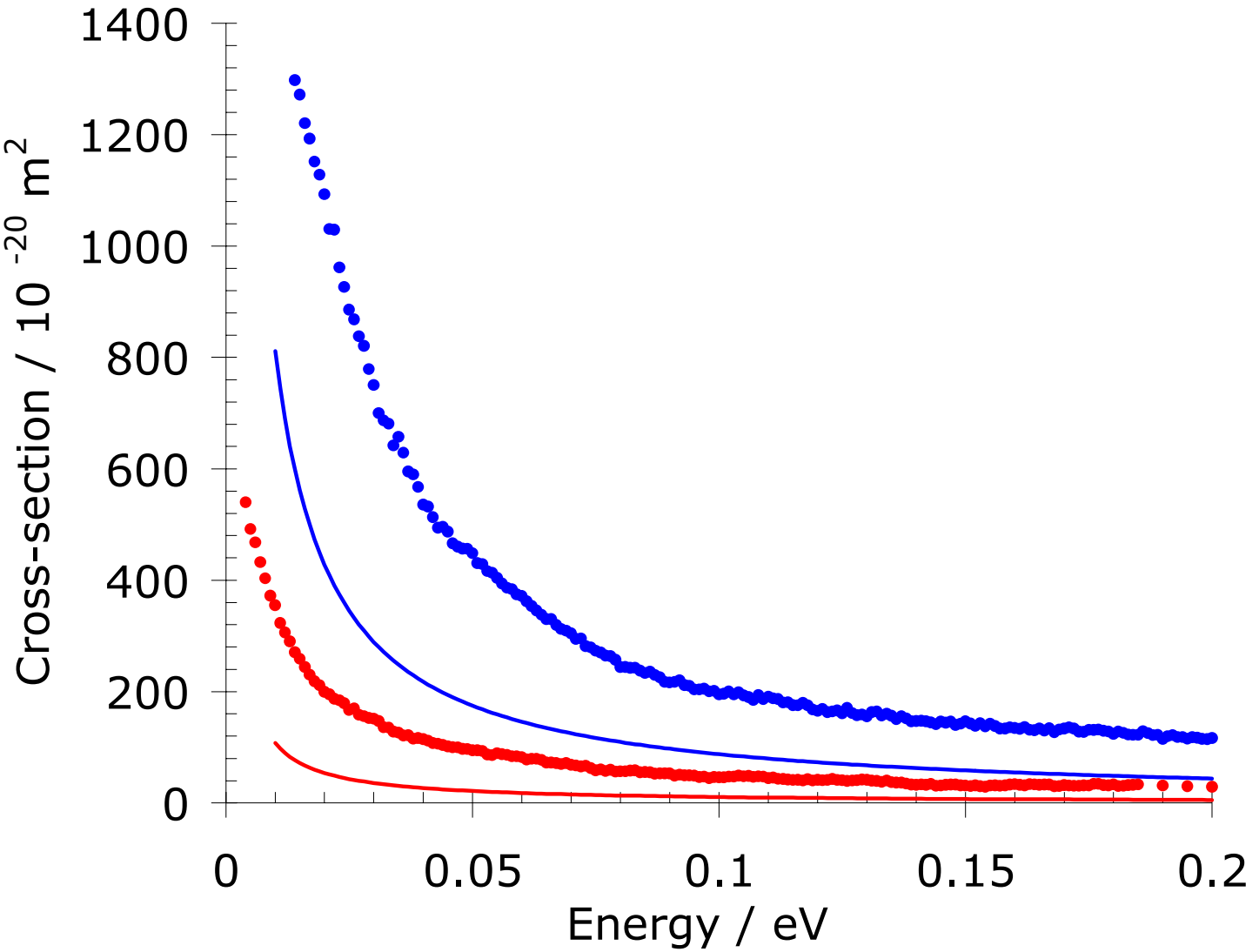
Treatment of Data

- Simple Born theory (first order) for the determination of rotationally inelastic scattering cross-sections gives the following relationship:

