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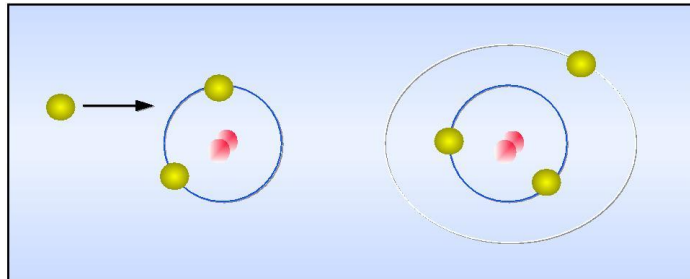
MOLECULAR PROCESSES II

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Electronic resonances

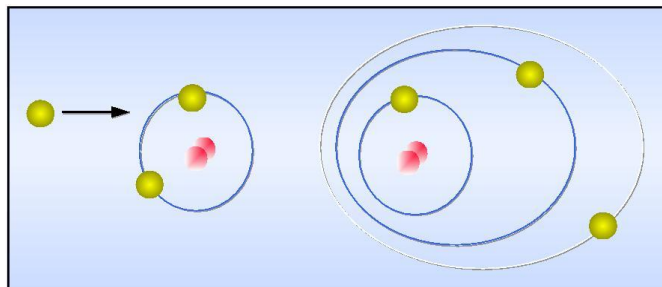
Metastable state where the electron is temporarily captured by target

Shape resonance: 1 particle



- Target in electronic ground state
- Can be modelled as a single-electron problem
- Visible in ETS experiments
- Short-lived

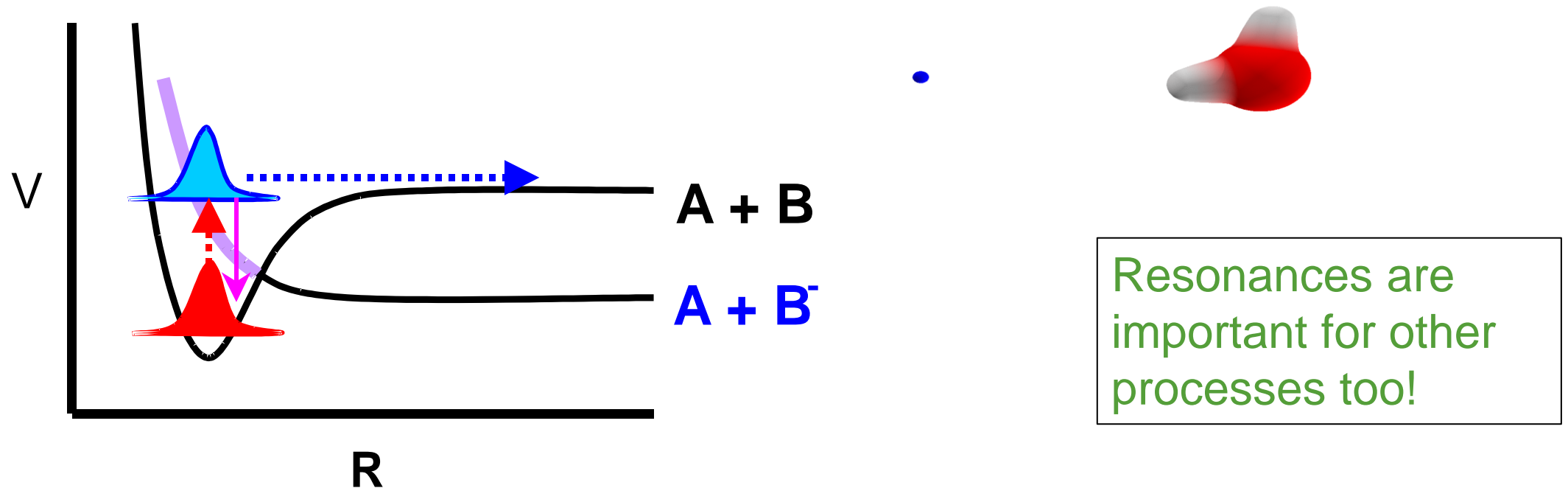
Core-excited: 2-particle, 1 hole



- Target in an excited state
- Multi-electronic description essential
- Shape or Feshbach
- Harder to observe (particularly Feshbach): EELS experiments
- Longer-lived

Resonances

Metastable state where the electron is temporarily captured by target. Decay by **autoionization**: energy and width (lifetime) or **dissociative electron attachment**.



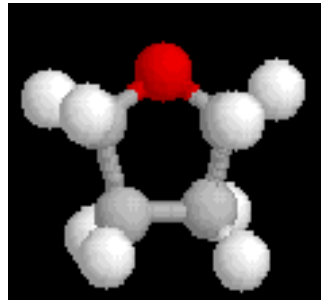
Resonances are important for other processes too!

DEA : resonant process initiated by formation of a **r resonance**:

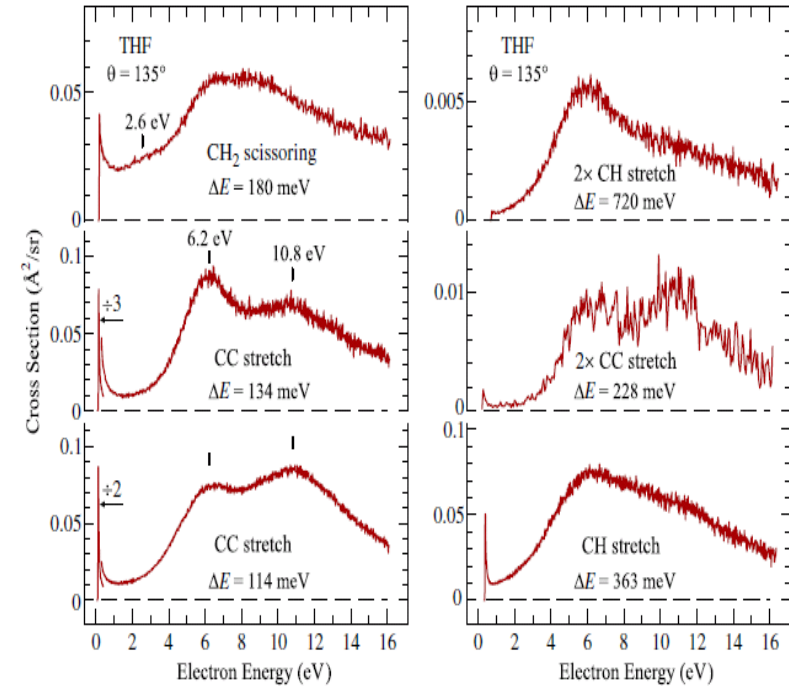
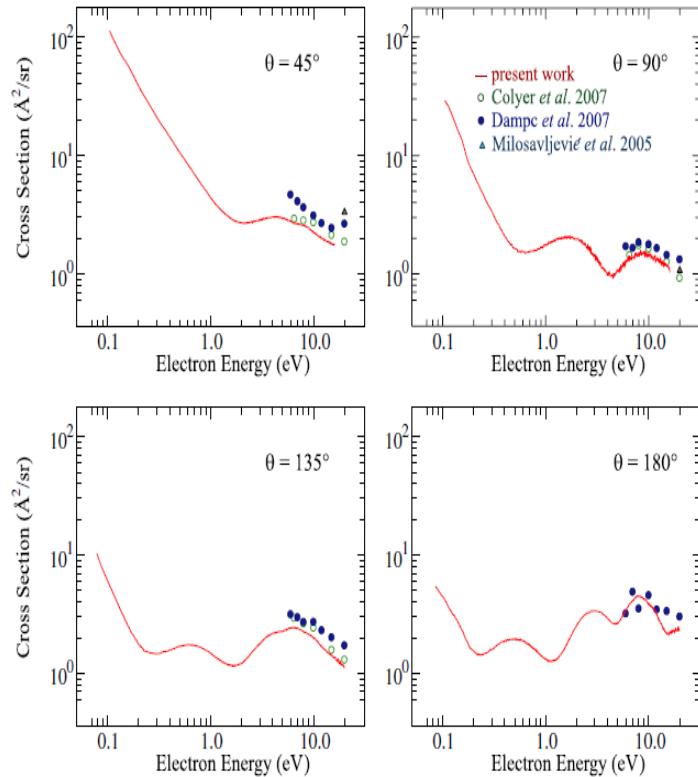


Resonance effect on scattering

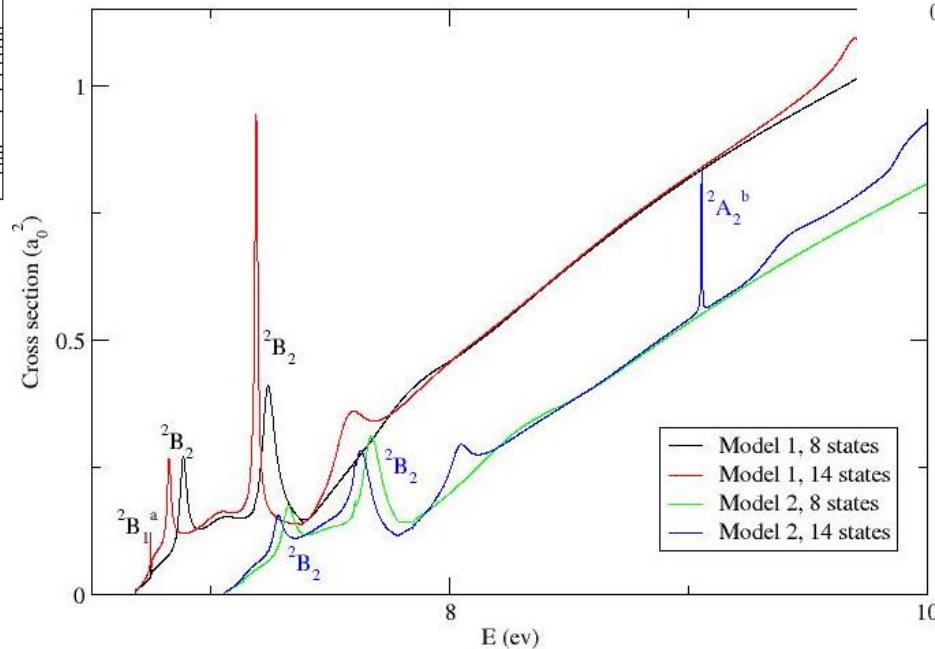
Allan *J. Phys. B.* **40** (2007)
3531–3544



