

Electronic Excitation of Molecules by Electron Impact: The Experimental and Theoretical Situation

by

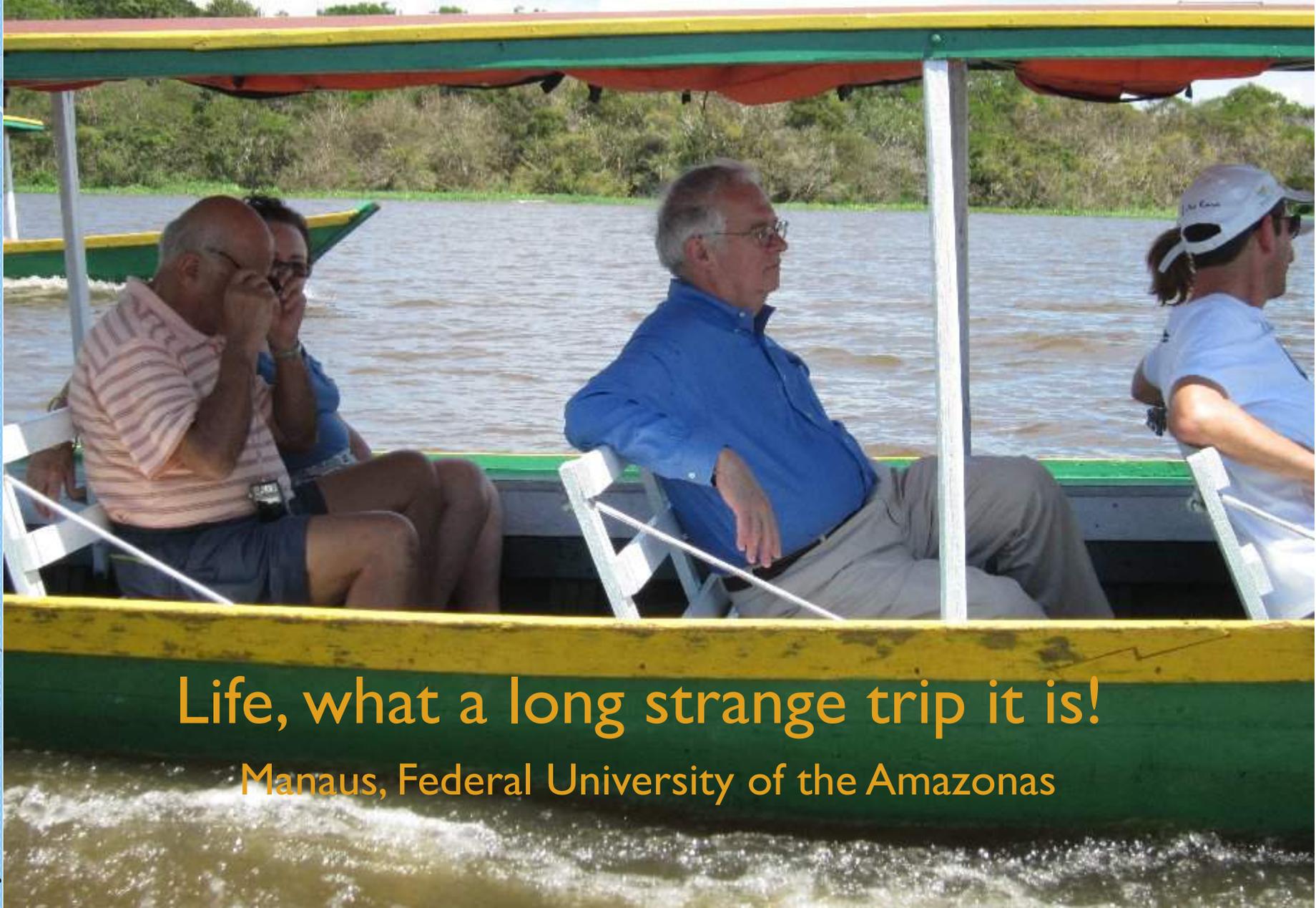
Marco A. P. Lima



UNICAMP

Honoring Prof. Vincent McKoy

Honoring Prof. Vincent McKoy



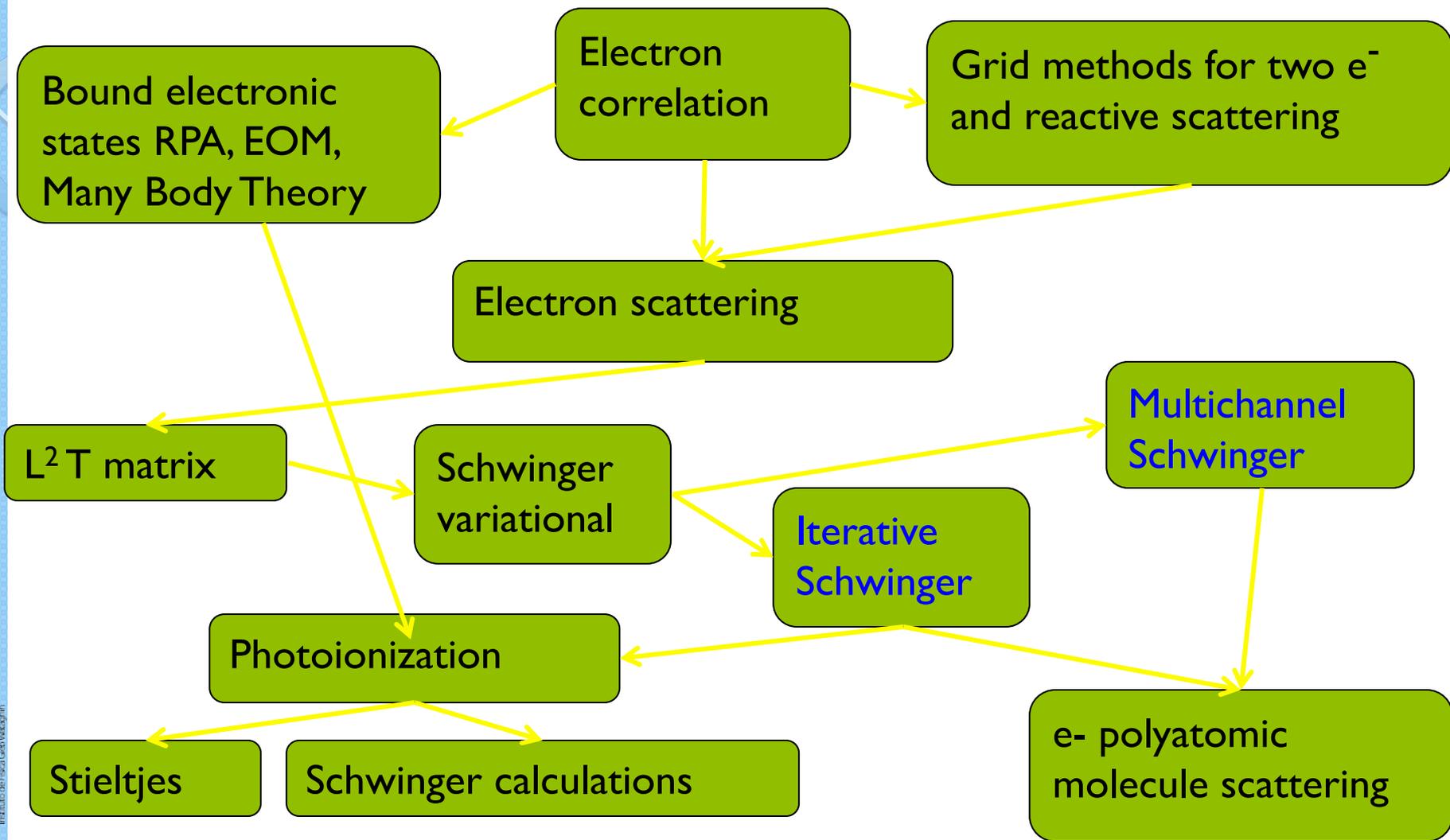
Life, what a long strange trip it is!

Manaus, Federal University of the Amazonas

IX ICPEAC July 1975 – Prof. McKoy had a long relationship with this community.



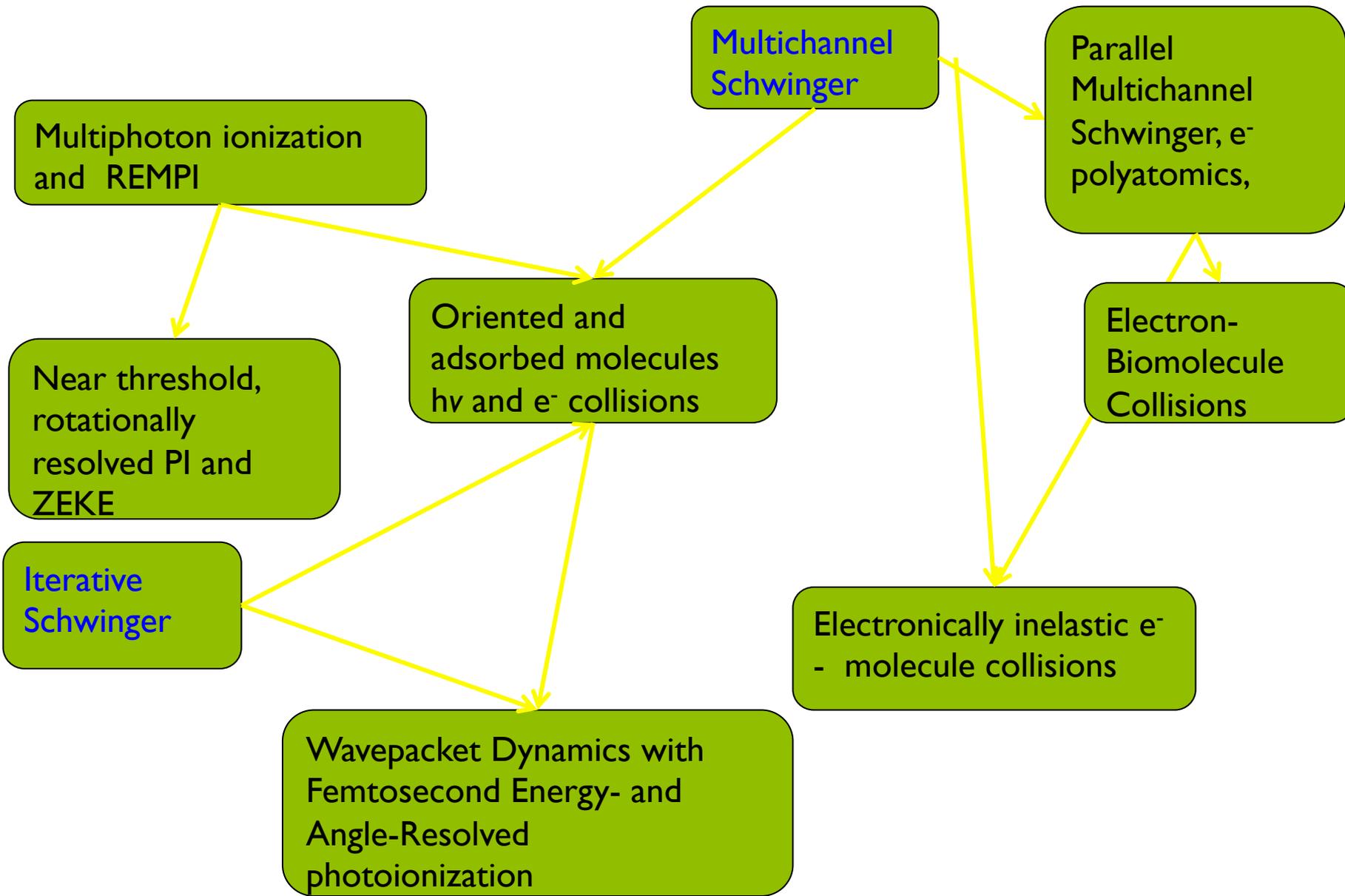
The flow of ideas of Vincent McKoy connected a lot of people.



This slide is a contribution from Bill McCurdy



The flow of ideas of Vincent McKoy connected a lot of people.



Honoring Vince

UFSCar

USP – UFABC – UFPR - UNICAMP

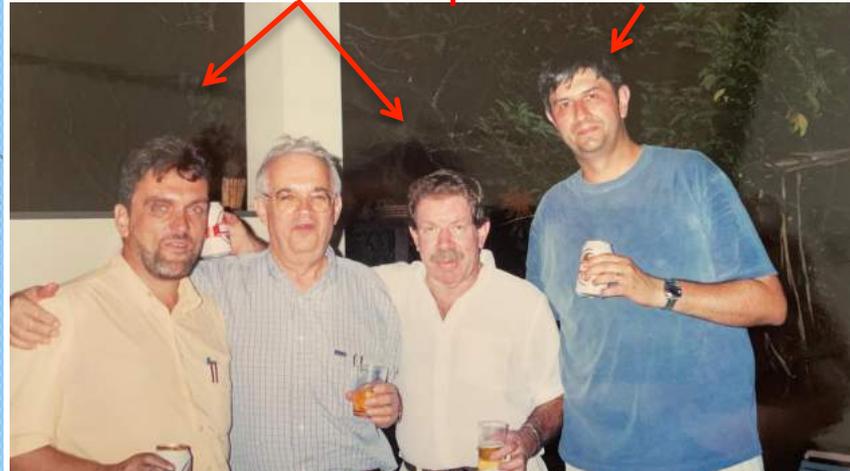


At lunch with director of CNPq, José Roberto Leite (USP, coordinator of the first collaboration agreement)

At Dinner with Scientific director of Fapesp, Carlos Brito Cruz, during visit of Kazuo Takatsuka