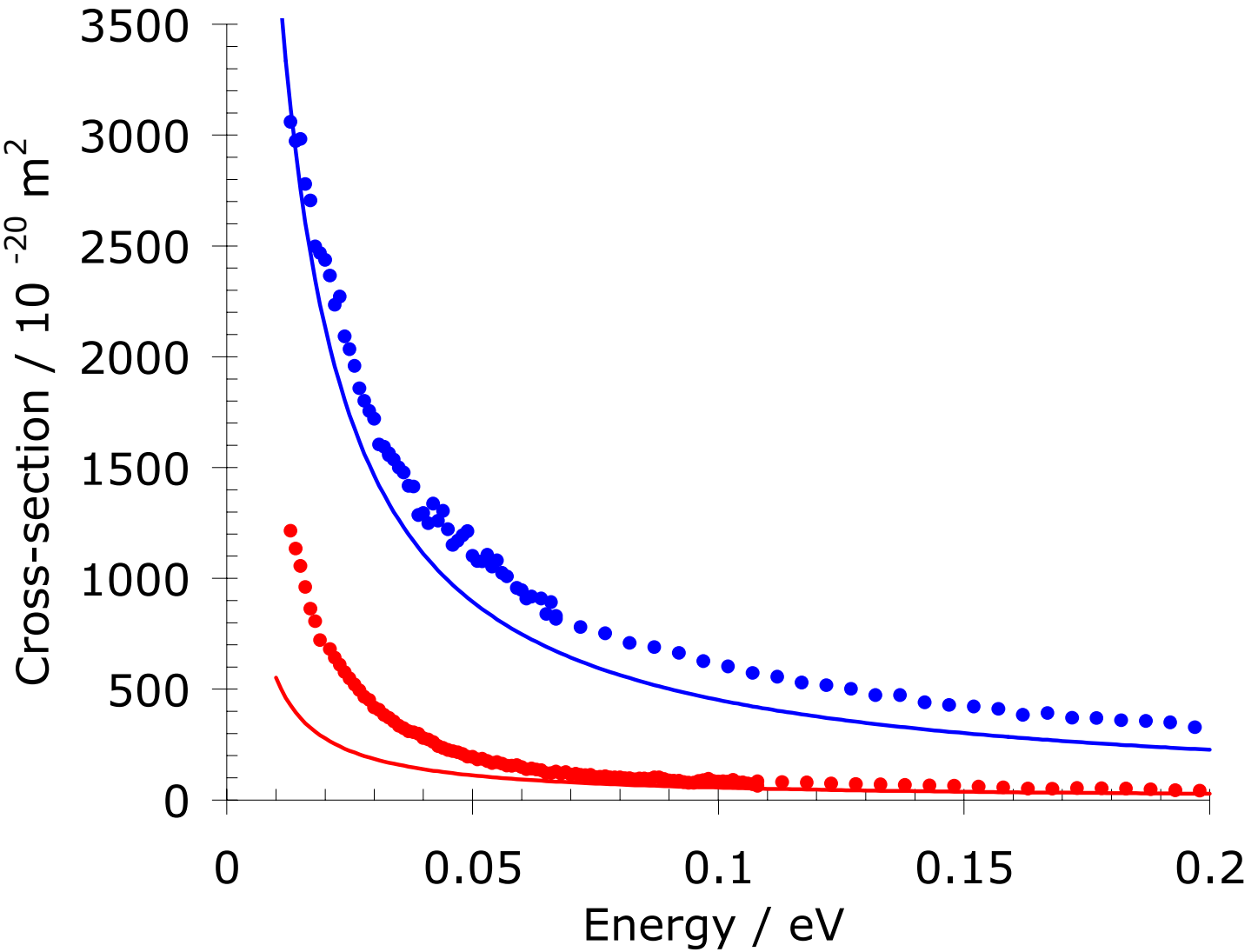
$$\sigma \propto \sim \left(\frac{4\pi}{3k^2}\right)\left(\frac{D^2}{(ea_0)^2}\right)$$

- The cross-section is approximately inversely proportional to the energy [$k^2=(2m_eE)/\hbar$] of the collision
- And proportional to the square of the dipole moment of the target molecule
- Born approximation makes predictions which would suggest strong forward scattering