THF

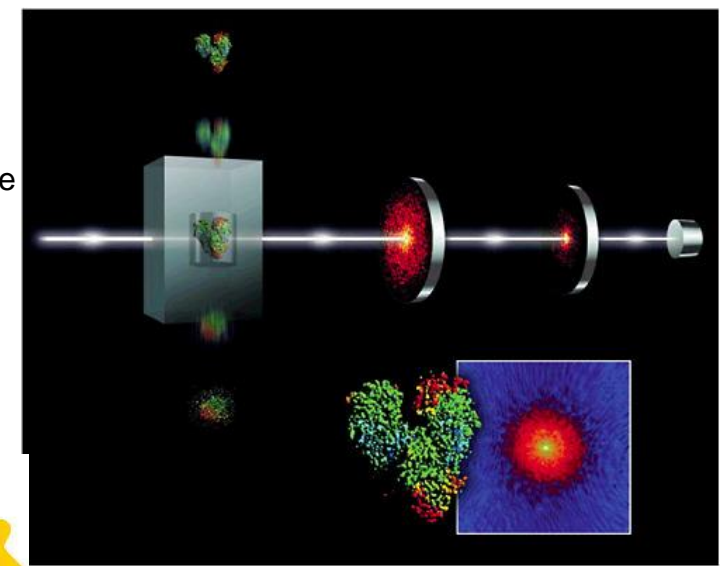


Bouchiha et al *J. Phys. B.*
39 (2006) 975



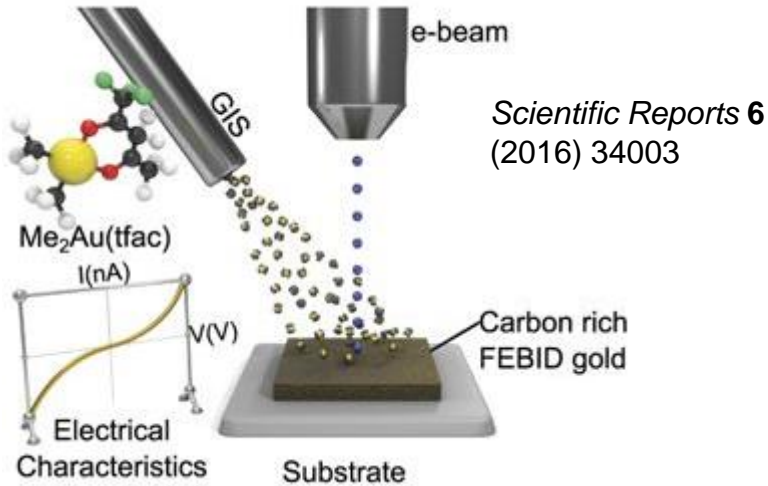
Applied relevance

Chapman, Lawrence Livermore National Laboratory



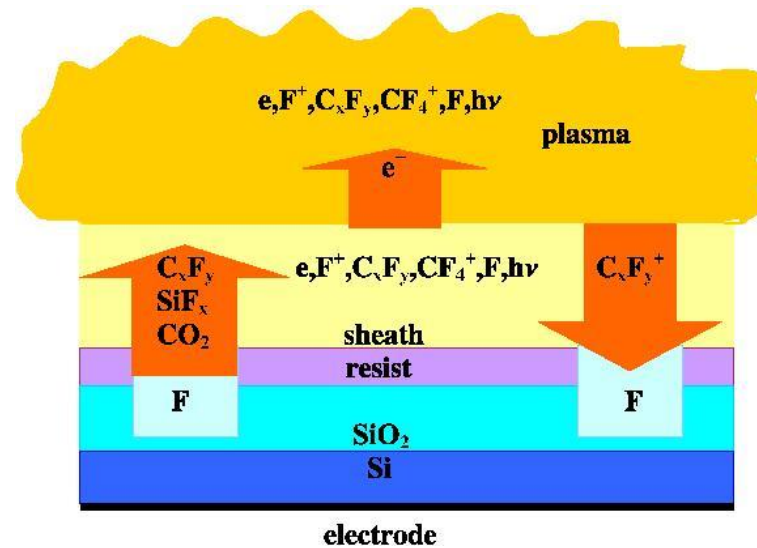
Radiation damage

Medical uses of radiation



Nanofabrication

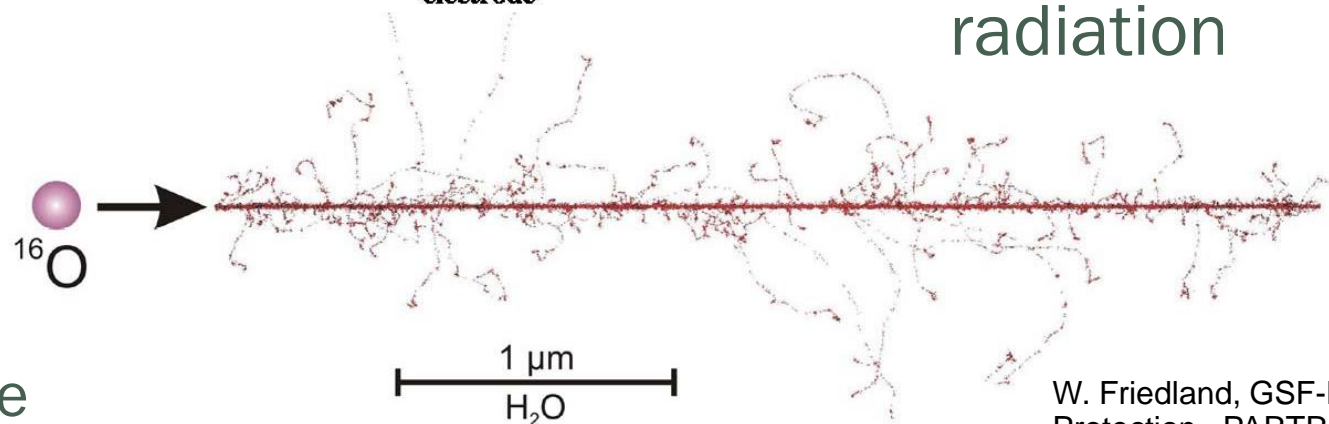
Plasma etching



Osaka University



Plasmas in medicine



W. Friedland, GSF-Institute of Radiation Protection . PARTRAC, MC simulation

Low energy e^- scattering calculations

- Quantum mechanical approach needed
- Time-independent approaches developed and implemented computationally for over 40+ years
- Electron in the continuum means **bound state Quantum Chemistry methods are not valid**
- Electronic transitions are treated in the **fixed-nuclei approximation**
- To treat rotational excitation: adiabatic nuclei rotation approximation
- To treat vibrational excitation: AN, Discrete Momentum Representation, etc.

Computational machinery

- Electronic scattering approaches:
 - R-matrix (UK, Czech Republic, India, etc.)
 - Schwinger multichannel (Brazil, USA)
 - Kohn variational method (USA)
 - Single-centre approaches (Italy, Poland)
 - Convergent Close-Coupling (Australia)
- In addition, to identify and characterize resonance, methods adapted from Quantum Chemistry: CAP, stabilization techniques, analytical continuation,....