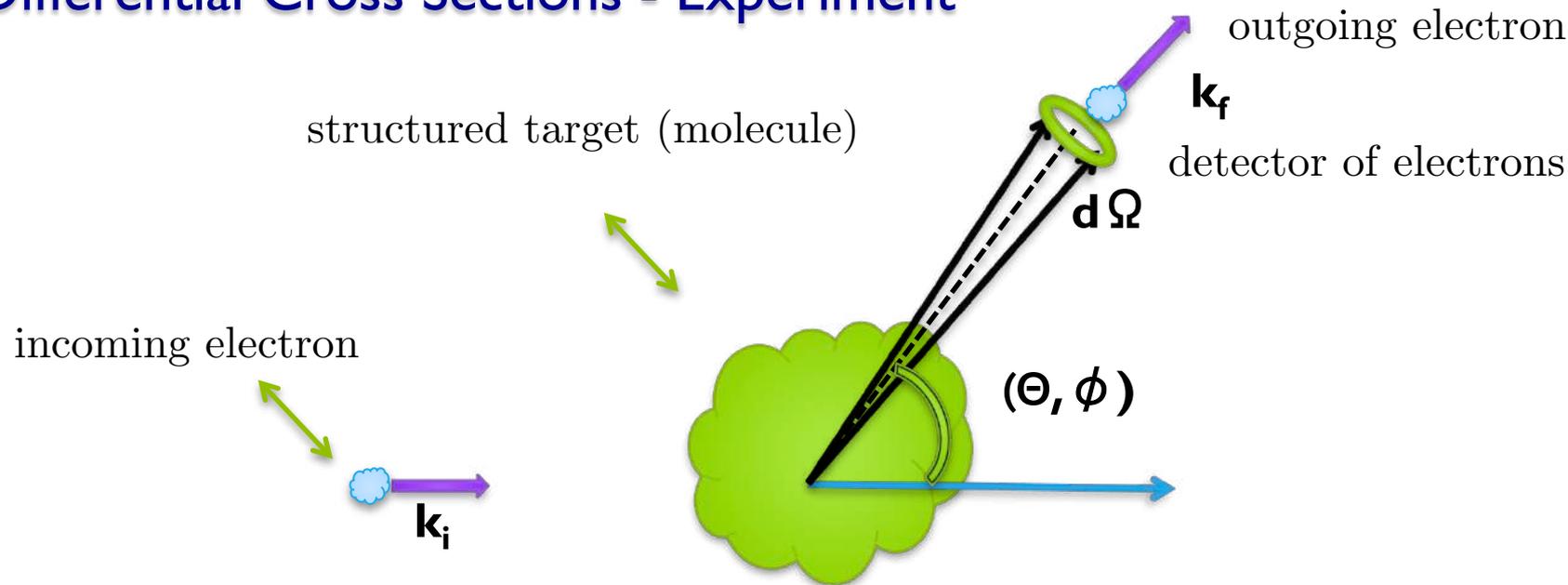
Unicamp

UFPR



UFSCAR and UFJF (influenced experiments in Brazil)

Differential Cross Sections - Experiment



$$dn \equiv \frac{\text{number of detected electrons}}{\text{unit of time}} \propto \begin{cases} \text{flux of incident electrons } F_i \\ \text{solid angle } d\Omega \end{cases}$$

The proportionality constant is the differential cross section:

$$dn = \frac{d\sigma^{i \rightarrow f}}{d\Omega} F_i d\Omega$$

$\frac{\# \text{ electrons}}{\text{unit of time}}$ $\frac{\# \text{ electrons}}{\text{time} \times \text{area}}$ solid angle

$\frac{\text{area}}{\text{solid angle}}$

Differential Cross Sections - Theory

- Time dependent Schrödinger equation ($N + 1$ electrons and N_α nuclei)

$$i\hbar \frac{d}{dt} \Psi_E(\mathbf{r}_1, \dots, \mathbf{r}_{N+1}, \mathbf{R}_\alpha, t) = H \Psi_E(\mathbf{r}_1, \dots, \mathbf{r}_{N+1}, \mathbf{R}_\alpha, t)$$



defines the structured molecular target

- Time independent Schrödinger equation solves the problem

$$\Psi_E = e^{-i\frac{E}{\hbar}t} \Psi_{\mathbf{k}_i}(\mathbf{r}_1, \dots, \mathbf{r}_{N+1}, \mathbf{R}_\alpha) \Rightarrow H \Psi_{\mathbf{k}_i} = E \Psi_{\mathbf{k}_i}$$

by applying the boundary condition

$$\Psi_{\mathbf{k}_i}(\mathbf{r}_1, \dots, \mathbf{r}_{N+1}, \mathbf{R}_\alpha) \xrightarrow{r_{N+1} \rightarrow \infty} \Phi_i e^{i\mathbf{k}_i \cdot \mathbf{r}_{N+1}} + \sum_f^{\text{open}} f_{i \rightarrow f}^B(\mathbf{k}_i, \mathbf{k}_f) \Phi_f \frac{e^{+ikr_{N+1}}}{r_{N+1}}$$

- The solution allows to obtain $f_{i \rightarrow f}^B(\mathbf{k}_i, \mathbf{k}_f) = -\frac{4\pi^2 m}{\hbar^2} \langle \Phi_f \mathbf{k}_f | V | \Psi_{\mathbf{k}_i}^{(+)} \rangle$
- Which is directly related to experiments, via differential cross sections,

$$\frac{d\sigma^{i \rightarrow f}}{d\Omega} = \frac{k_f}{k_i} |f_{i \rightarrow f}^L(\mathbf{k}_i, \mathbf{k}_f)|^2$$

Experimental and Theoretical requisites: molecular target description

target Hamiltonian

- Theory: the Hamiltonian is given by $H = \underbrace{\frac{p_{N+1}^2}{2m}} + \underbrace{H_N} + \underbrace{V}$, where the knowledge of

kinetic energy of the electron

potential electron-molecule

the target solution $H_N|\Phi_n\rangle = E_n|\Phi_n\rangle$ is the first step of calculation. The isolated target usually can be described in the Born-Oppenheimer (BO) approximation, where

$$\Phi_n(\mathbf{r}_i; \mathbf{R}_\alpha) = \underbrace{\Phi_{\text{elec}}(\mathbf{r}_i; \mathbf{R}_\alpha)} \underbrace{\Phi_{\text{nucl}}(\mathbf{R}_\alpha)}$$

electronic spectra

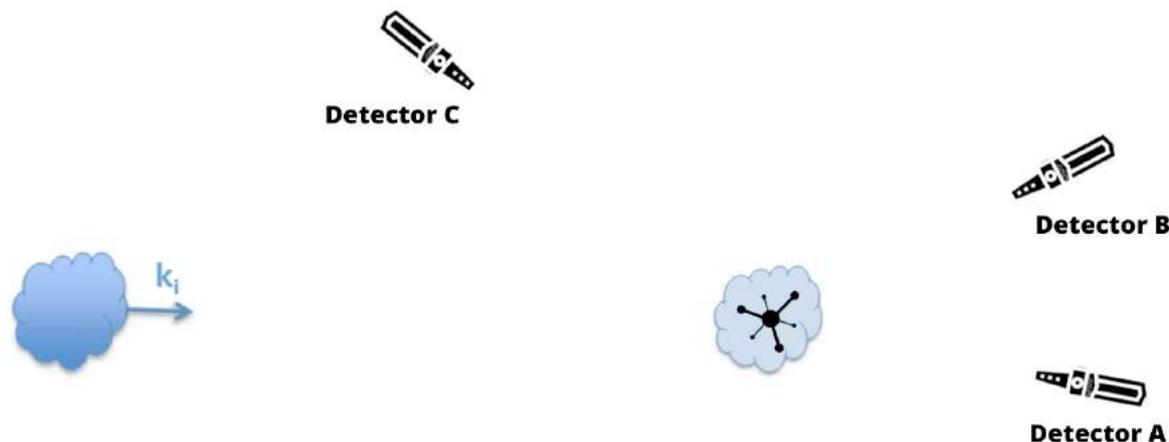
rotational and vibrational spectra

Justification for the BO-approximation: typical times of the electronic, vibrational and rotational transitions are very different

$$t_{\text{elec}} \approx 10^{-16} \text{ s} \ll t_{\text{vib}} \approx 10^{-14} \text{ s} \ll t_{\text{rot}} \approx 10^{-12} \text{ s}$$

- Experiment: measures energy loss of the scattered electron. This raises a very important question. *Which state is the target after the collision, considering that you only know the energy of the outgoing electron?*

The collision process



- What can happen? Any energy allowed composition of Rotational, Vibrational and Electronic excitations, including ionization, dissociation and combinations of all processes;
- Experimentalist: “They are all there, competing with each other, and I need to resolve the spectra in order to understand the measurements”;
- Theoretician: “I can run a multichannel calculation with a limited number of possibilities. BO approximation allows the separation of the processes, but resonances demand approximations beyond it”.

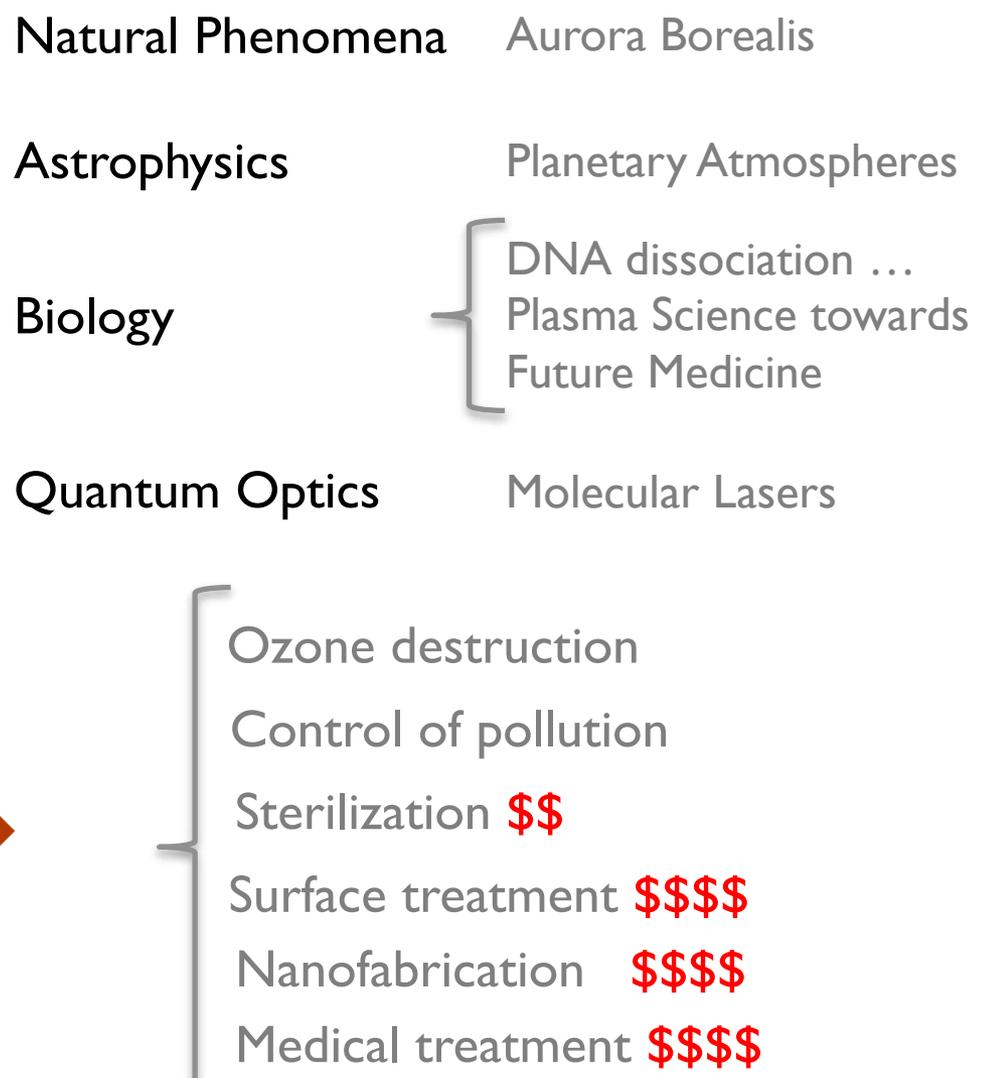
Electron scattering by Molecules

DISCHARGE ENVIROMENTS

This community was inspired by several basic science problems



and got further motivated by great applications



Surface treatment with Plasmas

Plasma
Processing
Gases

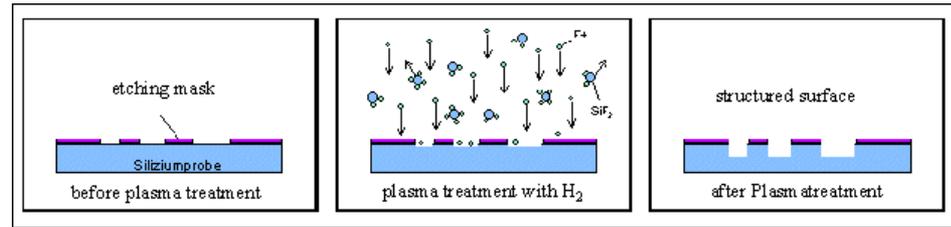


Several Industry Applications

Production
of reactive
species



ETCHING, DIAMANTIZATION,
POLIMERIZATION, NITRIDING,
CLEANING, and others



IMPROVEMENT NEEDS MODELING
AND MODELING NEEDS DATA



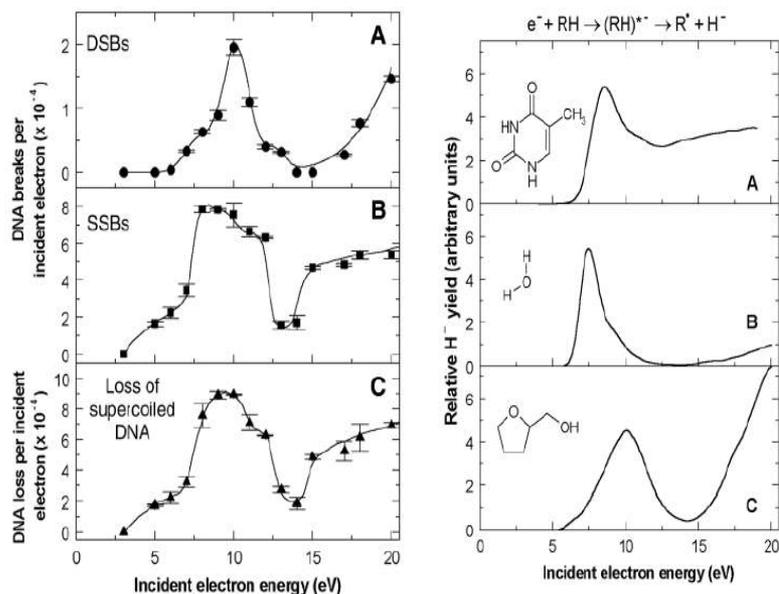
Electron collision
data: cross
sections for

Elastic
Inelastic: **electronic, rotational and vibrational excitation**
Ionization
Dissociation

Electron-Induced Damage to Biomolecules

Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons

Badia Boudaïffa, Pierre Cloutier, Darel Hunting,
Michael A. Huels,* Léon Sanche



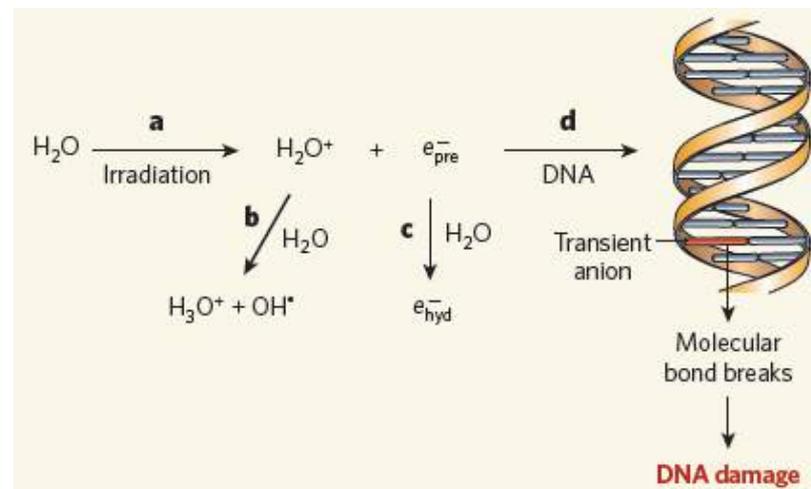
Science, **287** 1658 (2000)

BIOLOGICAL CHEMISTRY

Beyond radical thinking

Léon Sanche

Radiation-induced DNA damage has been attributed to hydroxyl radicals, which form when water absorbs high-energy photons or charged particles. But another product of water's radiolysis might be the real culprit.