$CHCl_3$ – with Born Calculations



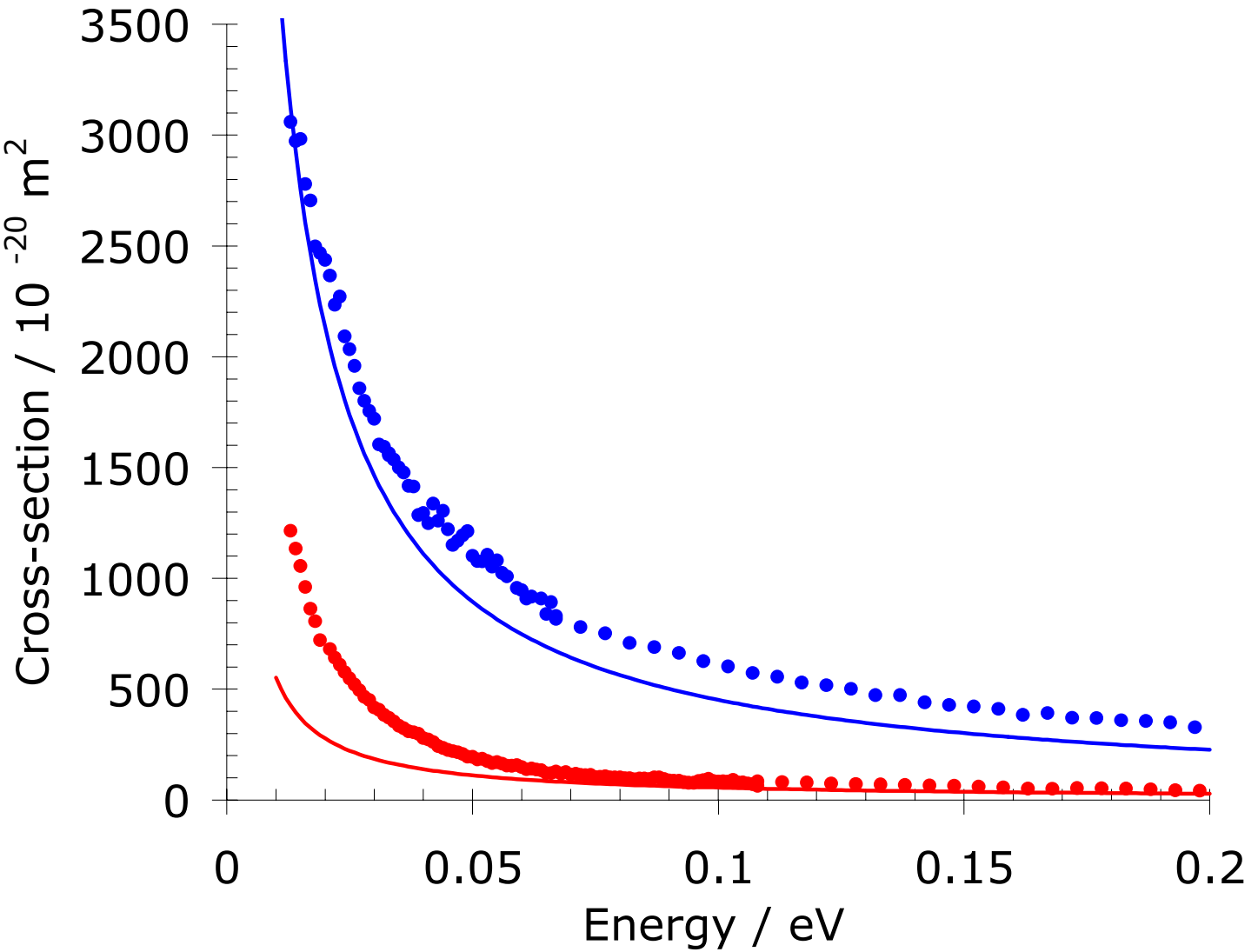
CH_3Cl – with Born Calculations



Treatment of Data

- Measured Total = Rotationally Inelastic + Elastic
- Can we obtain the two cross-sections separately?
- For example, subtract Born calculated values to give pure elastic scattering
- However Born theory is not good enough

CH_3Cl – with Born Calculations



Treatment of Data

- Measured Total = Rotationally Inelastic + Elastic
- Can we obtain the two cross-sections separately?
- For example, subtract Born calculated values to give pure elastic scattering
- However Born theory is not good enough
- Need theoreticians to calculate accurately either the rotationally inelastic or elastic scattering cross-sections.
- Elastic scattering contributions can be quite large, especially in backward scattering.
  [See UCL Node: Faure et al. J. Phys. B: At. Mol. Opt. Phys. 37 (2004) 801–807]

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Rotational Excitation and Attachment

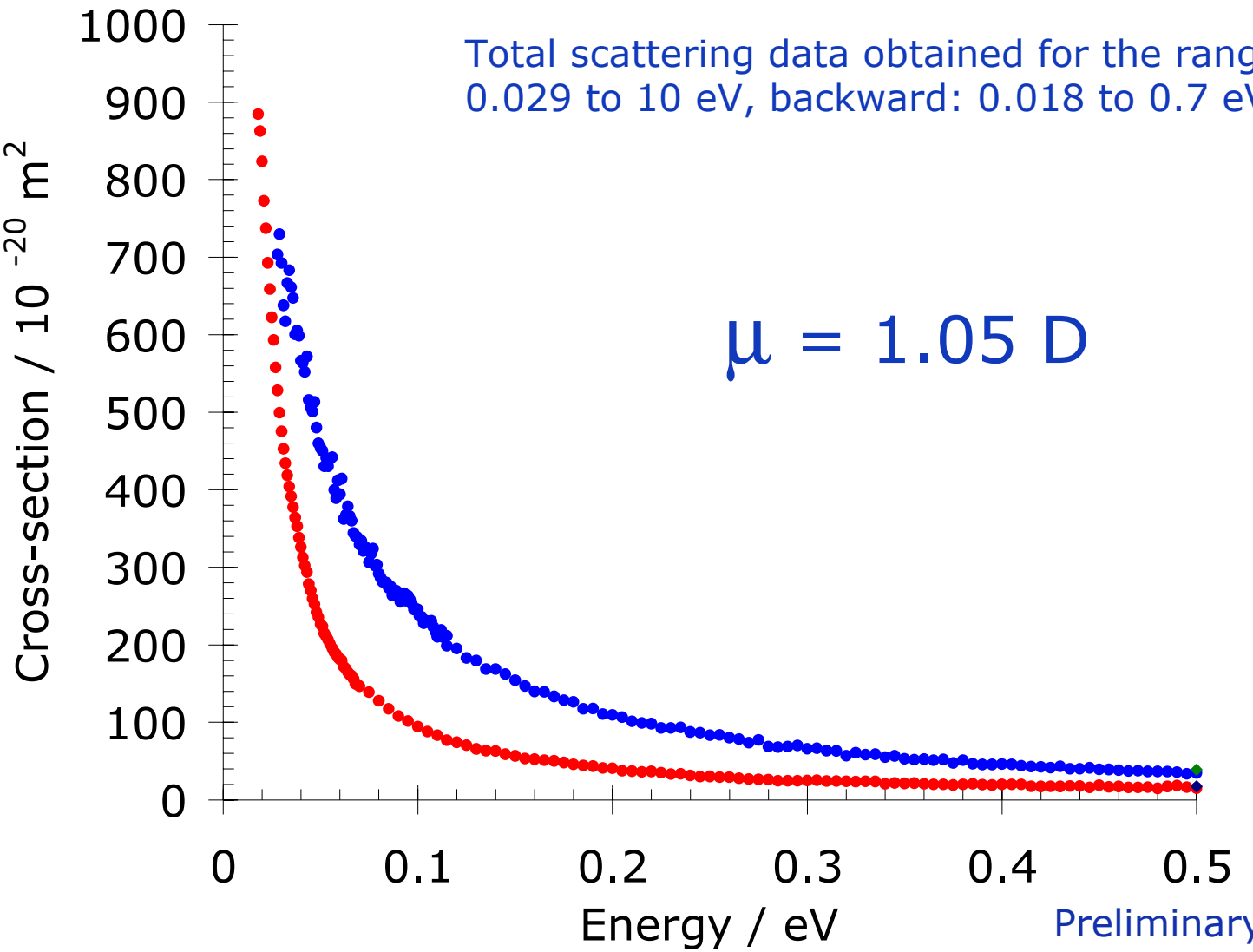
- If the attachment process has a lifetime long enough that the negative ion moves out of the line of sight of the detector