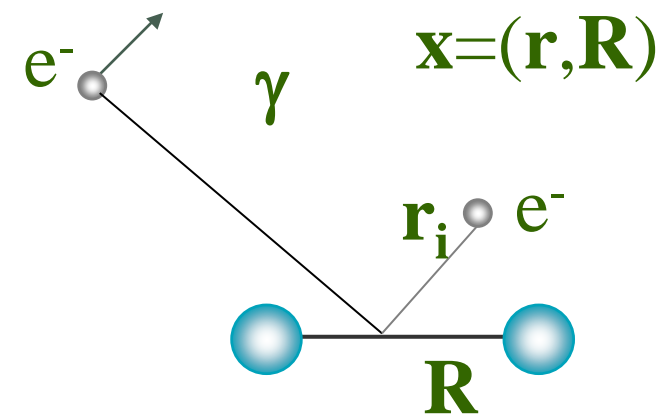
Low energy electron-molecule scattering

Time-independent approaches developed and implemented computationally over 40+ years

$$(H_{N+1} - E)\Psi_E(\mathbf{x}, \gamma) = 0$$

$$H_{N+1} = H_N(\mathbf{x}) + \hat{T}_e(\gamma) + \hat{V}_{\text{int}}(\mathbf{x}, \gamma)$$

subject to the appropriate boundary conditions



- Main issues: **description of continuum and electron correlation**
- Polarization is also an important effect, especially if target is non-polar

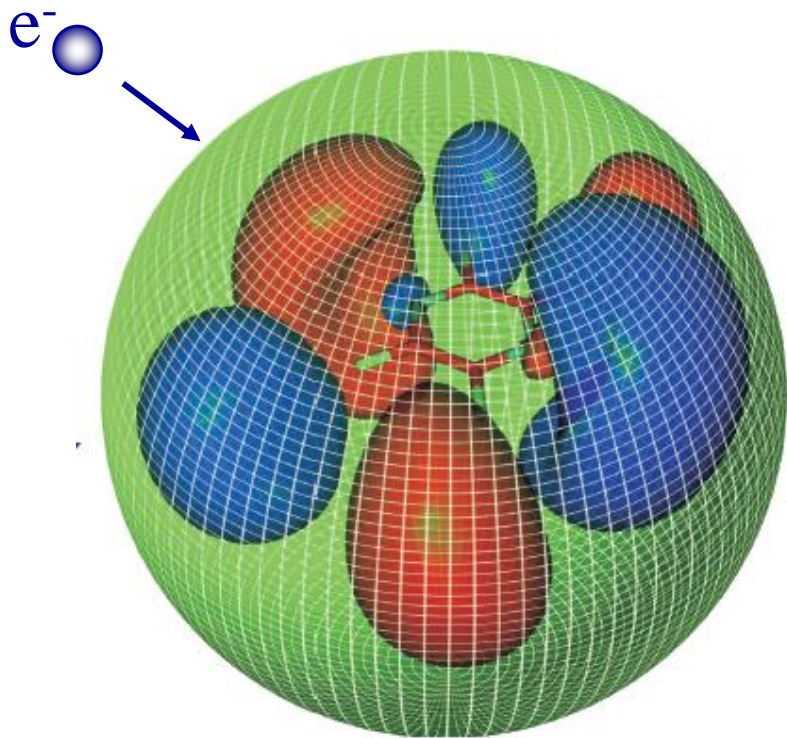
Exchange and correlation

- **Exchange** arises due to electrons being indistinguishable particles.
- Indistinguishability must be taken into account when wavefunctions are built.
- Electrons are fermions and must obey Fermi-Dirac statistics. (For bound electrons in atoms and molecules this translates into the Pauli Exclusion principle)
- Exchange integrals describing exchange interaction (with no classical equivalent) arise

- **Correlation** is due to the interaction of N moving charged particles, the electrons.
- Can be seen as the effect of the instantaneous repulsion felt by one electron due to all others.
- Can be difficult to model accurately for electron-rich molecules

Molecular R-matrix method

Fixed-Nuclei approximation but use of other software to treat nuclear motion



R-matrix sphere (box) of radius a

Inner region:

- exchange and correlation important
- Explicitly multielectronic
- Basis set methods
- Multicentre expansion

Outer region:

- exchange and correlation are negligible
- One explicit electron
- single centre expansion
- long-range multipolar interactions

Describing electronic target states

Use computational chemistry approaches

$$\Phi_i^N = \sum_{i,j} C_{i,j} \zeta_j^N$$

$$\begin{aligned} \zeta_j^N &= \text{N-electron configuration state function (CSF)} \\ &= \|\varphi_1 \varphi_2 \varphi_3 \dots \varphi_N\| \end{aligned}$$

φ_i = molecular orbitals

$C_{i,j}$ = variationally determined coefficients

Molecular R-matrix method

Inner region: close-coupling expansion

$$\psi_k^{N+1} = \mathcal{A} \sum_{i,j} a_{i,j,k} \Phi_i^N \eta_{i,j} + \sum_j b_{j,k} \phi_j^{N+1}$$

Choice of **continuum orbital** $\eta_{i,j}$, L^2 functions ϕ_j^{N+1} and **target states** Φ_1^N defines the quality of the calculation and model
Coefficients $a_{i,j,k}$ and $b_{j,k}$ obtained variationally

Static-Exchange (SE): Φ_1^N (HF ground state) + FEW L^2 functions

Static-Exchange plus Polarization (SEP): Φ_1^N (HF ground state) + L^2 functions

Close-Coupling (CC): Φ_i^N ($i=1,2,3,\dots$) + L^2 functions

Molecular R-matrix method

Implicit partial wave expansion

Outer region:

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 \right) F_i(r) = 2 \sum_j V_{ij}(r) F_j(r)$$

with inner region data providing initial conditions via R-matrix

$$w_{pk}(a) = \frac{1}{\sqrt{2}} \left\langle \Phi_p^\Gamma \frac{1}{r} \left| \psi_k^{N+1} \right. \right\rangle_{r=a} = \frac{1}{\sqrt{2}} \left\langle \Phi_{i_p}^N \frac{1}{r} X_{l_p, m_p}(\hat{\mathbf{r}}) \left| \psi_k^{N+1} \right. \right\rangle_{r=a}$$

$$w_{pk}(a) = \frac{1}{\sqrt{2}} \left\langle \Phi_p^\Gamma \frac{1}{r} \left| \psi_k^{N+1} \right. \right\rangle_{r=a} = \frac{1}{\sqrt{2}} \left\langle \Phi_{i_p}^N \frac{1}{r} X_{l_p, m_p}(\hat{\mathbf{r}}) \left| \psi_k^{N+1} \right. \right\rangle_{r=a}$$

At $r > 50-100 a_0$ K-matrices obtained $F_{ij} \sim \frac{1}{\sqrt{k_i}} \left((\sin(k_i r - \frac{1}{2} l_i \pi) \delta_{ij} + \cos(k_i r - \frac{1}{2} l_i \pi) K_{ij}) \right)$

$$\mathbf{S} = (\mathbf{1} + i\mathbf{K})(\mathbf{1} - i\mathbf{K})^{-1}$$

$$\mathbf{T} = \mathbf{S} - \mathbf{1}$$

$$\sigma(i \rightarrow i') = \frac{\pi}{k_i^2} \sum_s \frac{(2S+1)}{(2S_i+1)} \sum_{\Gamma l l'} |T_{i l i' l'}^{\Gamma S}|^2$$

UKRmol+ suite

Publication date:
January 15, 2021

DOI:
DOI [10.5281/zenodo.4442407](https://doi.org/10.5281/zenodo.4442407)

Keyword(s):
electron scattering, positron scattering, resonances, photoionization,

License (for files):
[GNU General Public License v3.0 or later](#)

Versions	
Version 3.1.1 10.5281/zenodo.4442407	Jan 15, 2021
Version 3.1 10.5281/zenodo.4120705	Oct 23, 2020
Version 3.0 10.5281/zenodo.3371125	Aug 19, 2019
Version 2.0.5	Jun 28, 2019

Source code:
<https://zenodo.org/> (cmake files and test suite included)

Mašin et al, CPC, **249**,
107092 (2020)
<https://doi.org/10.1016/j.cpc.2019.107092>
arxiv.org/abs/1908.03018

6 result(s) found

April 21, 2023 (1.0) Software Open

UKRmol-scripts

Houfek, Karel ; Benda, Jakub ; Mašin, Zdeněk

Perl scripts to automatically run the UKRmol+ codes for b photoionization for polyatomic molecules. Using a numbe

Uploaded on April 21, 2023

December 22, 2021 (3.2) Software Open

UKRmol+: UKRmol-in

Masin, Z. ; Benda, J. ; Harvey, A. G.; and 3 others

Inner region programs for the reengineered UK computat transition moments for the study of photon-induced proce

Uploaded on December 22, 2021

7 more versions exist for this record

December 22, 2020 (3.2) Software Open

UKRmol+: UKRmol-out

UK R-matrix community

Outer region programs for the re-engineered UK comput

UKRmol+ suite

Electron scattering:



Positron scattering:



change the sign

Photoionization:



half a collision

- **Positron**-molecule collisions (excluding Ps formation)
- **Photoionization** of molecules
- Input for **R-matrix with time** approach that solves TDSE to model strong-field processes

UKRMol-scripts: A Perl-based system for the automated operation of the photoionization and electron/positron scattering suite UKRmol+

Houfek et al, CPC, **298**, 109113 (2024)
<https://doi.org/10.1016/j.cpc.2024.109113>

UKRmol+ suite

- Initial code for electron-diatomic molecules (early 80s). Polyatomics: mid-90s. Parallelization and modernization early-00s. Overhaul of most of the programs 2010s: UKRmol+ a interfacing with time-dependent R-matrix with time (RMT) codes for strong-field processes. Multiphoton ionization...