Sanche, Nature **461**, 358 (2009)

J|A|C|S
COMMUNICATIONS

Chun-Rong Wang, Jenny Nguyen, and Qing-Bin Lu*

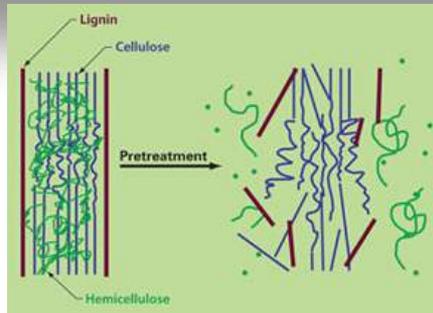
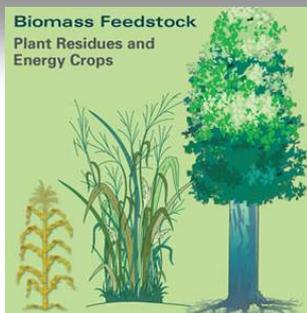
J. AM. CHEM. SOC. 2009, **131**, 11320–11322

SPECIAL MOTIVATION (Brazil)

Biomass is Made Up with Fermentable Sugars



First generation ethanol: crushing the cane for the juice



Experimental Cross sections for:

- Alcohol molecules: Morty Khakoo collaboration;
- Biomass components: Michael Brunger collaboration and his network.

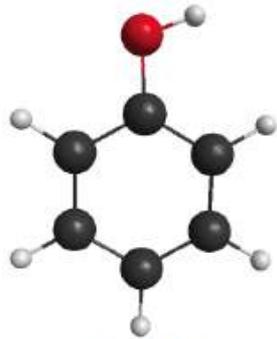
Plasma applications (Dr. Jayr Amorim) hosted by CTBE (National Lab for Bio-ethanol) with support of CNPq & Fapesp

Pretreatment: bio- and physical-chemical processes to expose the cellulose fibers

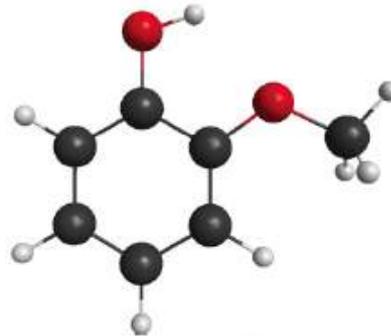
RAPID COMMUNICATIONS

Shape resonance spectra of lignin subunits

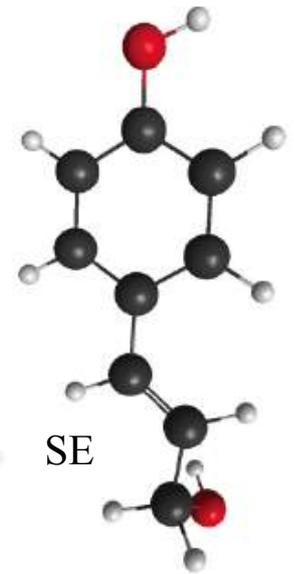
PHYSICAL REVIEW A **86**, 020701(R) (2012)



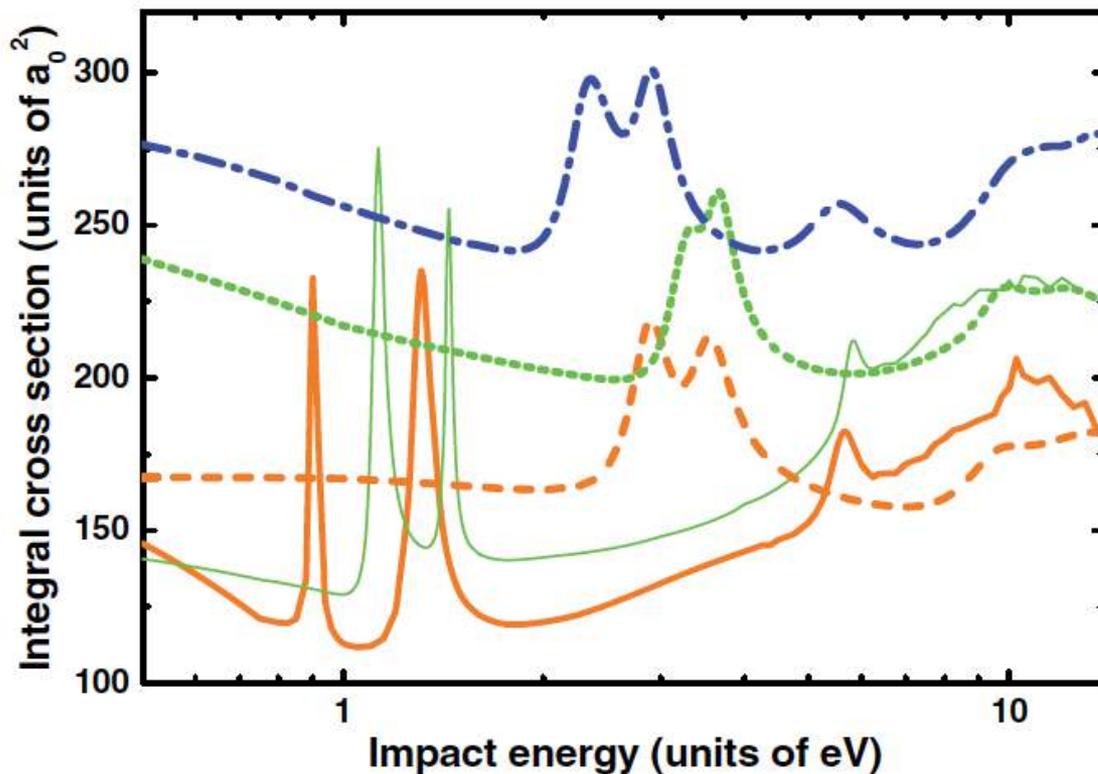
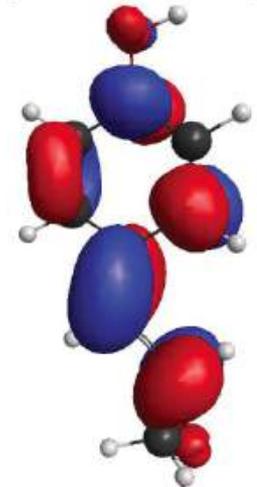
phenol



guaiacol



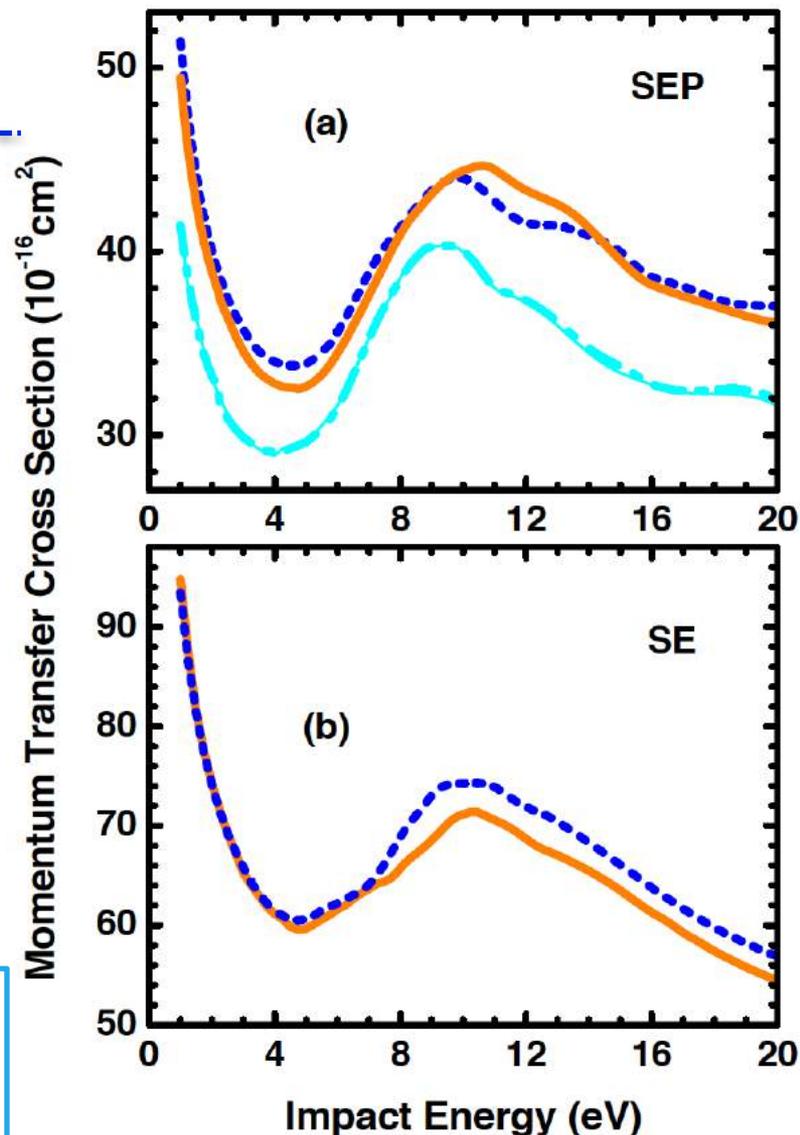
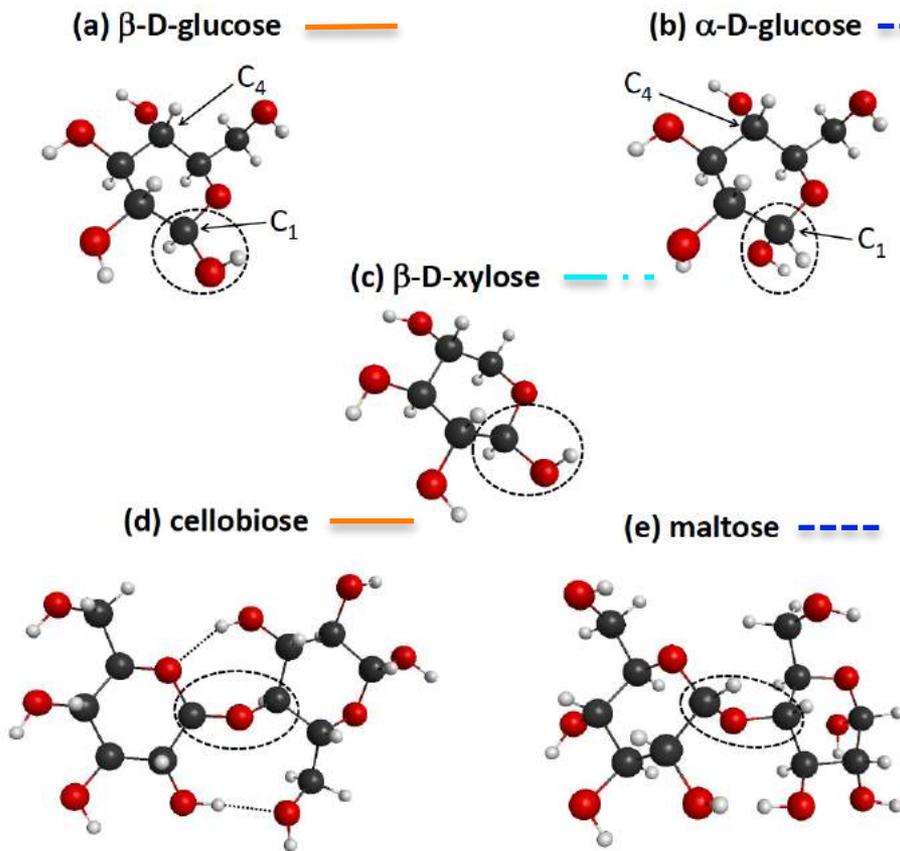
p-coumaryl alcohol
p-Cu (LUMO)



Lots of low-energy resonances!

Low-energy electron scattering by cellulose and Hemicellulose components

Phys. Chem. Chem. Phys. **15**, 1682 (2013).