- Then with a magnetic field applied we measure the sum of
  - the *integral* attachment cross-section and
  - all inelastic and elastic scattering events into the backward hemisphere

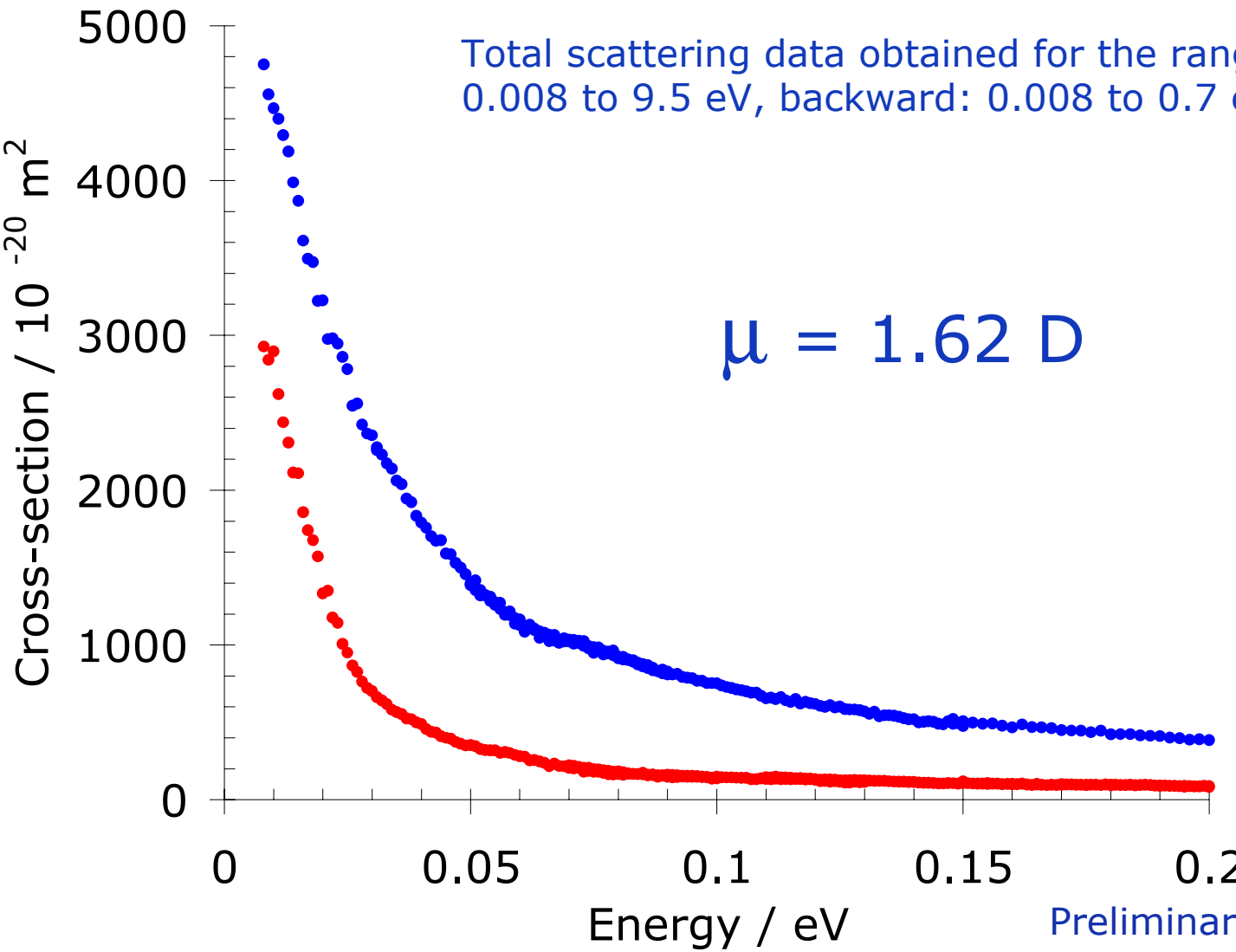
  $\sigma_B = \sigma_{int}(\text{attachment}) + \sigma_{back}(\text{elastic+inelastic})$