Capabilities:

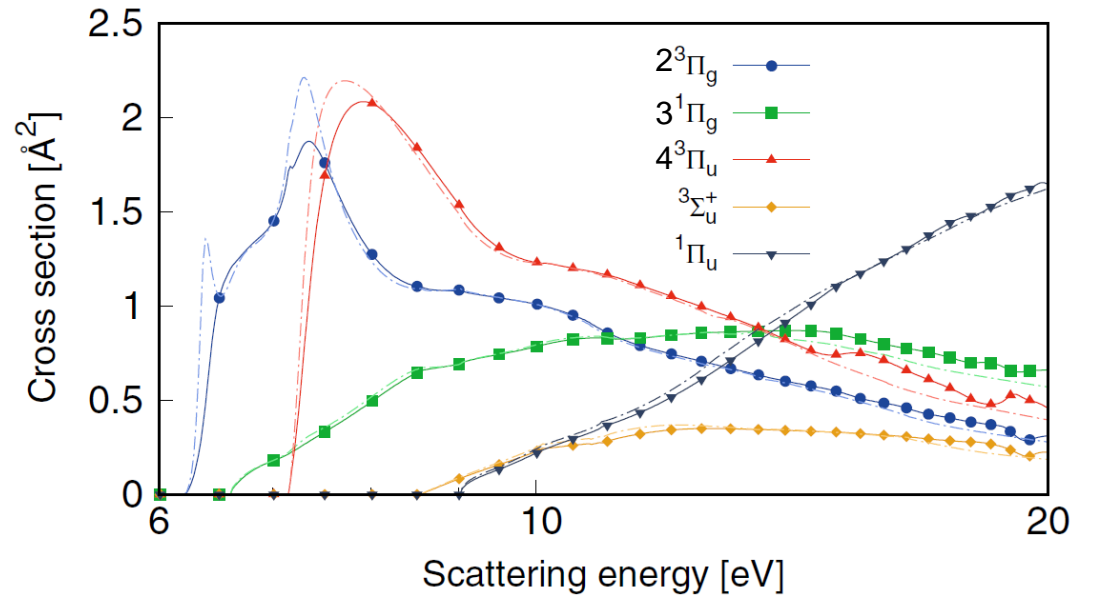
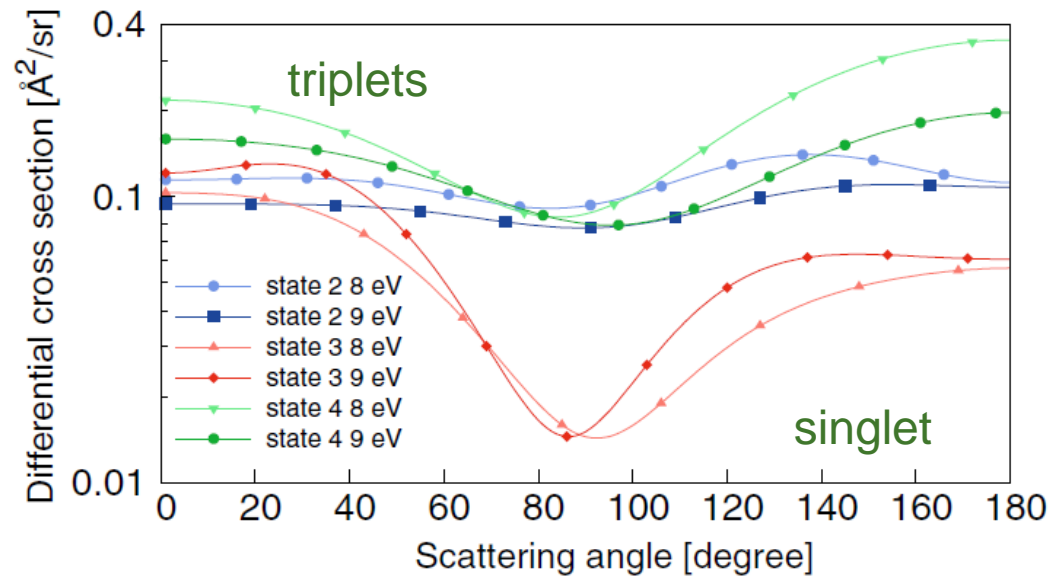
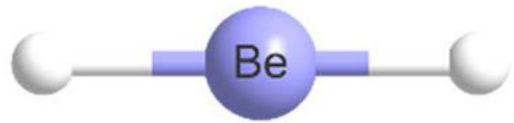
- 2000: electronic excitation of H₂O: 10 e⁻, 9 electronic states, 60 channels (per symmetry)
- 2014: CH₄ > 1000 channels (Brigg *et al* JPB)
- 2016: electronic excitation of pBQ, 56 e⁻ (Loupas PCCP); 2017: elastic scattering from thymine-(H₂O)₅. > 100 e⁻ (Sieradzka JCP)
- 2020: H₂, $a = 100 a_0$ (Meltzer *et al* JPB). Excellent agreement with CCC.

In practice:

- < 1 hour on a desktop computer for elastic scattering for mid-size molecules
- > days on a supercomputer for electronic excitation of molecules with 40+ electrons
- Finding appropriate model can take some effort!

Inelastic cross sections BeH₂

Present in plasma in divertors
of thermonuclear fusion
reactors (e.g. ITER)



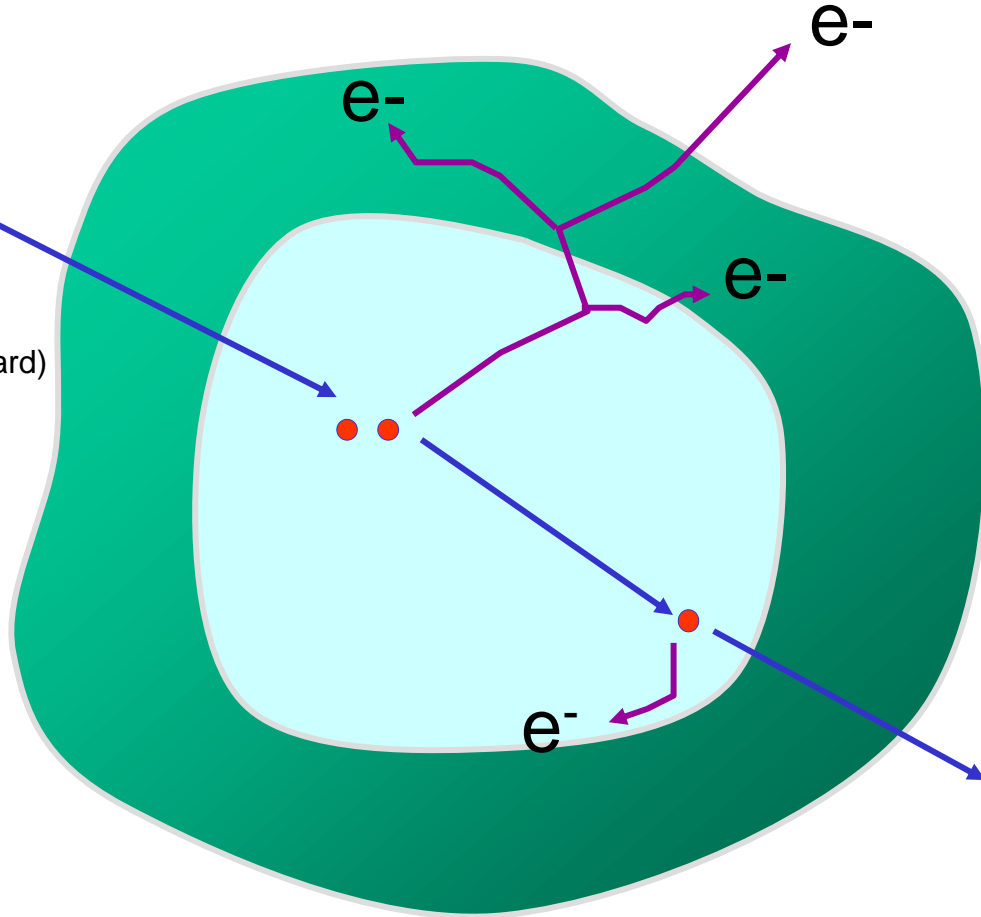
State-to-state integral and DCS
for electron excitation
Expected behaviour for singlets
and triplet states

Radiobiological damage

Ionizing radiation

(Adapted from M. Folkard)

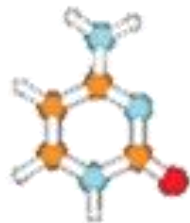
2 μm



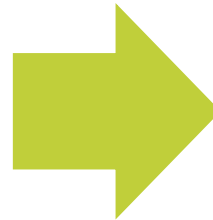
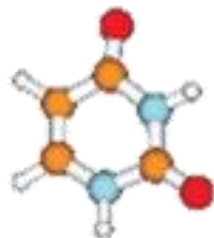
Thymine