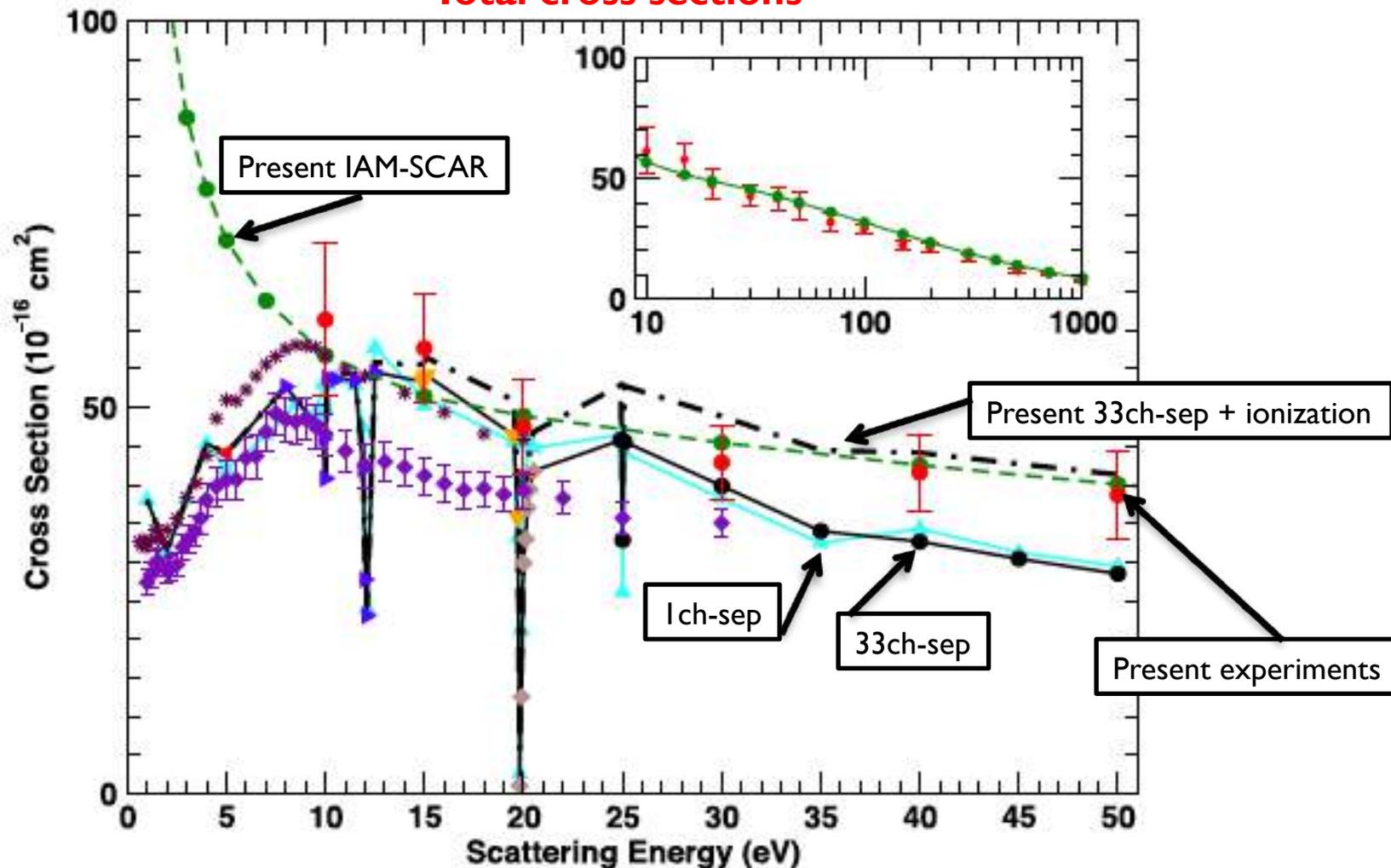


No low-energy resonances! Is this sufficient to explain why the discharge attacks the lignin and not so much the cellulose and hemicellulose?

Electron-phenol scattering: elastic, electronic excitation and total cross sections

- D. B. Jones, G. B. da Silva, R. F. C. Neves, H.V. Duque, L. Chiari, E. M. de Oliveira, M. C.A. Lopes, R. F. da Costa, M.T. do N.Varella, M. H. F. Bettega, M.A. P. Lima, and M.J. Brunger, *J. Chem. Phys.* **141**, 074314 (2014)
- R. F. da Costa, E. M. de Oliveira, M. H. F. Bettega, M.T. do N.Varella, D. B. Jones, M. J. Brunger, F. Blanco, R. Colmenares, P. Limão-Vieira, G. Garcia, and M.A. P. Lima, *J. Chem. Phys.* **142**, 104304 (2015).
- R. F. C. Neves, D. B. Jones, M. C.A. Lopes, K. L. Nixon, G. B. Da Silva, H.V. Duque, E. M. de Oliveira, R. F. da Costa, M.T. do N.Varella, M. H. F. Bettega, M.A. P. Lima, K. Ratnavelu, G. García, and M. J. Brunger, *J. Chem. Phys.* **142**, 104305 (2015).

Total cross sections



Message from Prof. Hiroshi Tanaka Experiments (Sophia University)

A message to all of EMS (2021) participants

Dear All of Friends

Marco, I appreciate your kindness, for giving me this kind of opportunity.

As you know, this year, 2021, we have celebrated the 100 Anniversary of Ramsauer-Townsend Experiment. That triggered the development of "Quantum Mechanics", of course, with Franck-Hertz Experiment. For centuries, "Concept of Quantum" extended to Quantum Chemistry, Solid State Physics, Fundamental Particle Physics, and so on. Our AMO theoretical and experimental in itself has changed our understandings of Universe, Biology, Technology, and so on. There have been, still and always, a growing demand for our filed.

According to my own experiences, for cross-section data to be applicable to any of those practical problems, they must fulfill the threefold requirement that the data be correct, absolute, and comprehensive. We need more computational and experimental collaboration; when it is experimentally difficult to obtain cross section, the computational approach may be applied to estimate the cross section, or vice versa. That reminded me of the Late Professor V. McKoy, having contributed so much in our community.

The AMO will stay forever, like "Renaissance Culture", in Science and Technology!!

Good luck and Wishing all of you success in the EMS 2021

Best wishes,

Hiroshi

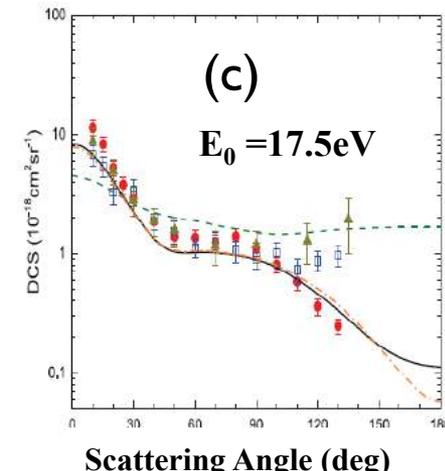
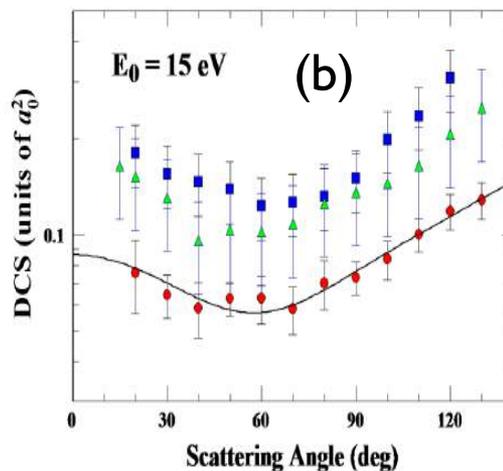
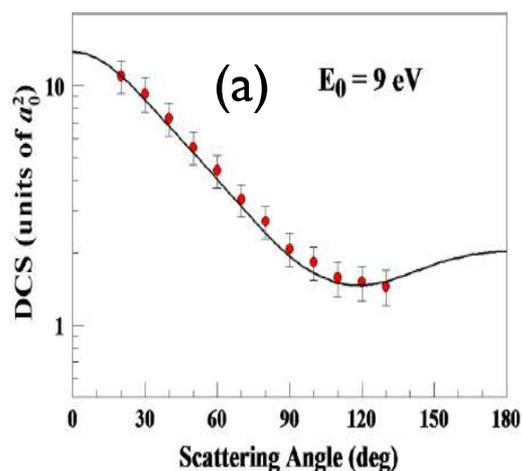
Message from Prof. Morty Khakoo Experiments (Fullerton University)

DIFFERENTIAL ANGLE ELECTRON SCATTERING FROM MOLECULAR TARGETS.

Recent Progress (Success):

Elastic and Inelastic Differential Cross Sections for H₂.

M. Zammit et al. PRL 116, 233201 (2016); Essentially exact solutions for scattering from H₂. Theory: Convergent Close-coupling Method (CCC; 2-electron systems only). Curtin University, Western Australia.



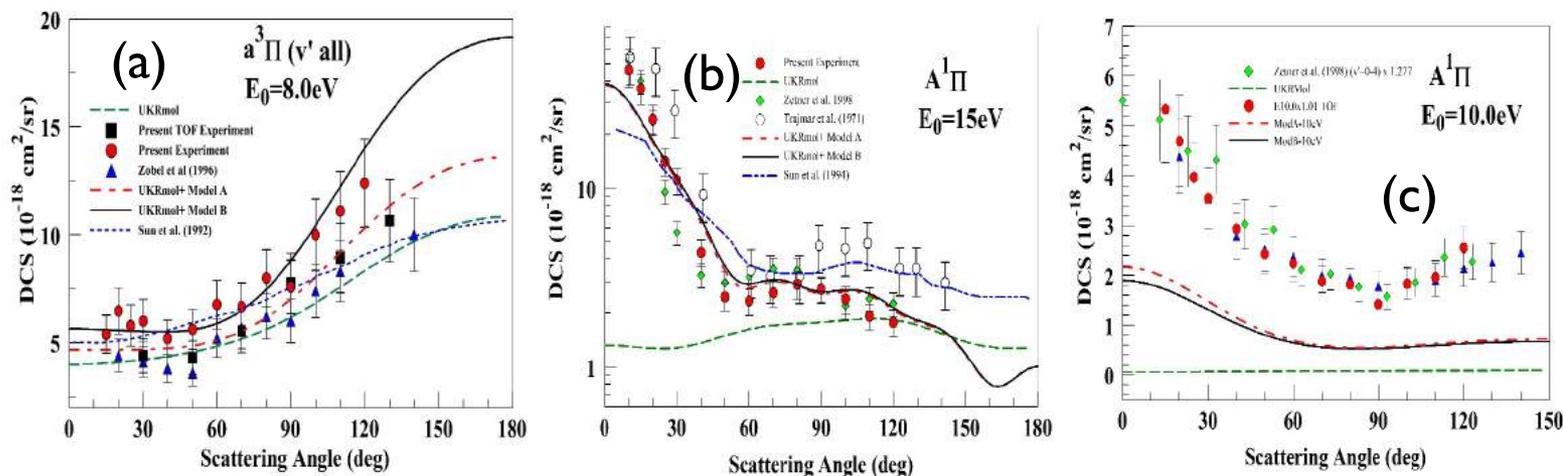
- (a) Elastic Scattering; • Experiment CSUF Muse et al. JPB 41 (2008) 095203; Theory CCC (2016) ———
- (b) Inelastic Scattering $b^3\Sigma_u^+$; • Experiment CSUF Zawadzki et al. PRA 98 (2018) 062704; Theory CCC (2016) ———
- (c) Inelastic Scattering $B^1\Sigma_u^+$; • Experiment CSUF Hargreaves et al. JPB 50 (2017) 225203; Theory CCC (2016) ———
- (d) and - - - - ; Theory R F da Costa et al. - - - - MCS *Min. Orb. Basis – for Sng. Config. Int.* (MOB-SCI) method.

DIFFERENTIAL ANGLE ELECTRON SCATTERING FROM MOLECULAR TARGETS.

Recent Progress (Mixed):

Elastic and Inelastic Differential Cross Sections for CO.

J. Tennyson, Z. Masin and A. Dora. UCL London, UK.



Inelastic Scattering $a^3\Pi$; • Experiment CSUF Zawadzki et al. JPB 53 (2020) 165201;

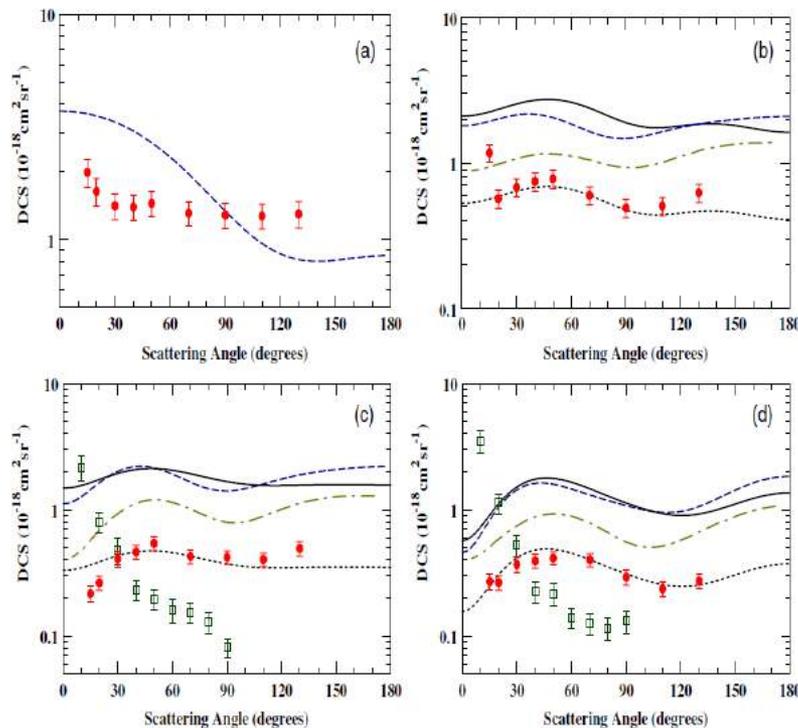
— Theory Rmatrix UKR Mol +

(a) $a^3\Pi$ near threshold E_0 ; (b) $A^1\Pi$ above threshold E_0 ; (c) $A^1\Pi$ near threshold E_0 .

DIFFERENTIAL ANGLE ELECTRON SCATTERING FROM MOLECULAR TARGETS.

Recent Progress (Needs future work):

Elastic and Inelastic Differential Cross Sections for H₂O. Hargreaves et al. 2012 JPB 45



Inelastic Scattering H₂O a³B₁; • Experiment CSUF Hargreaves et al. JPB 45 (2012) 201001; — Theory Schwinger MC (a) 9 eV, (b) 12 eV, (c) 15 eV and (d) 20 eV. Theory is scaled onto experiment: Scaling factors are large : 0.25(b); 0.20(c); 0.27(d).

Initiatives for Differential Angle Electron Excitation of Molecules.

1. CCC restricted to 2-electron systems. So future progress for larger diatomics and polyatomic molecules will need to come from Rmatrix (close-coupling) and MCS (perturbative) theoretical models. Presently the Rmatrix has also shown excellent agreement in H_2 (recent collaboration between UCL and Curtin/ Los Alamos).
2. Presently, agreement with Rmatrix method for CO and N_2 for excitation of *valence states* looks good and also is showing promising improvement for overall agreement. Agreement for diatomics using MCS is also good, and showing similar promising improvement. More work on this from world-wide groups.
3. Presently, agreement with Rmatrix method for CO and N_2 for excitation of *Rydberg states* looks poor; this is similar for MCS Theory. It needs to improve. Should tackle homonuclear diatomics: N_2 , O_2 and heteronuclear diatomics CO, NO regarding *Rydberg* states in collaboration with Rmatrix and MCS methods. *Rydberg states* important because majority of dipole-allowed (radiative) transitions are *Rydberg* \rightarrow Ground State.
4. *Excitation of polyatomics is a daunting challenge!* Presently this is inhibitive for close-coupling methods due to much-raised target centers + electrons (and thus electronic, vibrational and rotational channels!). Much better chances with perturbative methods especially the MCS method (with pseudo-states) which restrict number of open channels. Should tackle triatomics e.g. CO_2 , H_2O , N_2O , NO_2 and notable aromatic hydrocarbons (e.g. methane, ethane, ethylene, acetylene, etc.) and aliphatic hydrocarbons (e.g. benzene and its derivatives) plus furan and its simple derivative biomolecules.