- Ion trajectories are unaffected by the field of 20G

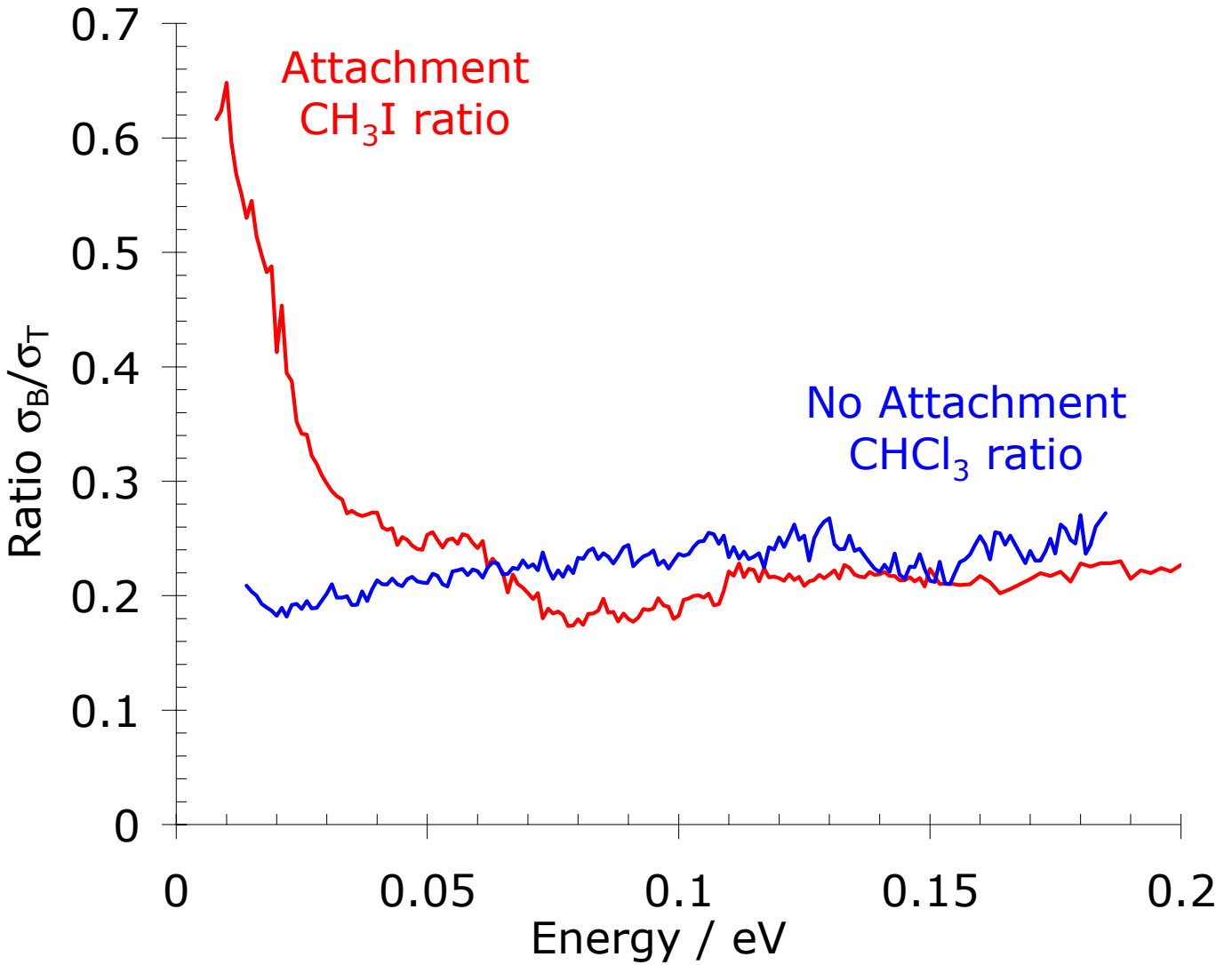
Trifluoro-iodomethane – CF_3I



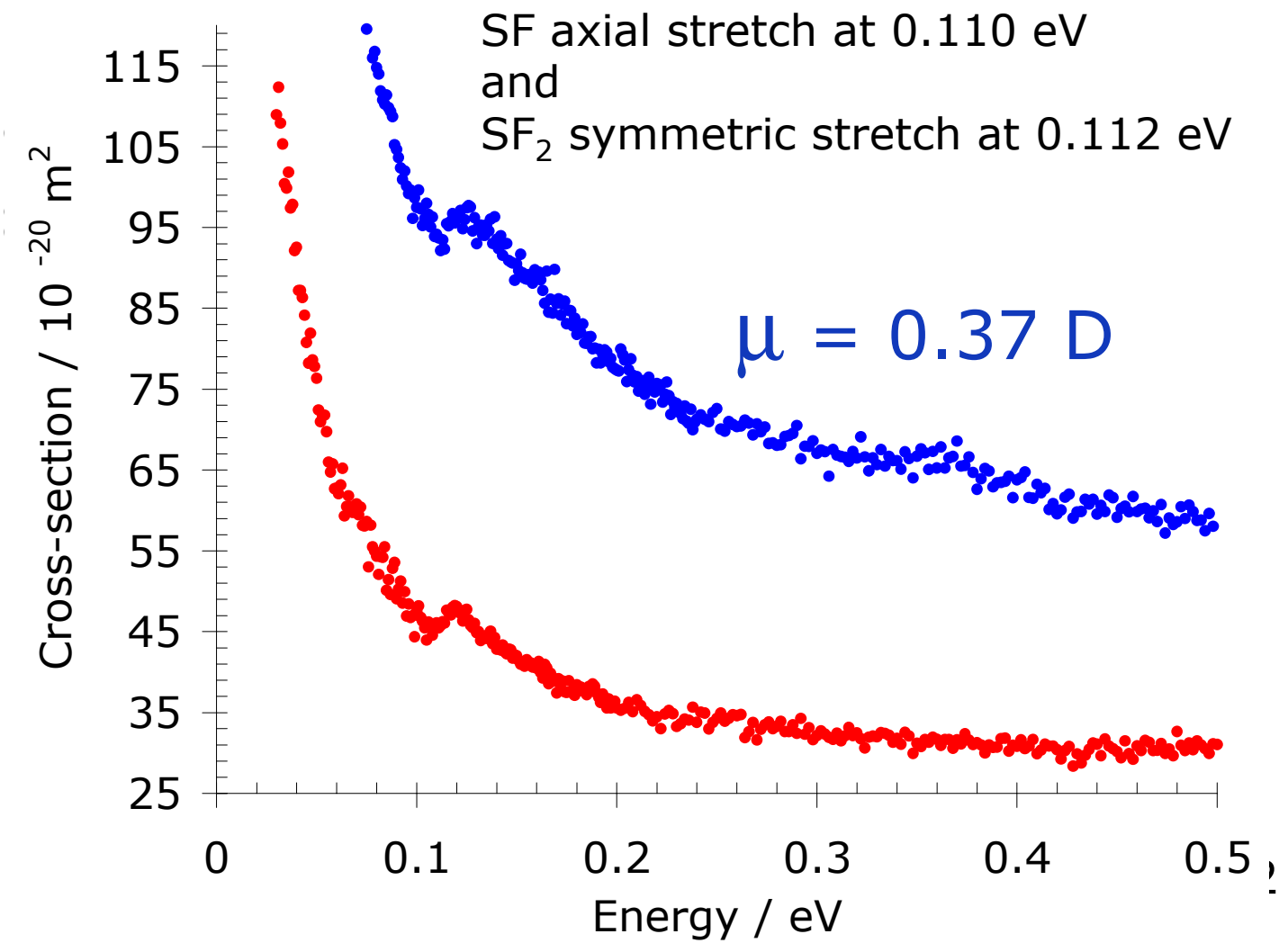
Methyl iodide – CH_3I