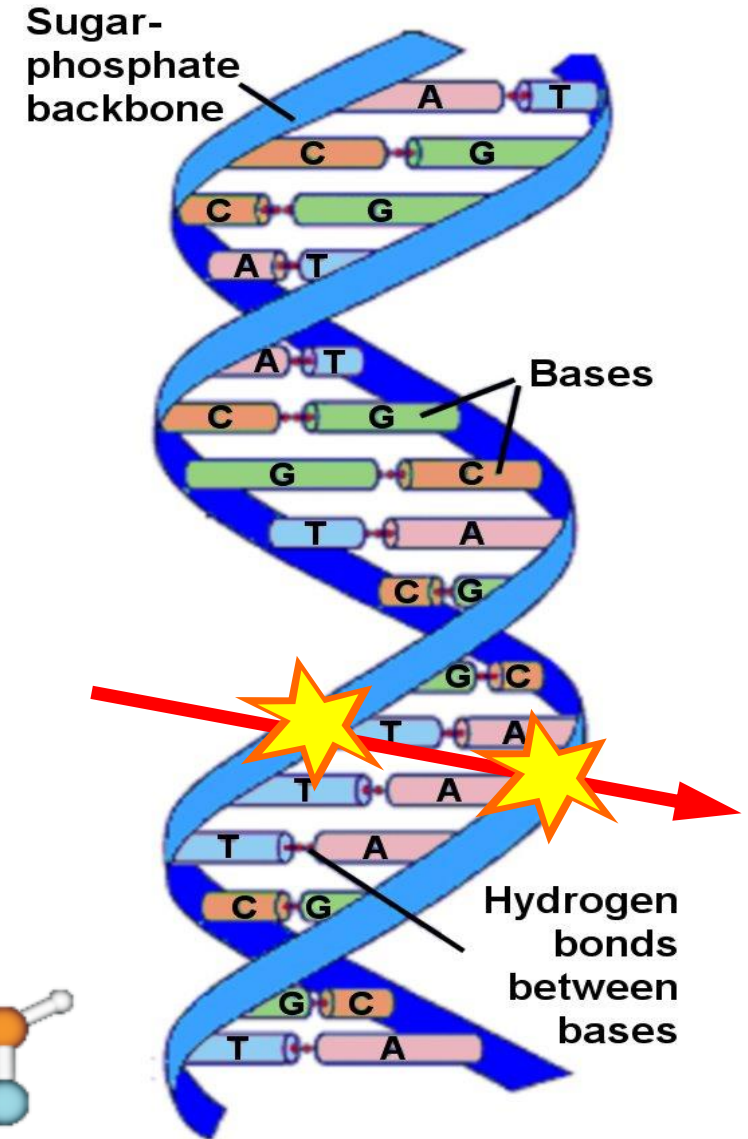
Cytosine



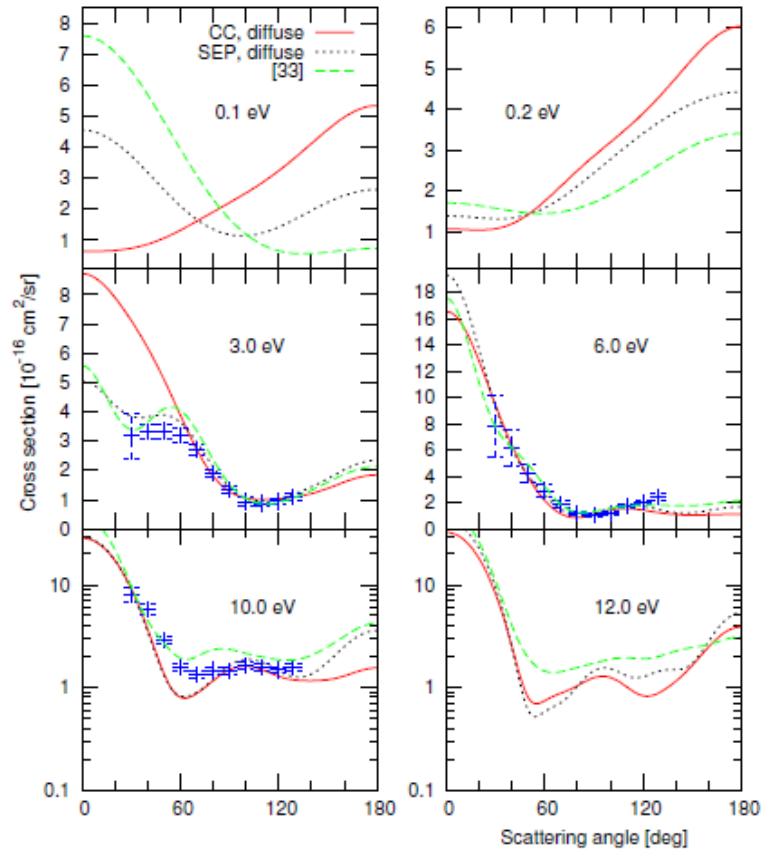
Uracil



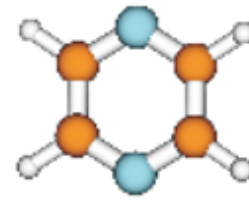
Pyrimidine



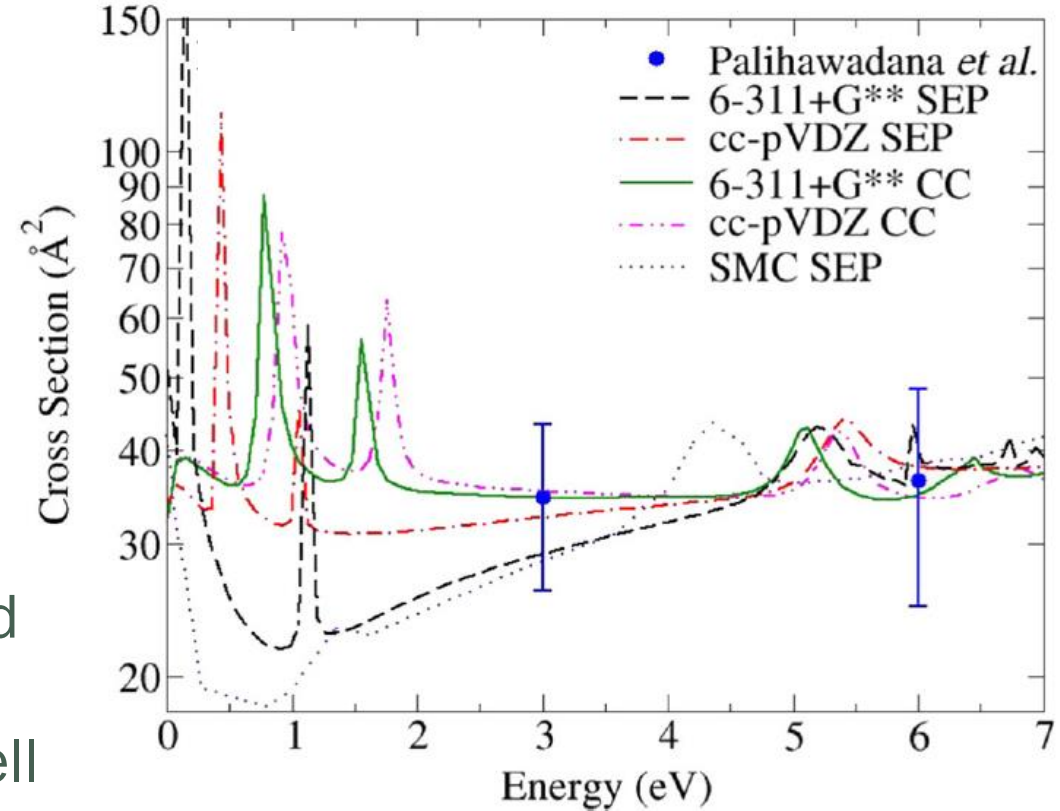
Elastic scattering from pyrazine



Elastic DCS



Elastic cross sections in good agreement if polarizability well described



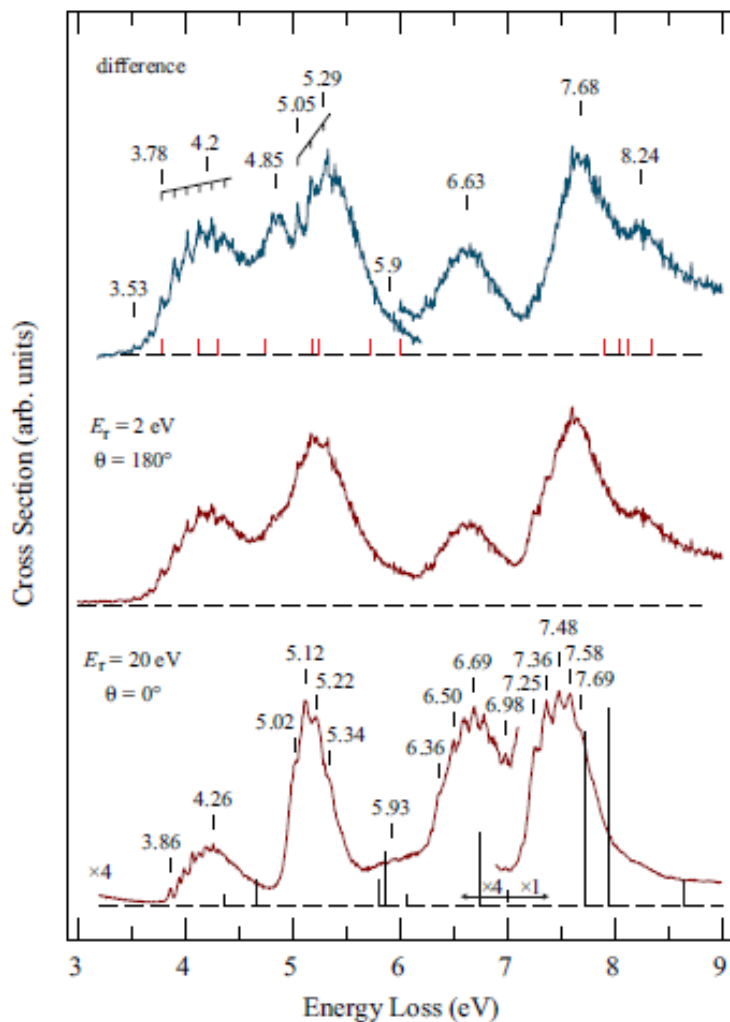
Integral elastic cross section

Experiment: Palihawadana *et al.*, *JCP* **137** (2012);
Theory: Winstead and McKoy *PRA* **76** (2007);