Message from Prof. Michael Allan Experiments

Electronic excitation of noble gasses by electron impact

Dramatic progress has been achieved by **Klaus Bartschat** and **Oleg Zatsariny** with their Breit–Pauli B-spline R-matrix method with non-orthogonal orbital sets.

The Fribourg experiment provided suitable data for comparison:

- Absolute differential cross sections
- All scattering angles, 0° - 180°
- Data down to very close to threshold (≈ 20 meV)
- Good resolution (≈ 15 meV) to resolve sharp resonant features

The original version of the theory did not include relativistic effects. It was spectacularly successful for Ne, as shown on the next slide.

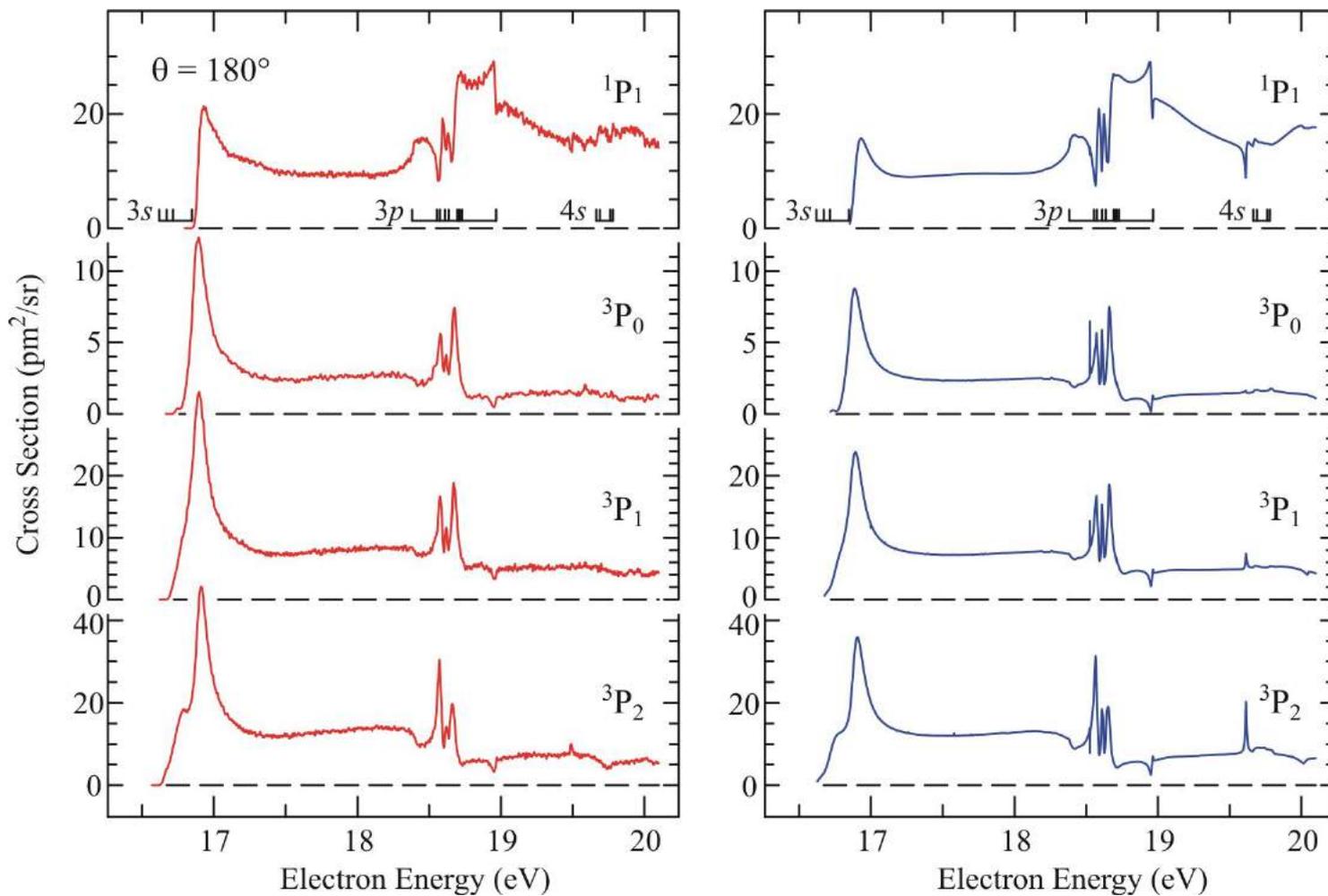
Note that:

- The vertical scales, i.e., the absolute values, are independent for theory and experiment. The absolute values of the cross sections agree very well.
- The data refers to the scattering angle of 180° , non trivial both for experiment and theory.
- The positions, widths and shapes of the sharp resonant features agree very well.
- The cross sections plotted as a function of scattering angle also agree well.

The calculations were later extended to a fully relativistic Dirac B-spline R-matrix (DBSR) framework. An example of the theoretical and experimental data for Kr and Xe is shown below. The capacity of theory to reproduce both the absolute values and the intricate details of the narrow resonant structures is excellent.

Ne

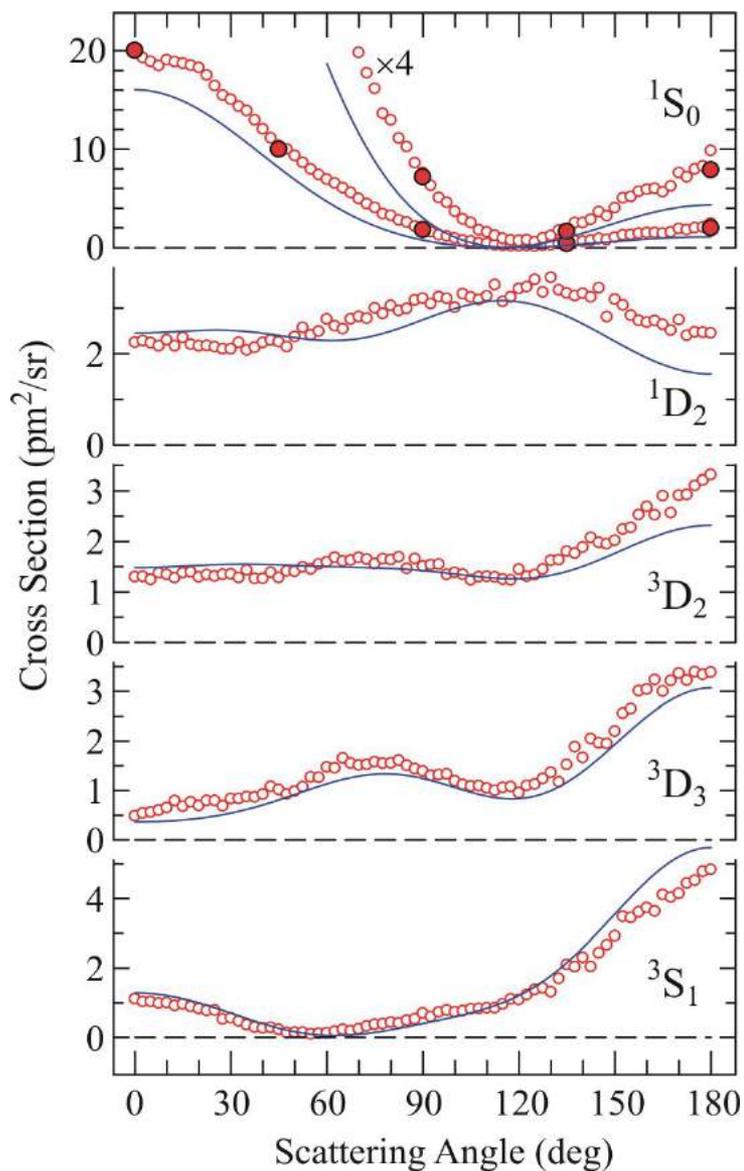
Absolute cross sections for excitation of the Ne ($2p^53s$) states at $\theta = 180^\circ$.



M. Allan, K. Franz, H. Hotop, O. Zatsarinny, and K. Bartschat: $\left\{ \begin{array}{l} \text{J. Phys. B 2006, 39, L139} \\ \text{J. Phys. B 2009, 42, 044009} \end{array} \right.$

Ne

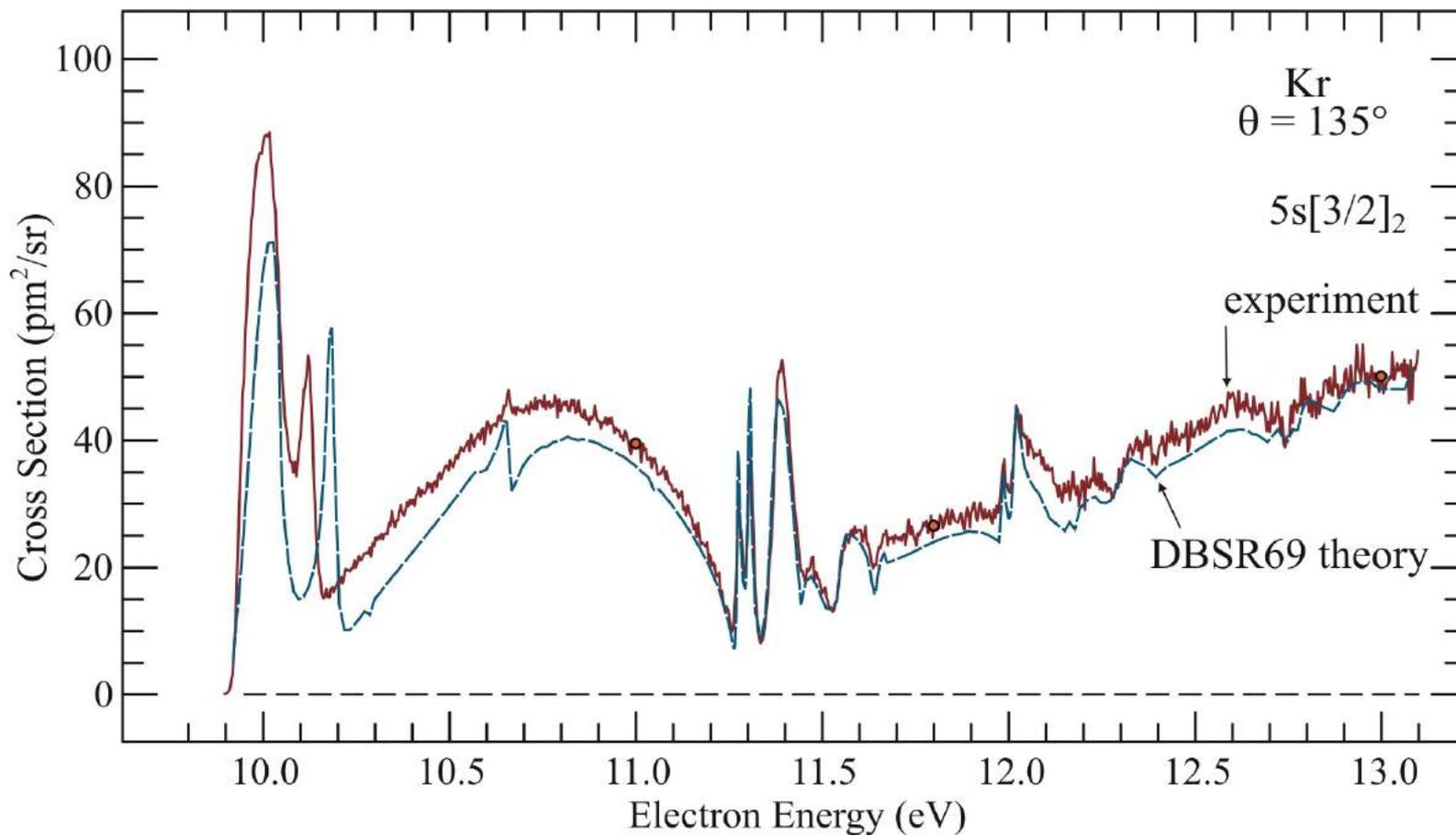
Angle-differential cross sections
for excitation of the Ne
($2p^5 3p$) states at $E = 19.3$ eV.



M Allan, K Franz, H Hotop,
O Zatsarinny and K Bartschat
2008

Kr

Absolute cross sections for excitation of the Kr ($4p^55s$) states:
high-resolution electron scattering experiments and B-spline
R-matrix calculations.

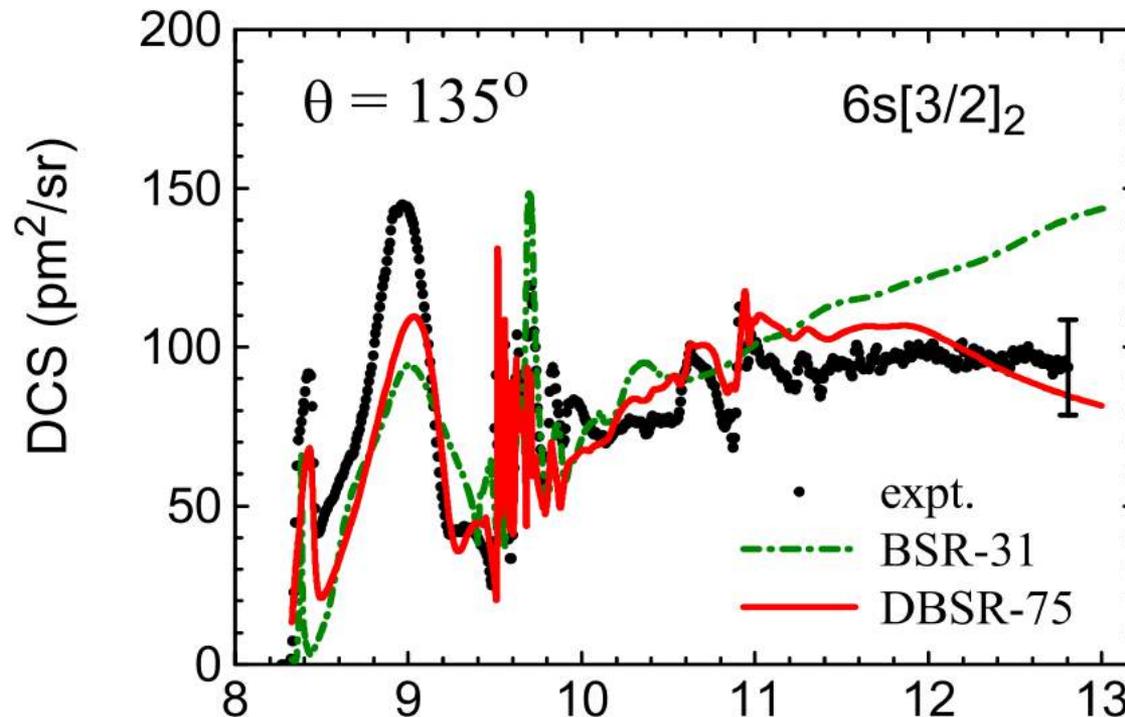


M. Allan, O. Zatsarinny, K. Bartschat: *J. Phys. B* **44**, 065201 (2011); *J. Phys. Conf. Ser.* 2012, 388, 042017;
Phys. Rev. A 2011, 83, 032713

Xe Absolute cross sections for excitation of Xe at $\theta = 180^\circ$

Experiment: black dots

best theory: red line



M. Allan, O. Zatsarinny and K. Bartschat, Phys. Rev. A 2006

Oleg Zatsarinny and Klaus Bartschat, J. Phys. B 2010

Conclusion for atoms:

- Spectacular success of the DBSR theory

Challenges for the future:

- Extend work to other interesting (but hard-to-measure) atoms, Fe etc.
- Extend the calculations to small molecules?