Comparison of Ratios



Trifluoromethyl pentafluorosulphide - SF_5CF_3



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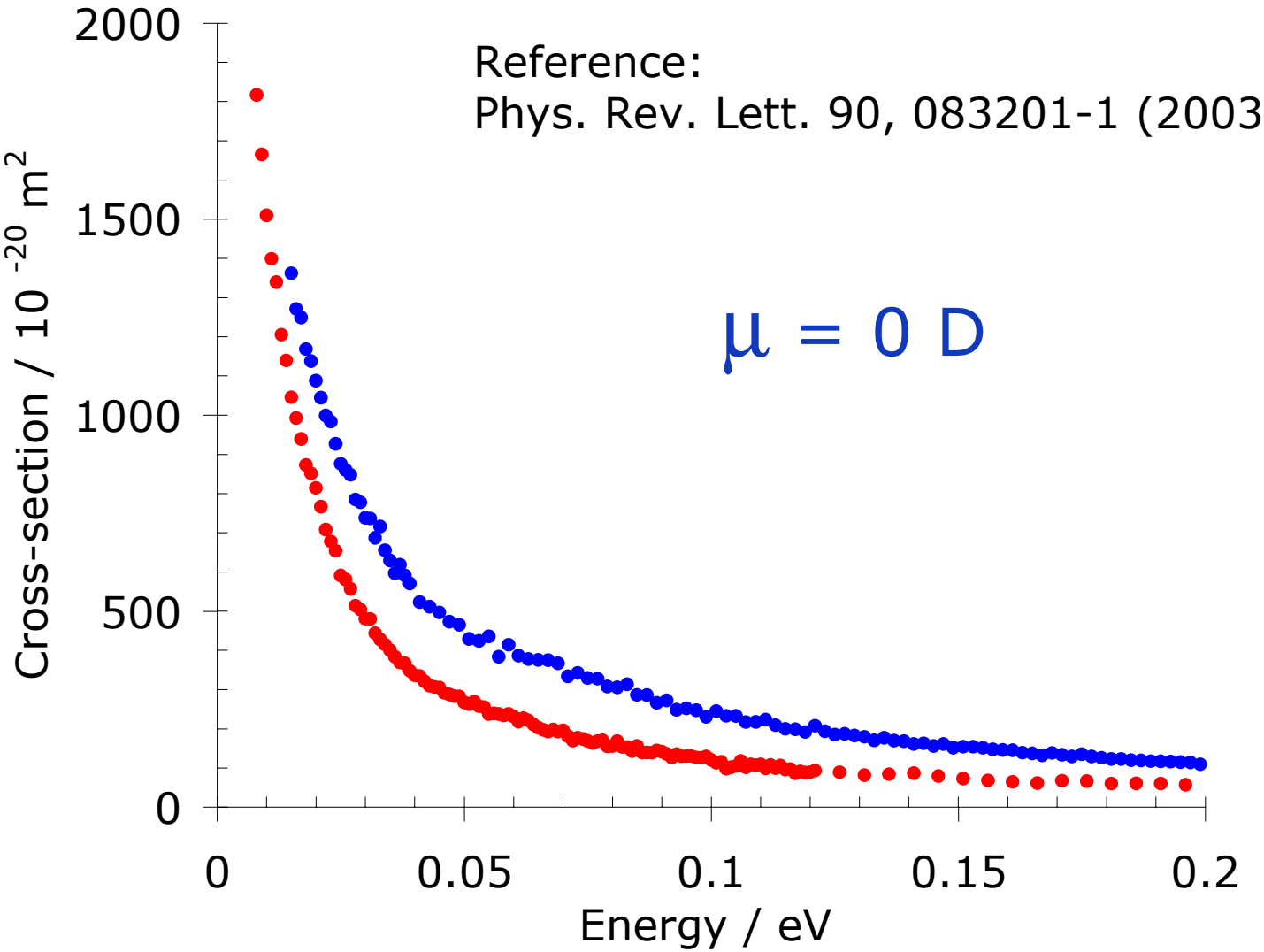