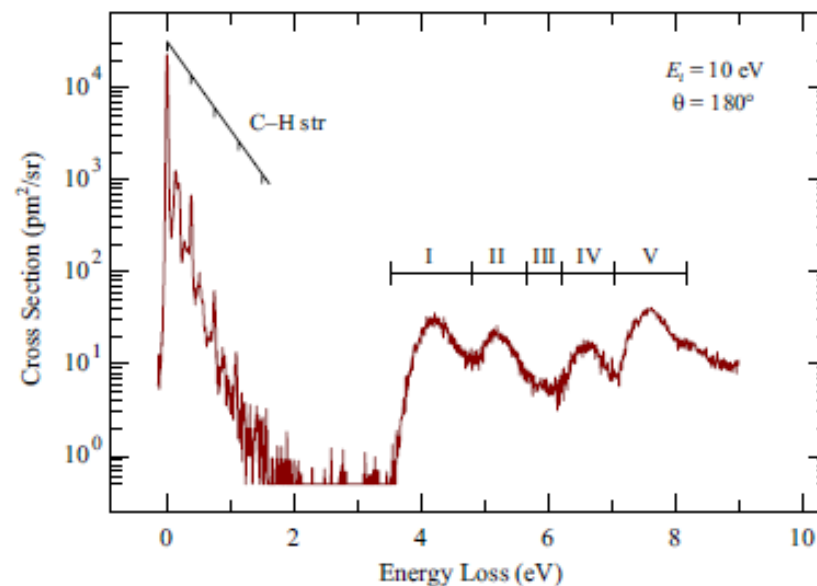
Z. Mašín and J. D. Gorfinkiel, *JCP* **137**, 204312 (2012), V. H. Graves and J.D. Gorfinkiel, *EPJD* (2022) **76**:43 <https://doi.org/10.1140/epjd/s10053-022-00371-0>

EELS: Pyrimidine

EELS: measurement of **absolute** electronic excitation cross sections using relative flow technique and accurate calculated cross sections for He.

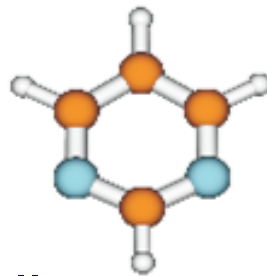


Representative EEL spectra

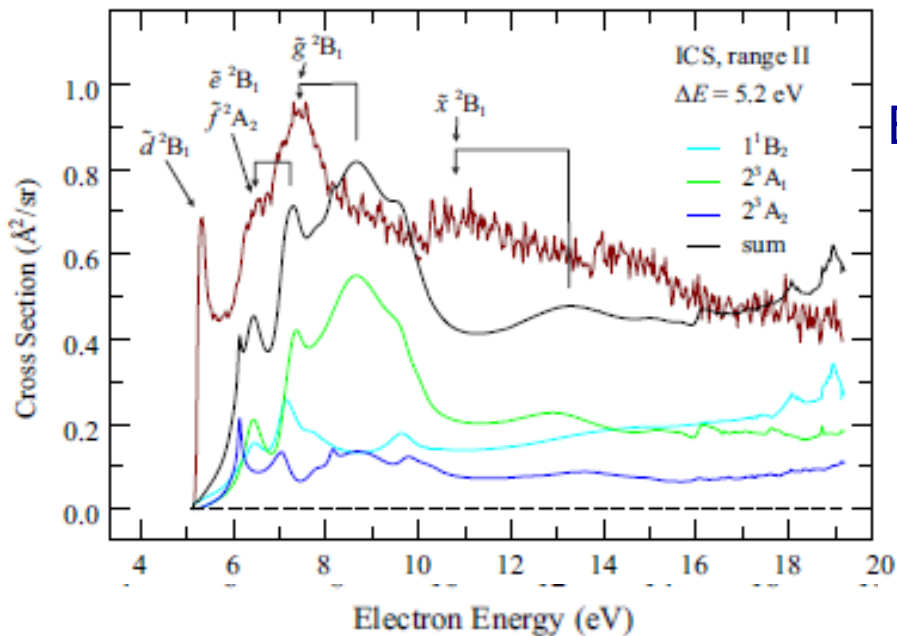
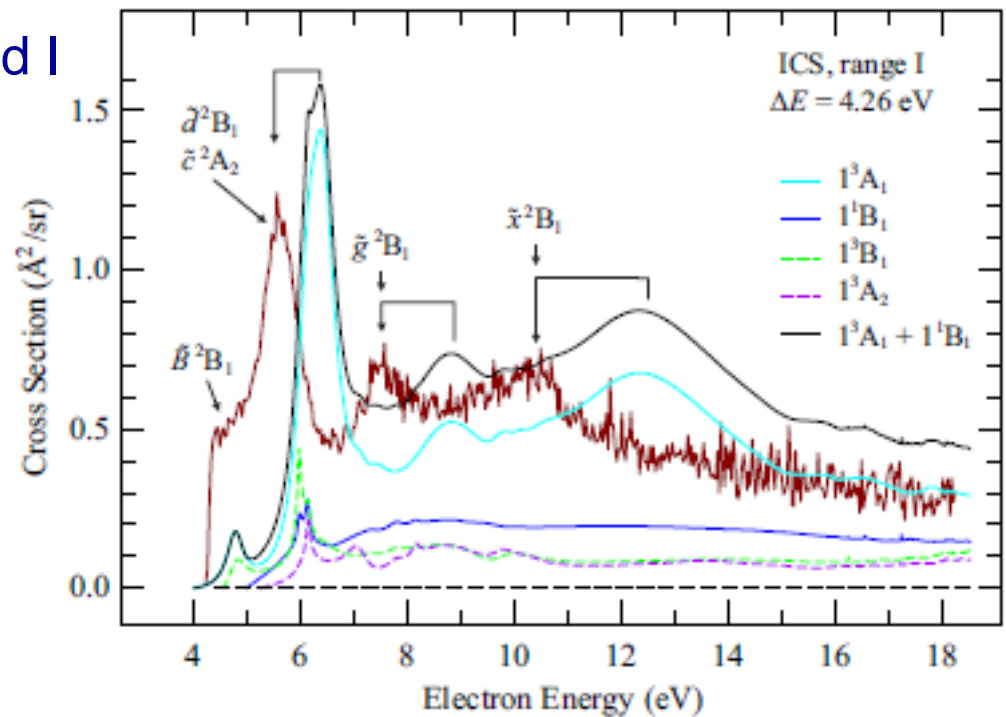


State overlap implies EEL measurements for **bands** not individual states.

Electronic excitation of Pyrimidine



Band I



Band II

- ✓ 42 electrons
- ✓ cc-pVDZ, SA-CASSCF
- ✓ CC calculation: 29 states
- ✓ GTO continuum ($l_{\max}=4$)
- ✓ C_{2v} point group

- Quantitative inelastic cross sections
- 7 core-excited shape resonances confirmed

Regeta et al, JCP **144** (2016)