Electronic excitation (EE) of polyatomic molecules by electron impact

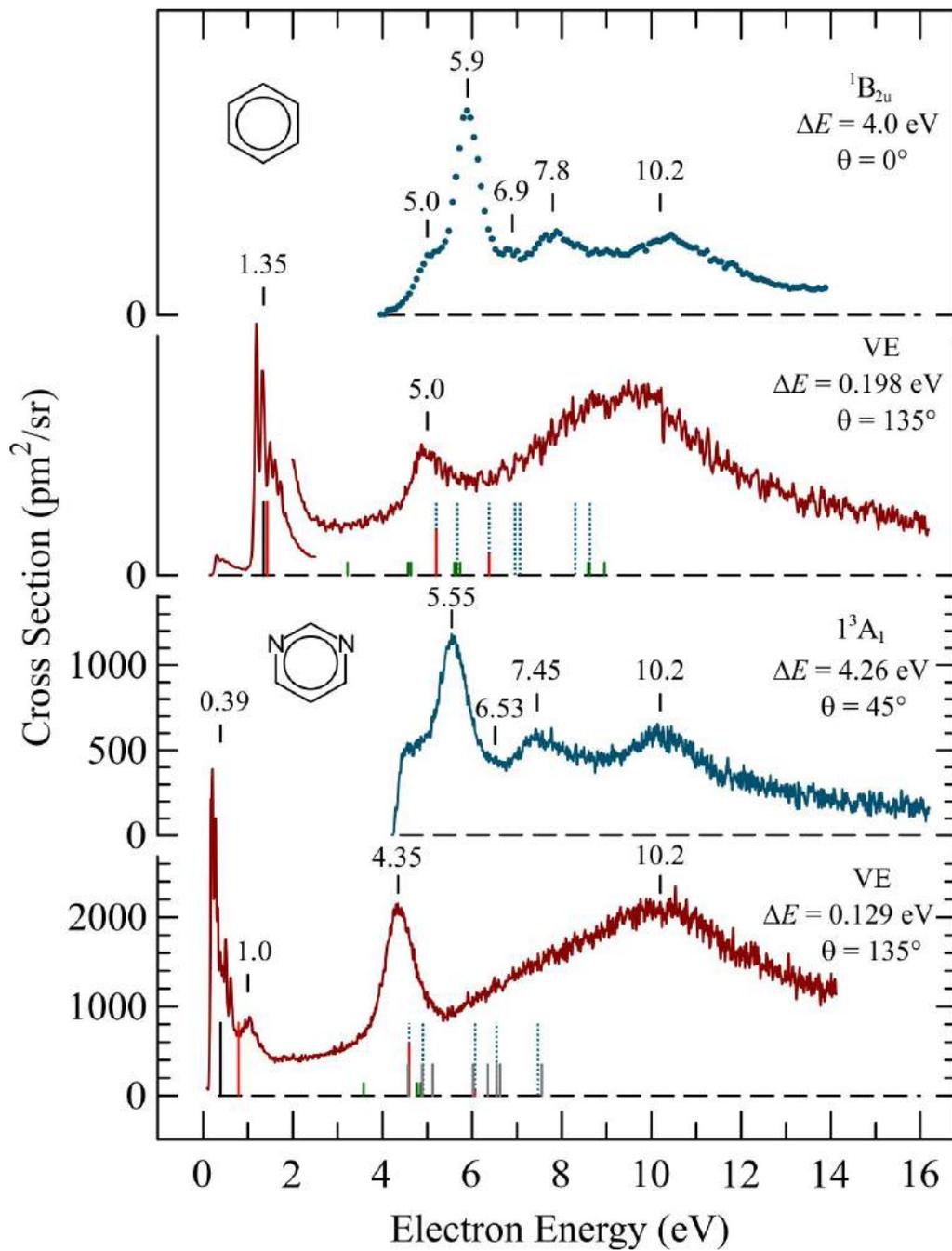
Relevance:

Initial step in electron-impact induced chemistry



History:

- I measured my first electronic excitation cross section (in benzene) in 1982 (Helv. Chim. Acta 65, 2008 (1982))
- Instrument (magnetically collimated spectrometer) was unsatisfactory: Cross sections were not absolute, only one scattering angle.
- The spectra showed fascinating resonances which I would have liked to understand. (see next slide)
- But no calculations were available to satisfy my curiosity.
- The next slide shows the old EE cross section of benzene (top curve; data from 1982), compared to more recent data of pyrimidine.
- Vibrational cross sections are shown for comparison; they indicate the shape resonances.
- Note the resonances: they are very similar in benzene and pyrimidine.



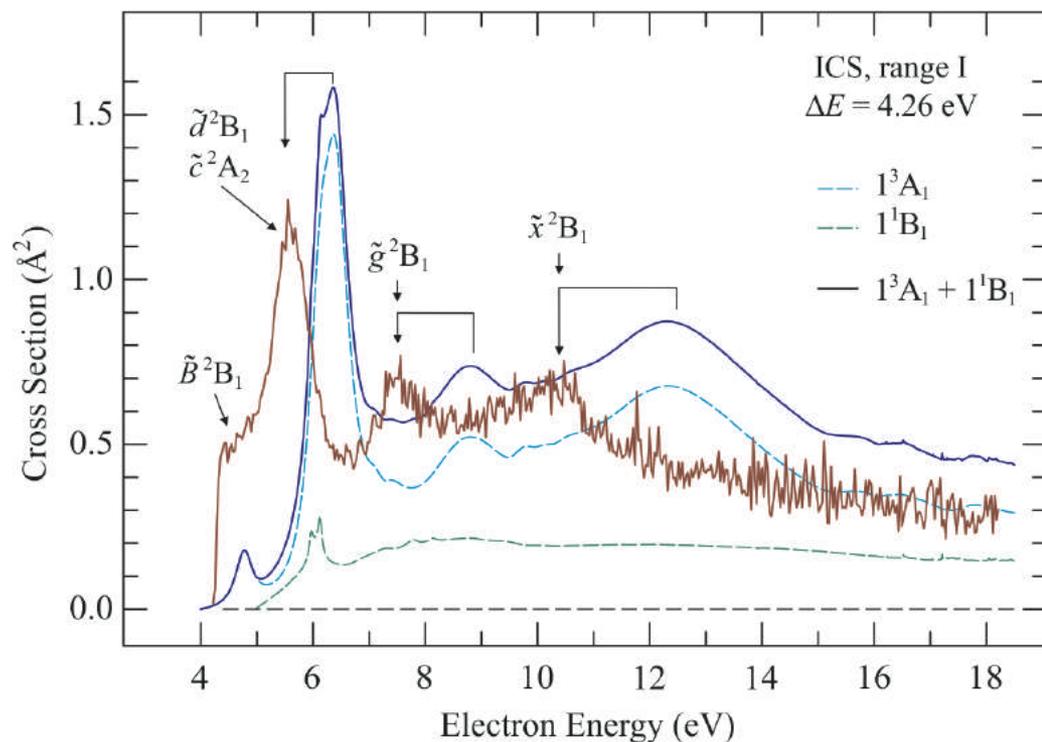
Benzene

Pyrimidine

Pyrimidine

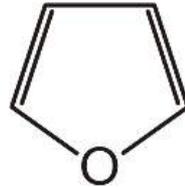
Pyrimidine:

- Red line: Experiment.
- Dark blue, solid line: Theory, sum of the cross sections for two final states which overlap and thus cannot be resolved experimentally.
- Green and blue-green lines: The cross sections for the two final states, shown individually.
- The four resonances discerned in the experiment are reproduced by the theory.
- Theory provides assignment of the resonances.
- The resonances are calculated too high. This is excusable because the reason is known: it is insufficient polarizability of the target.



Khrystyna Regeta, Michael Allan, Zdeněk Mašín, and Jimena D. Gorfinkiel

J. Chem. Phys. 2016



Furan:

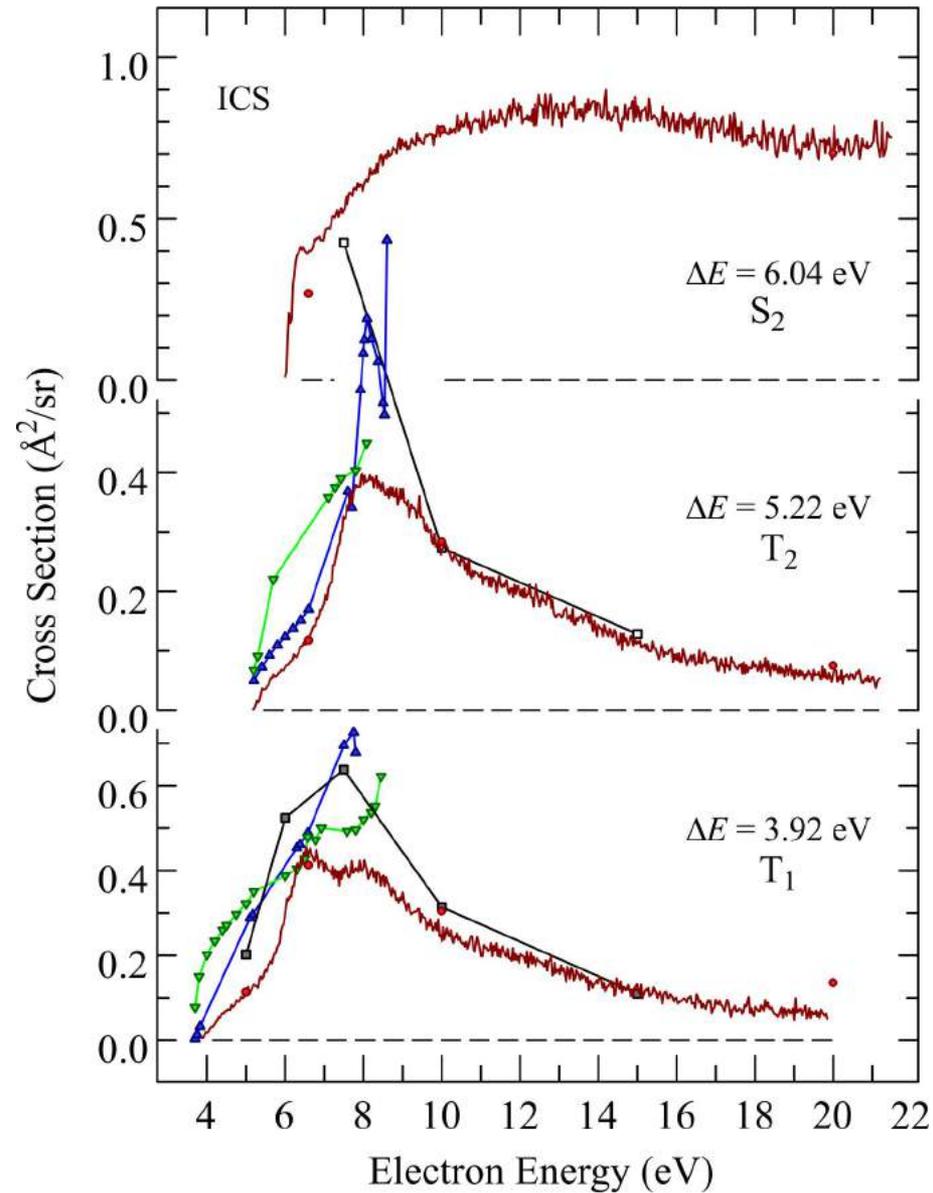
- The experiments of Khakoo and from Fribourg agree well.
- The Schwinger multichannel method reproduces the absolute values of the cross section well.

Theory: ▲ ▼

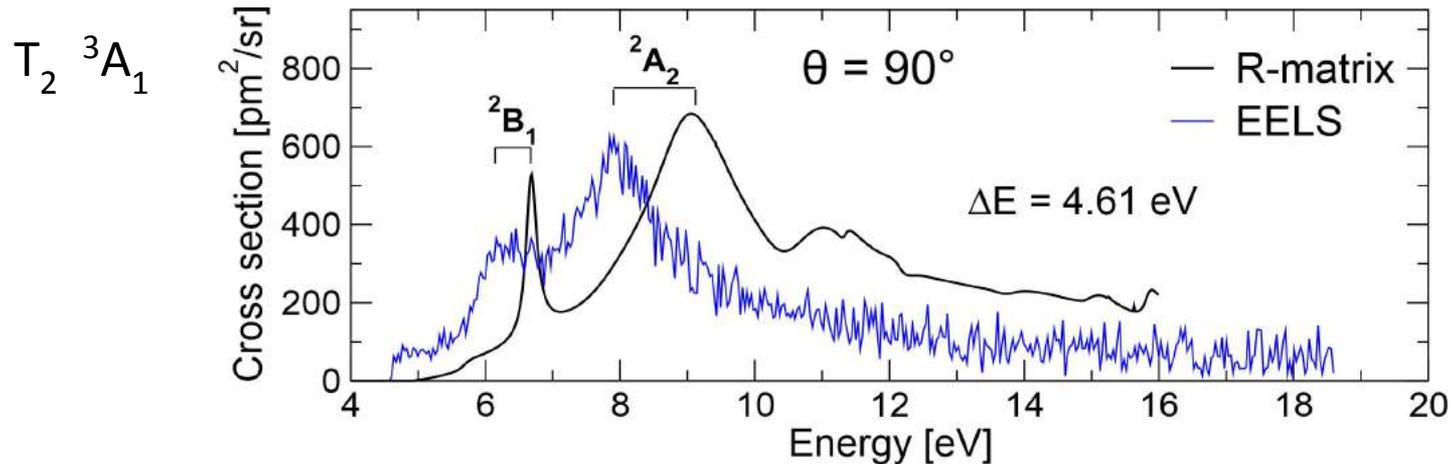
R. F. da Costa, M. H. F. Bettega,
M. A. P. Lima, M.C.A. Lopes,
L. R. Hargreaves,
G. Serna, and M. A. Khakoo,
Phys. Rev. A (2012)

Experiment Khakoo: □

Experiment Fribourg:



Thiophene

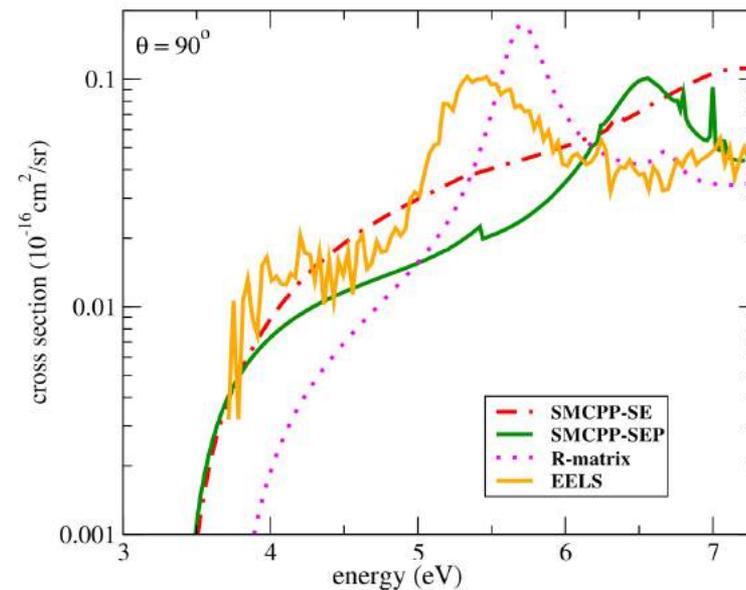


Alexandra Loupas, Khrystyna Regeta, Michael Allan, and Jimena D. Gorfinkiel, J. Phys. Chem. A 2018

Schwinger multichannel method,
implemented with
pseudopotentials
in the static-exchange plus
polarization approximation
(SMCPP-SEP)

G M Moreira, F Kossoski, M H F Bettega and
Romarly F da Costa, J. Phys. B 2020

$T_1 \ ^3B_2$



Conclusions for polyatomic molecules: electronic

Amazing success of theory:

- Magnitude of the cross section correct.
- Resonant structure in the spectra correct.
- Inspection of the time-delay identifies all resonances.
- Provides assignment of the resonances.
- Characterizes the resonances in terms of their parent state(s).
- Shape and core-excited resonances are treated on the same footing!
Their mixing (!) is thus revealed. Similarly valence-Rydberg mixing.

Challenges for the future:

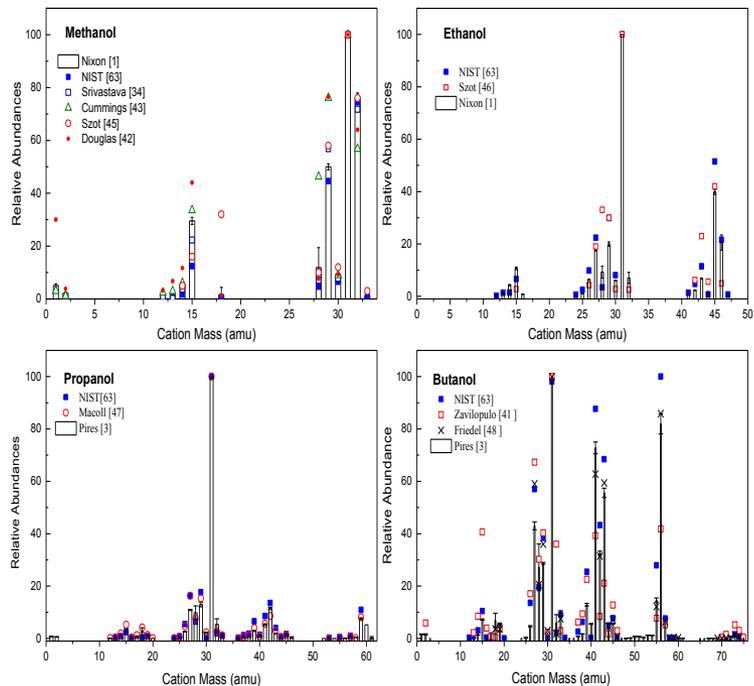
- Improve the accuracy of calculated resonance energies.
- Extend the calculations to higher energies.
- Calculate the dynamics of the resonant states. To this end calculate the parameters (energy, width) of the resonant states as a function of the positions of the nuclei, including nonadiabatic couplings and conical intersections. Then calculate how do the nuclei move on the potential surfaces, in particular calculate rapid decays by conical intersections.

Message from Prof. Maria Cristina A. Lopes Experiments (UFJF)

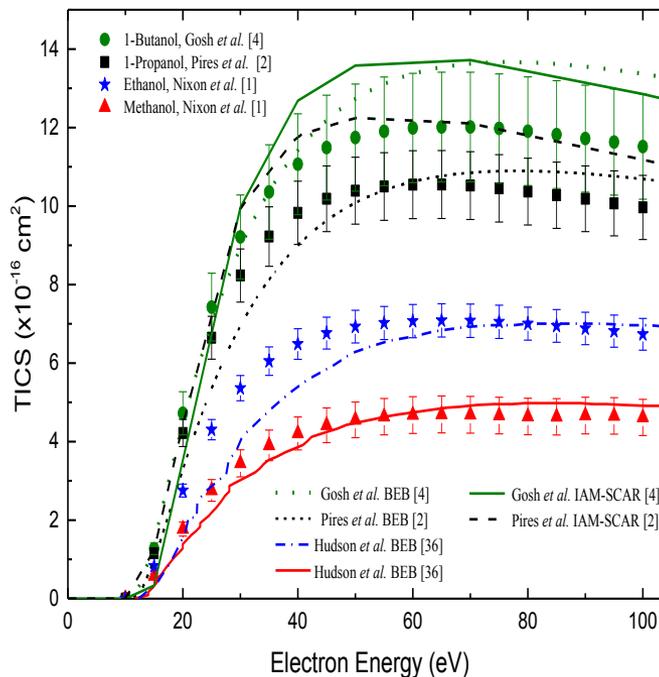
Electron Impact Ionization and Fragmentation of Biofuels

Universidade Federal de Juiz de Fora – Brazil, Flinders University – Australia,
Consejo Superior de Investigaciones Científicas - Spain

Mass Spectrum

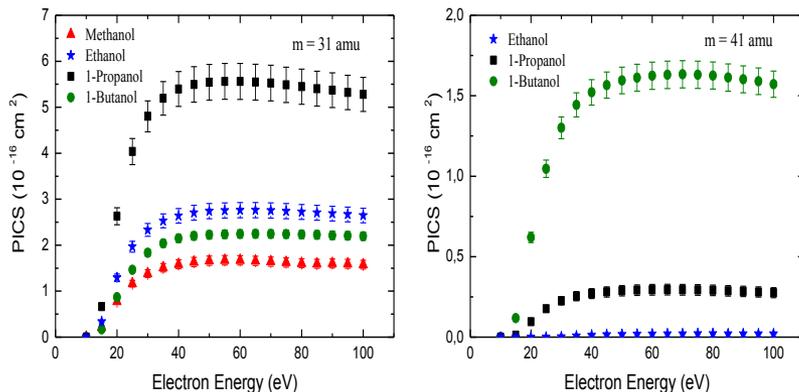


TICS - Total Ionization Cross Section

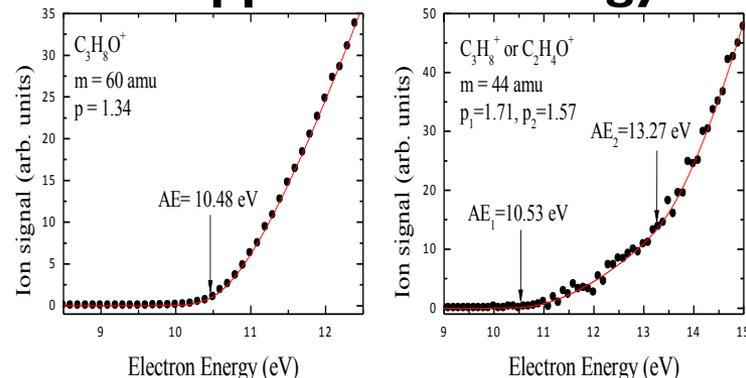


- [1] Nixon et al., *Int. J. Mass Spectrom.* 404 (2016) 48.
[2] Pires et al., *Int. J. Mass Spectrom.* 422 (2017) 32.
[3] Pires et al., *Int. J. Mass Spectrom.* 430 (2018) 158.
[4] Lopes et al. *Eur. Phys. J. D* 74 (2020) 88.

PICS - Partial Ionization Cross Section



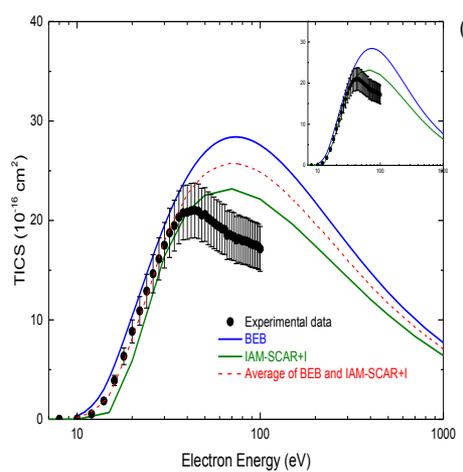
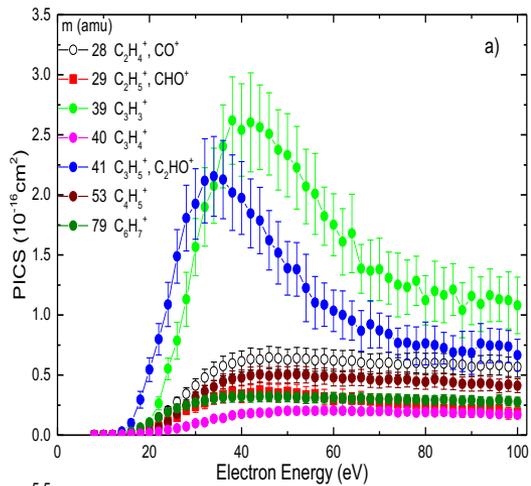
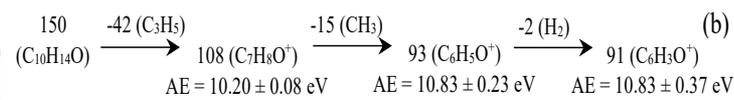
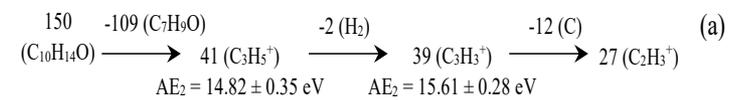
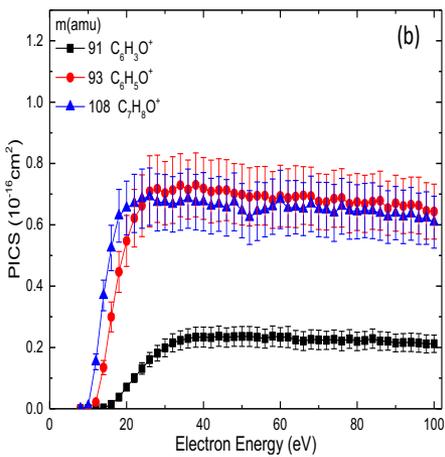
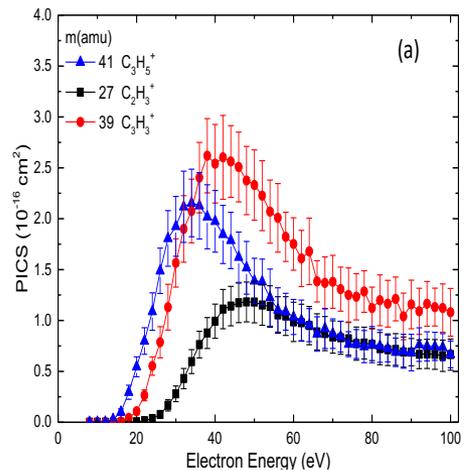
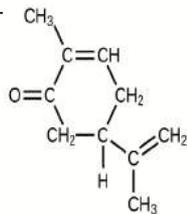
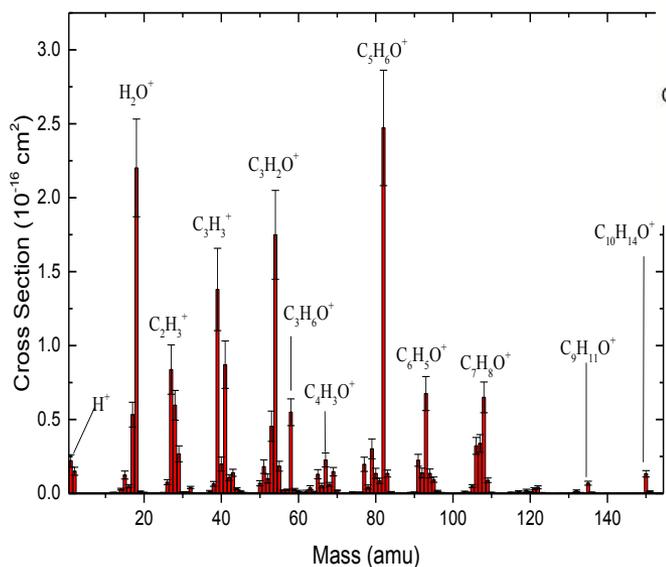
AE - Appearance Energy



Electron Impact Ionization and Fragmentation of R-Carvone

Universidade Federal de Juiz de Fora, Brazil; Flinders University, Australia; Consejo Superior de Investigaciones Científicas, Spain

Mass Spectrum



[1] M. C. A. Lopes et al., *Int. J. Mass Spectrom.* **456**, 116395 (2020)
 [2] R. A. A. Amorim et al., *Int. J. Mass Spectrom.* **464**, 116556 (2021)
 [3] R. A. A. Amorim et al., *Eur. Phys. J.* (2021), in press.

Message from Prof. Michael Brunger Experiments (Flinders University)

I) Apparatus Developments

- While there is now a good understanding by the community, in terms of taking appropriate experimental precautions in order to make *bona fide* electronic-state cross-section measurements, **the challenge remains to get the best possible energy resolution** (currently typically $\sim 40\text{--}60$ meV) but with high enough incident electron fluxes so that statistically viable (i.e. excellent signal-to-noise) energy-loss spectra can be obtained.
- Currently, at ANU, measurements are underway with a traditional electron source (e.g. hairpin filament and thermionic emission) in conjunction with a Surko trap and rotating wall. The technology for the latter is well established in the positron community, with preliminary data suggesting good incident electron currents at energy resolutions ~ 40 meV. Furthermore, **if the Surko group's work on a cryogenic trap proves to be successful, routine energy resolutions ~ 20 meV (or better), with good electron flux, potentially become available.** While this development is probably of more direct relevance to diatomic molecules, it might also assist with the interpretation of polyatomic-molecule energy-loss spectra.