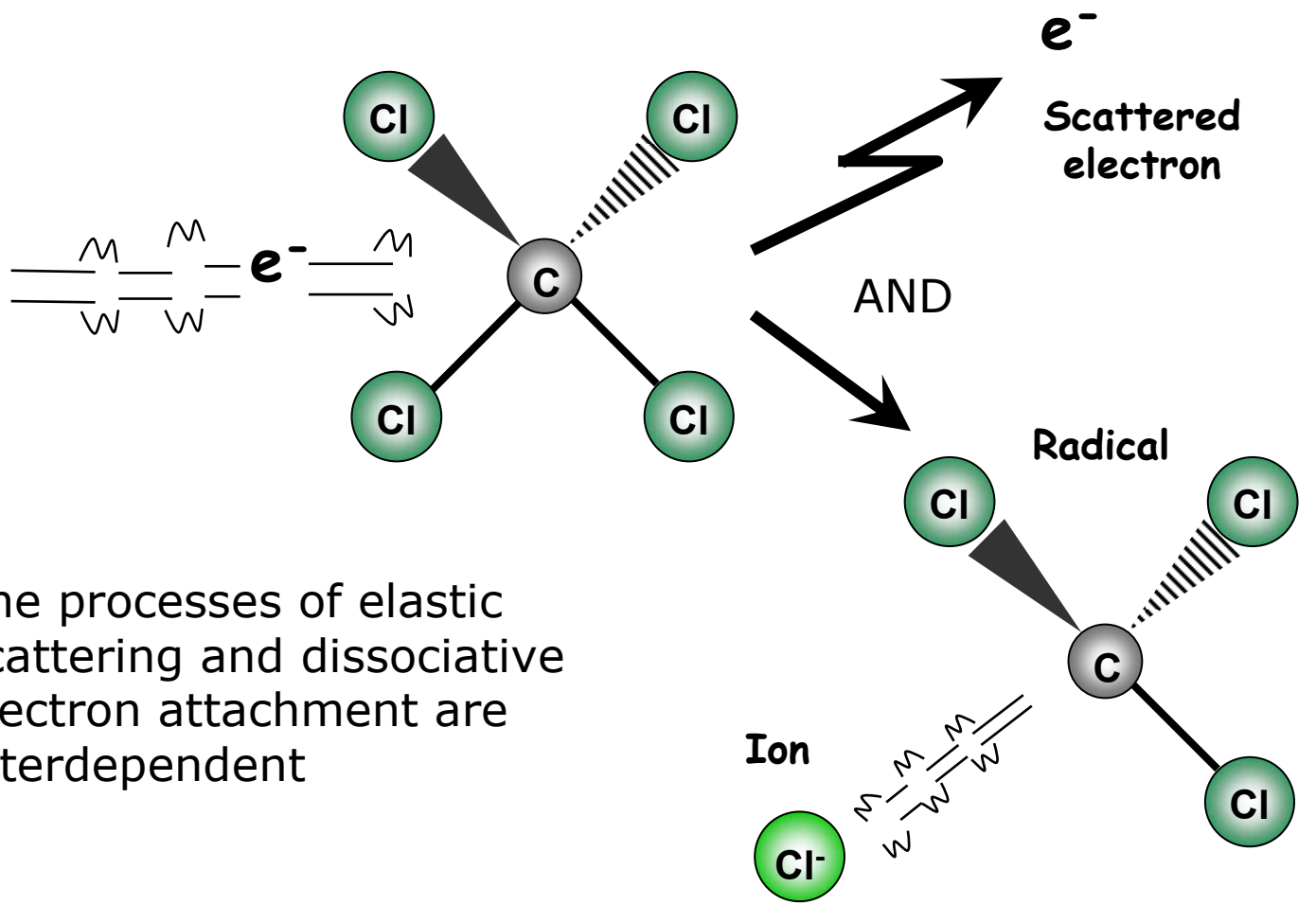
Carbon tetrachloride – CCl_4



Dissociative electron attachment



The processes of elastic scattering and dissociative electron attachment are interdependent