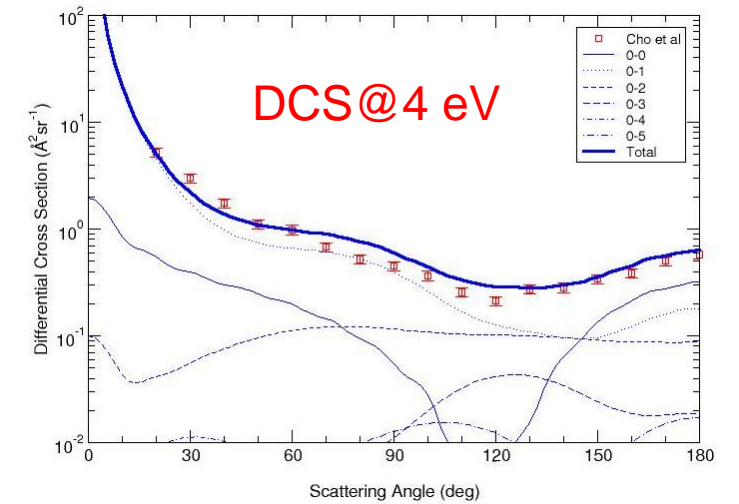
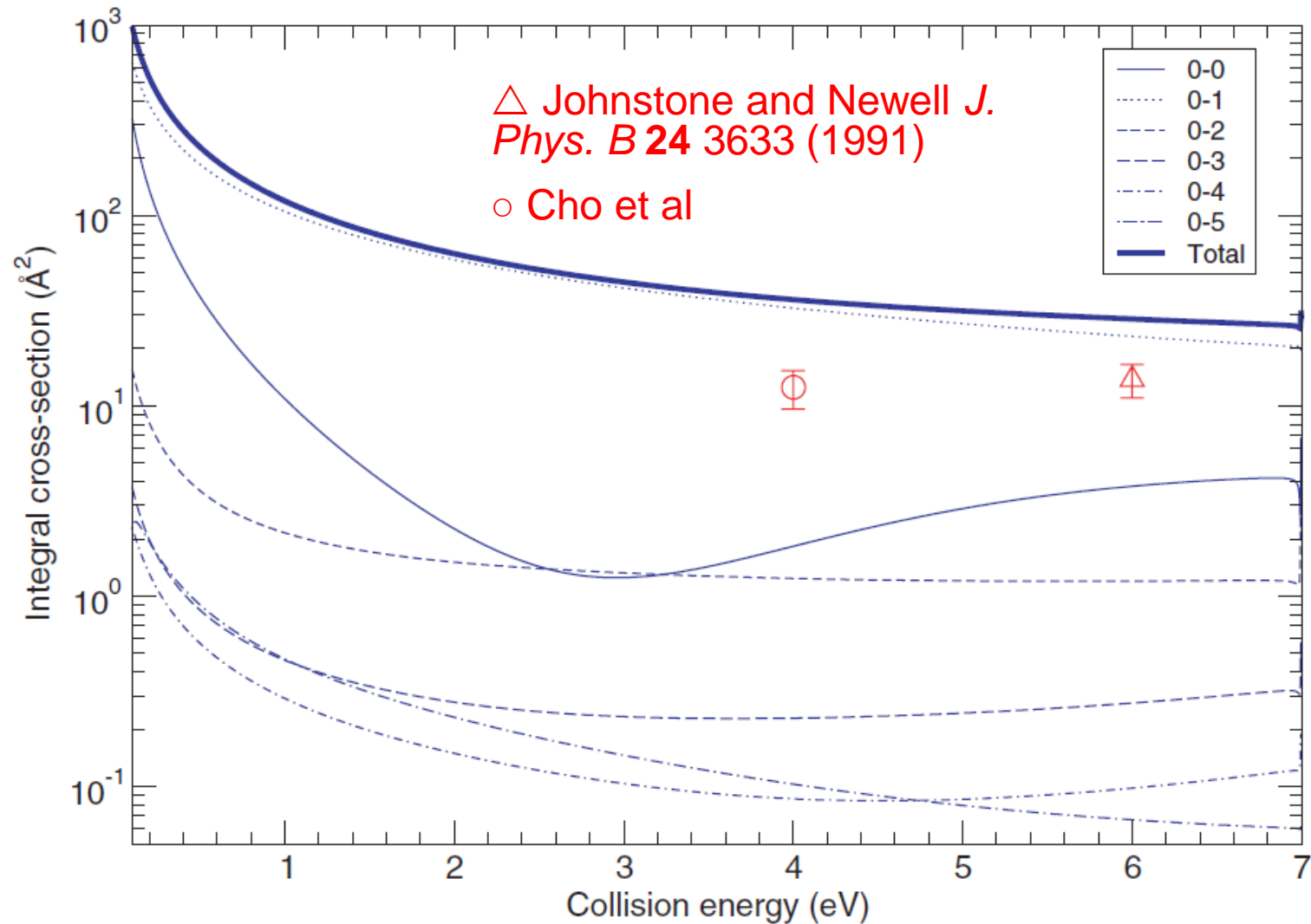
label	exp.	R-matrix	conf.	ETS ^a	ETS ^b
\tilde{X}^2A_2	0.27 ^c	0.53	2*	0.25 ^c	0.39 ^c
\tilde{A}^2B_1	0.70 ^d	0.96	1*	0.77	0.82
\tilde{B}^2B_1	4.35	4.78	3* + 1, 2* ² + 1, 1* ²	4.24	4.26
\tilde{a}^2A_1	-	5.96	$n-, 1^*2^*$	-	-
\tilde{b}^2A_1	-	6.15	$n-, 1^*2^*$	-	-
\tilde{c}^2A_2	5.55	6.11	1, 1*2* + 2, 2* ²	-	5.5
\tilde{d}^2B_1	5.55	6.37	2, 2*1* + 1, 1* ² + 1, 2* ²	-	5.5
\tilde{e}^2B_1	6.52	7.11	-	-	-
\tilde{f}^2A_2	6.52	7.33	-	-	-
\tilde{g}^2B_1	7.45	8.47	-	-	-
\tilde{x}^2B_1	10.3	12.3	-	-	-

Rotational excitation

- Adiabatic nuclei rotation (ANR) method (Lane 1980)
- Assumes that the electron loses no energy in the inelastic collision
- Cross-section is expressed as a partial-wave expansion
- For low partial-waves contribution from FN T-matrices obtained via the R-matrix calculations: electronically elastic scattering
- Born approximation to obtain the cross section for the high partial-waves not included in the FN T-matrices (Crawford & Dalgarno 1971). Essential for dipolar molecules
- Final cross-section calculated as the sum of two contributions: can be regarded as a short-range correction to the Born approximation

$$\frac{d\sigma_{j_0, \mathbf{P} \rightarrow j, \mathbf{P}_j}}{d\Omega} = |f_{j_0, \mathbf{P} \rightarrow j, \mathbf{P}_j}^B(\cos \theta)|^2 + \sum_{L=0}^{L_{max}} (A'_L - A_L^B) P_L(\cos \theta)$$

Rotational excitation of water



Disagreement between experiment and theory due to effect of dipole :
Experiment uses extrapolation procedure at forward angles
Theory needs top-up procedure to complete the partial wave expansion

Vibrational resolution in R-matrix calculations

Simple approach: use of **Franck-Condon factors** and equilibrium geometry (R_0) scattering data.

- ❑ Electronically inelastic scattering (and vibronically elastic)

Alternatively, **vibrational averaging (adiabatic nuclei, AN)**

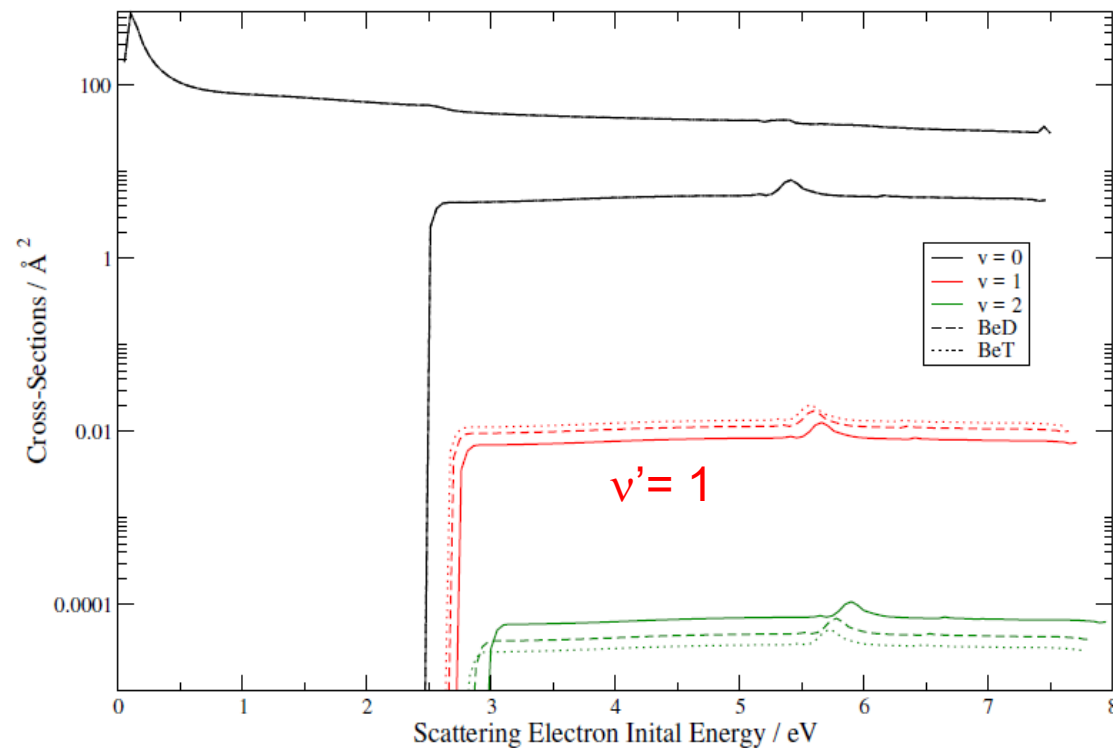
- ❑ No energy balancing: works best when electronic energy curves are parallel (energy difference is the same for all geometries)
- ❑ Can't model effect of resonances
- ❑ Used for diatomics but could in principle be used for normal modes of polyatomics
- ❑ Reduces to FN if T-matrix dependence on R where vibrational wf is non-negligible is small (no good near thresholds)

$$F_{i\nu_i f\nu_f} = \left| \int \chi(R)_{i\nu_i} \chi(R)_{f\nu_f} dR \right|^2$$
$$\sigma(i\nu_i \rightarrow f\nu_f) = \sigma(i \rightarrow f)(R_0) F_{i\nu_i f\nu_f}$$

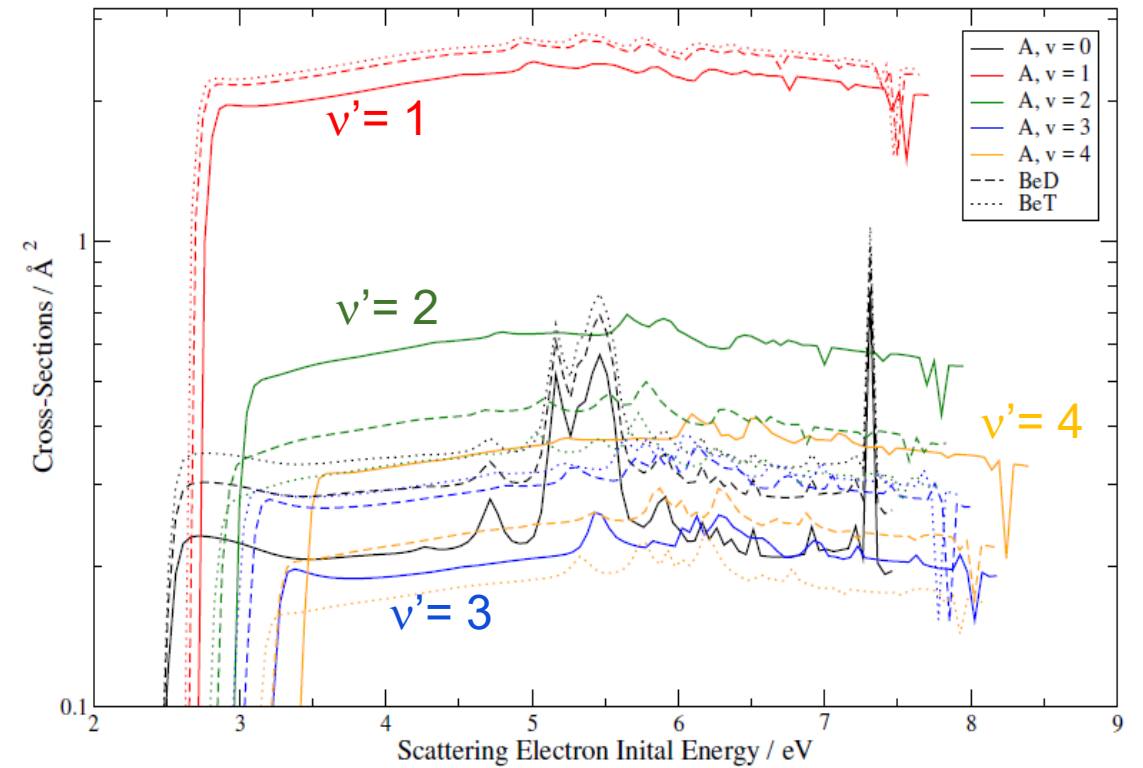
$$T_{l'v',lv} = \int \chi_{v'}(R)^{\text{FN}} T_{l',l}(R) \chi_v(R) dR$$

Vibrational resolution

- Transitions from ground vibronic state to lowest electronic excited state of BeH/BeD/BeT
- Size of vibrationally resolved cross sections very different for both models



FN



AN

Other low energy approaches

da Costa et al EPJD [69 159](#) DOI:
[10.1140/epjd/e2015-60192-6](https://doi.org/10.1140/epjd/e2015-60192-6)

Schwinger multichannel method (SMC)

- based on Lippmann–Schwinger integral equation
- applied within the FN approximation
- restricted to closed-shell molecular targets
- uses many strategies similar to R-matrix: GTOs used to bound and scattering orbitals, Hartree–Fock description for target state, Born top-up procedure...
- Elastic cross sections (integral and differential) of similar quality to R-matrix

SCMPP

- Analytic pseudopotentials used to describe the nuclei and core electrons
- Reduces computational cost
- Allows study of targets with electron-rich atoms (e.g. halogen atoms)

Other low energy approaches

Zammit et al 2017 JPB 50 123001
DOI 10.1088/1361-6455/aa6e74
Scarlett et al 2020 EPJD74 36
DOI 10.1140/epjd/e2020-100549-0

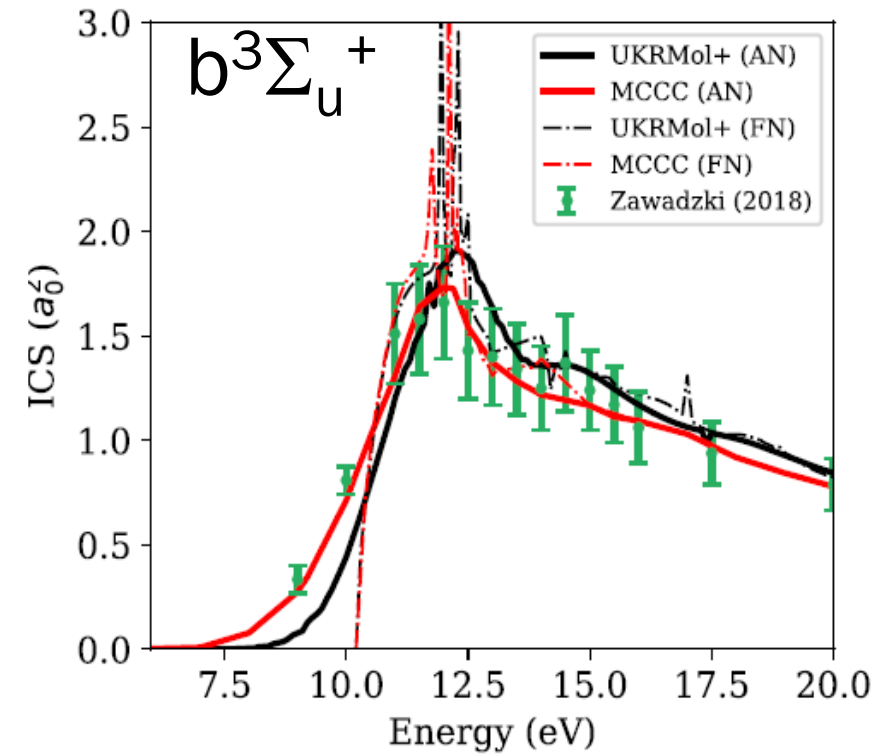
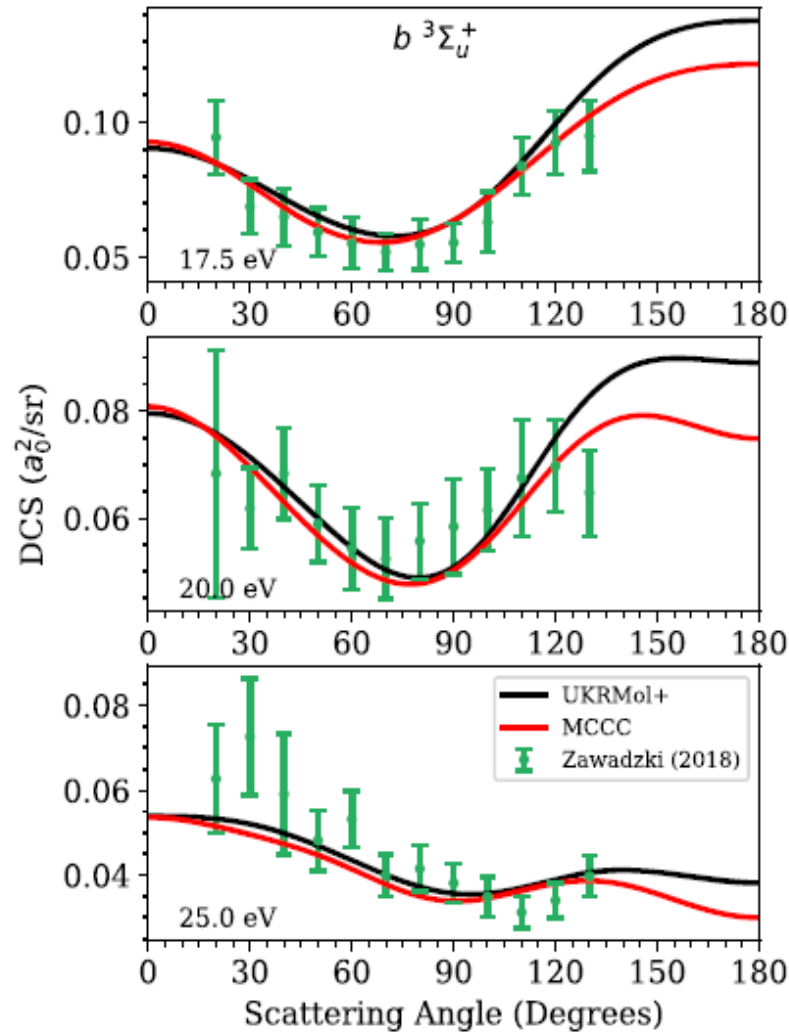
Convergent close-coupling (MCCC)

- For quasi-one and two-electron targets
- Uses close-coupling expansion
- Orbitals built from products of Laguerre polynomials, $\exp(-\alpha r)$ and spherical harmonic
- Works well at intermediate energies (pseudostates)
- Uses Born top-up
- Applied within the FN approximation but also beyond: AN for vibrationally resolved calculations
- Vibrational wavefunctions are obtained diagonalizing the vibrational Hamiltonian in a basis of above Laguerre functions
- Integral and differential cross-sections for elastic, vibration and electronic excitation, ionization and neutral dissociation



- Simplest multielectronic molecule
- High quality calculations available and converged

Excellent agreement between theoretical methods: UKRmol+ (R-matrix) and MCCC (molecular convergent close-coupling)



- ✓ 2 electrons
- ✓ t-aug-cc-pVTZ
- ✓ Full CI
- ✓ 98 target states
- ✓ $a = 100 a_0$
- ✓ B-splines only continuum

What is still hard at low energies

- Calculations for
 - very big or electron rich targets
 - vibrationally resolved cross sections for molecules with many vibrational modes
- Very accurate elastic cross sections for dipolar molecules
- Data for molecules not initially in their ground state
- Neutral dissociation and dissociative electron attachment (DEA) beyond triatomics (and even then....). Experiment can measure DEA (in general yields not cross sections) but neutral dissociation is very hard

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Harald Friedrich, Springer
- ▶ Roadmap on photonic, electronic and atomic collision physics: Light–matter interaction, Electron and antimatter interactions, Heavy particles: with zero to relativistic speeds (Journal of Physics B, Volume 52, Number 17, 2019, 171001-171003) <https://doi.org/10.1088/1361-6455/ab26dJ>
- ▶ Plasma Modeling, Methods and applications, Gianpiero Colonna and Antonio D'Angola Eds
IOP Publishing <https://doi.org/10.1088/978-0-7503-3559-1>