Elastic scattering and reaction cross-sections

- For CCl_4, s-wave attachment occurs
- Cross-sections are represented by:

$$\sigma_{T,I} = \sigma_I^{el} + \sigma_I^{att} = \frac{2\pi}{k^2}\left[4 - \varepsilon_0 \cos 2\eta_0 - 3\cos 2\eta_1\right]$$

$$\sigma_{T,B} = \sigma_B^{el} + \sigma_I^{att} = \frac{\pi}{2k^2}\left[6 - \varepsilon_0^2 \cos 2\eta_1 - 3\varepsilon_0 \cos 2(\eta_0 - \eta_1)\right]$$

$$\sigma_I^{att} = \frac{\pi}{k^2}\left[1 - \varepsilon_0^2\right]$$

- The elastic cross-sections depend on the attachment channel via ε_0

Extracting attachment cross-sections

- By fitting to our data we can extract absolute attachment cross-sections
- No prior knowledge of rate coefficients or cross-sections from other experiments is necessary.
- Phase shifts are written as simple expansions in the k-vector

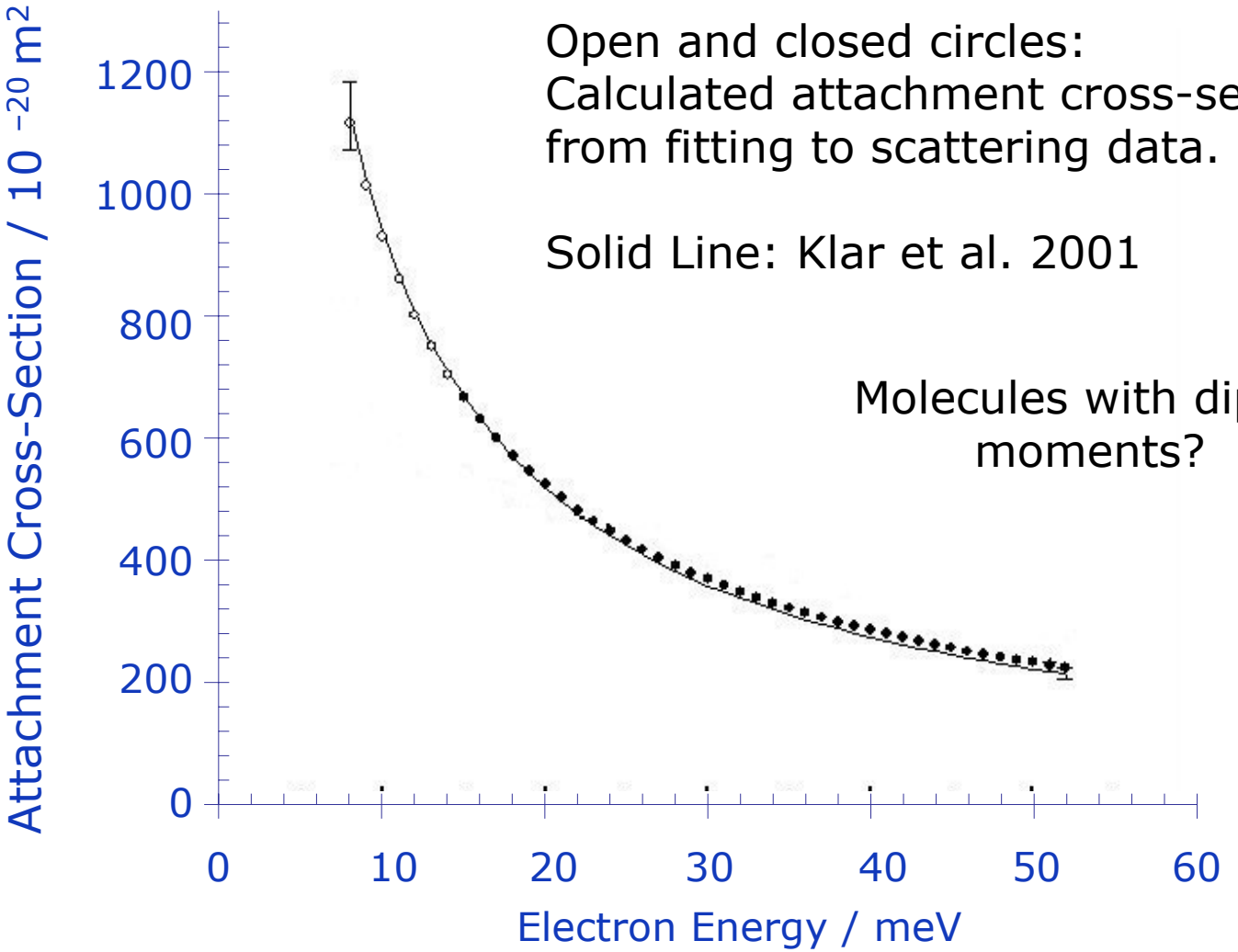
$$\eta_\ell = \sum_{n=0}^{4} c_n^\ell k^n$$

- and ε_0 is parameterised as

$$\varepsilon_0 = 1 + a_1 k + a_2 k^2$$

where c_n^ℓ, a_1 and a_2 are fitting coefficients

Calculated Attachment Cross-sections



Open and closed circles:
Calculated attachment cross-section from fitting to scattering data.

Solid Line: Klar et al. 2001

Molecules with dipole moments?

Summary

- Numerous molecules investigated following the EPIC programme.
- Display a wide variety of processes, in particular rotationally inelastic scattering, elastic scattering and attachment.
- We can extract absolute attachment cross-sections at very low energy from scattering experiments. For polar molecules theoretical input is required.