2) Spectral Deconvolution Developments

- Least squares fitting approaches, for extracting cross sections from energy-loss spectra, have also developed since the pioneering work of Cartwright, Trajmar and their colleagues. In particular, uncertainty estimates on the deconvoluted spectral components (i.e. relative cross sections) are now available. Nonetheless, issues relating to the uniqueness of the extracted cross sections remain.
- In this respect, coupling your interpretation of the measured energy-loss spectra with a high-resolution (< 10 meV) photoabsorption spectrum of the species in question, which favours optically allowed transitions, and with high-level quantum chemistry computations, seems a prudent approach to take.

3) Using AI (Machine Learning) in conjunction with Swarm Measurements and Simulations

- White's group (JCU) have recently been applying machine learning techniques, in conjunction with a multi-term Boltzmann equation solver, the LXCAT cross section data base, and measured swarm data, in order to evaluate the self-consistency of proposed ('complete') cross section sets for a species in question.
- Of course to make use of this approach you not only need the electronic-state cross sections (ICSs in this case) you have measured, but all the relevant cross sections for the available open channels at some incident electron energy (E_0).
- All those ICSs can typically be assembled from results of other measurements and theory in the literature (or derived from the independent TCS assuming the ICS sum rule holds). Of course this is quite a lot of extra work, but ultimately it provides a detailed test for the validity of your electronic-state ICSs. This follows as for some regions of E/n_0 , the measured and simulated transport coefficients are sensitive to those electronic-state ICSs.

[see P.W. Stokes *et al.*, J. Chem. Phys. **154**, 084306 (2021)]

Message from Prof. Gustavo Garcia Experiment&Theory (IFF-CSIC)

Research group: Radiation-Matter Interactions (RMI)

Led by: **Gustavo García (IFF-CSIC)**

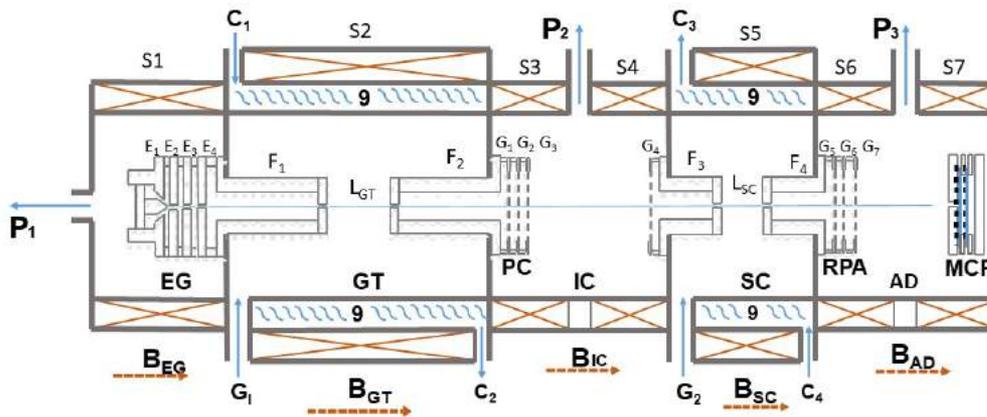
Objectives:

- Experimental electron and radical interaction reference data: Total cross sections, total and partial ionisation cross sections
- Theoretical electron scattering cross sections over a wide energy range (10-10000 eV), IAM-SCAR+I method.
- Modelling electron and radical transport in gaseous and condensed media, LEPTS simulation procedure.
- Biological damage induced by secondary electrons and radicals

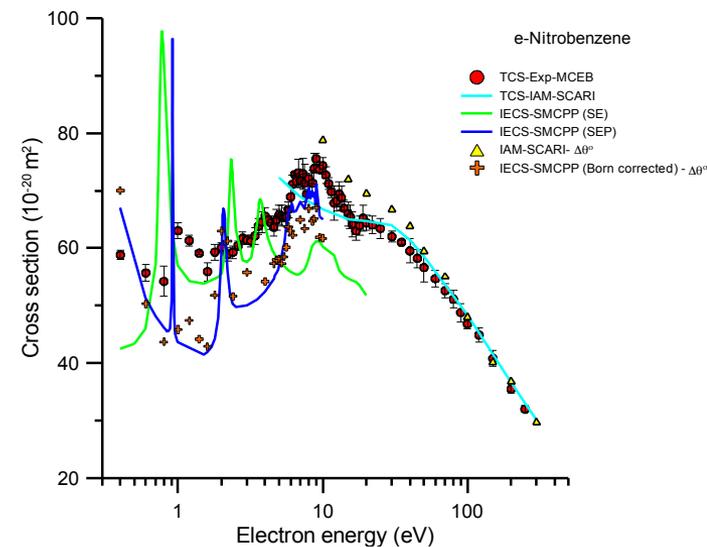
Electron and radical interaction reference data

- Total electron scattering cross sections: experiment and theory

Magnetically confined electron transmission apparatus

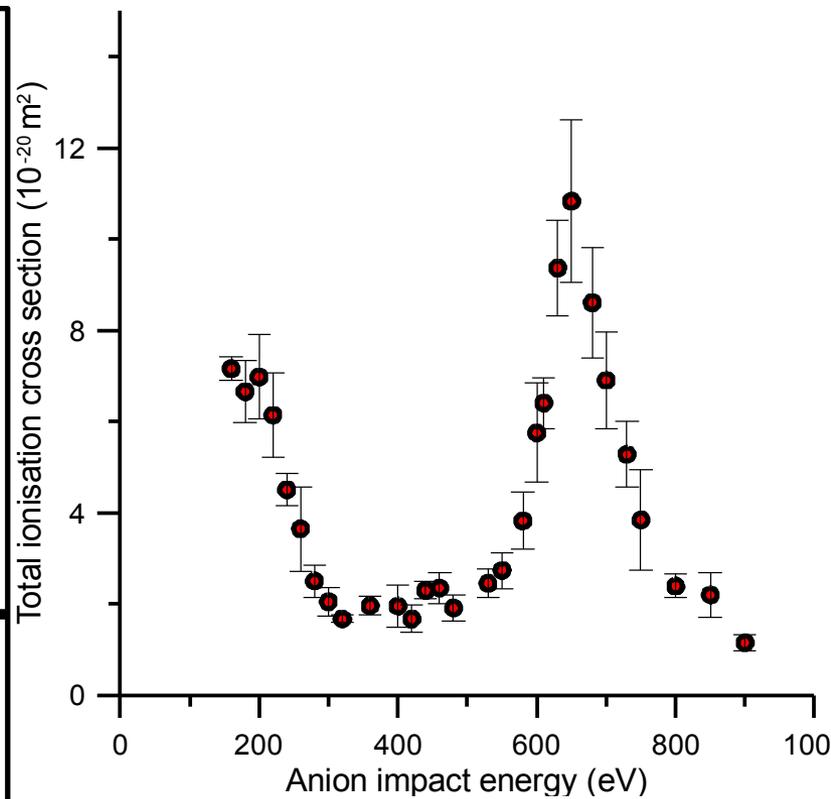
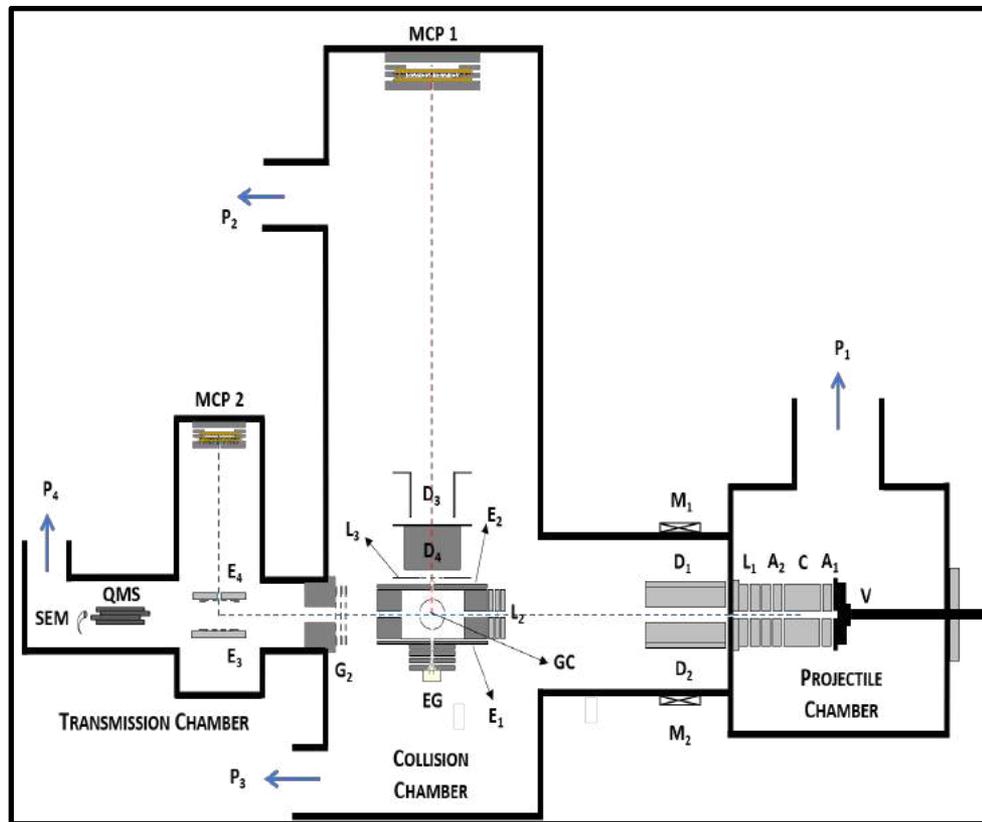


Total electron scattering cross sections for nitrobenzene



Electron and radical interaction reference data

- Total electron detachment and induced cationic fragmentation cross sections for oxygen anion collisions with molecules: Benzene (Bz)



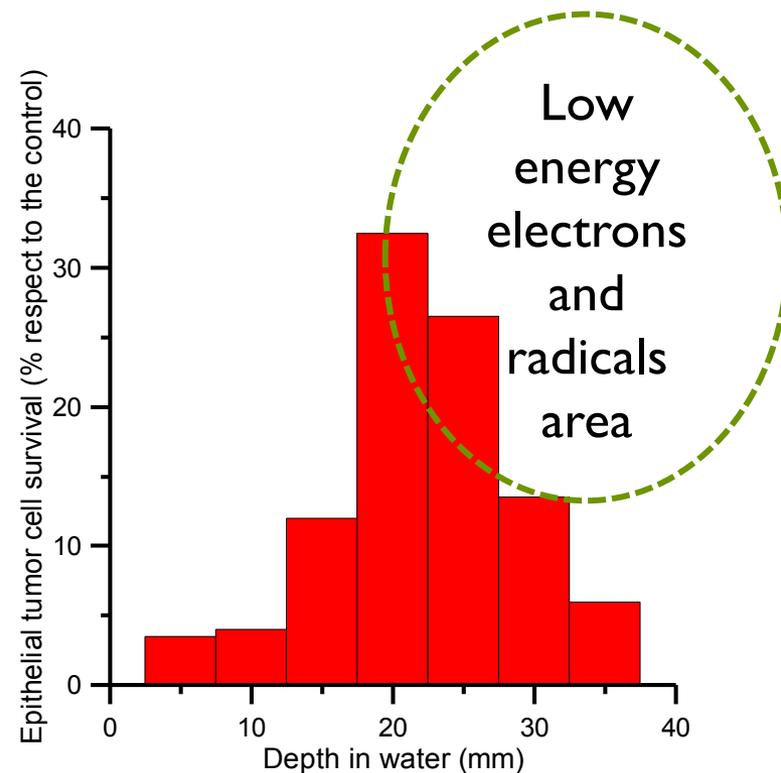
Biological damage induced by secondary electrons and radicals

Intraoperative radiotherapy with electrons: LIAC accelerator (Hospital Ramón y Cajal, Madrid)



Sample holder with epithelial tumor cells

Initial electron energy: 6 MeV
Constant irradiation dose: 5 Gy



Message from Prof. Stephen Buckman Experiments (ANU)

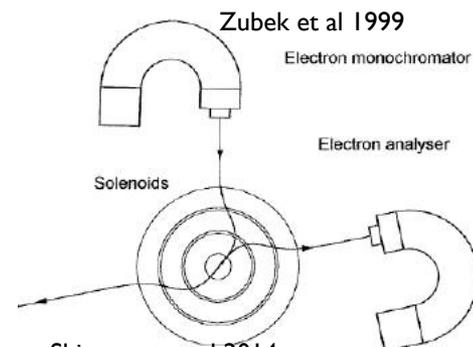
Dear Marco, thanks for the invite to contribute to your Plenary Address to EMS, which is a great honour for you and your extended Group, and a recognition of both yourself and your research - I recall we first met 30 years ago at Aarhus !! - it has been an absolute pleasure to know and work with you!

Ok, as an experimentalist, let me indulge myself on what I think are the few most important developments in the last 30 years or so – it is a personal view and apologies to those I may have missed ...

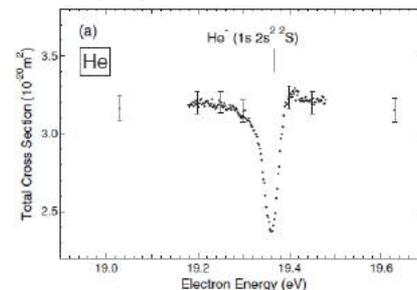
Magnetic Angle Changer – Frank Read, Mariusz Zubek, and collaborators. What an AMAZING idea, Brilliant ! Enables scattering measurements to 180° - Adopted by a few groups, Michael Allan, Hyuck Cho, and ourselves at ANU

Threshold Ionization Electron Sources – another brilliant idea that had its laser roots in the 80's (Gallagher, Kennerley, van Brunt) and early 2000's (Hotop and colleagues), and its synchrotron roots in the 80's (e.g. Field and colleagues) and 2010's (Kitajima and co-workers)

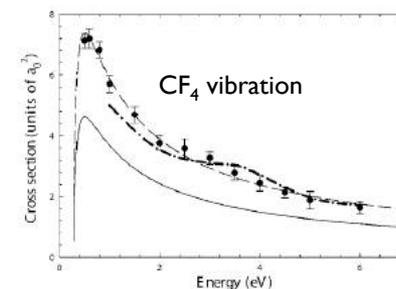
Buffer Gas Traps – developed by Surko and colleagues for high-resolution positron studies, they have revolutionised the field over the past 20 years. Applied to electron collisions only once (to date) so also an opportunity there



Shigemura et al 2014
 $\Delta E = 6$ meV



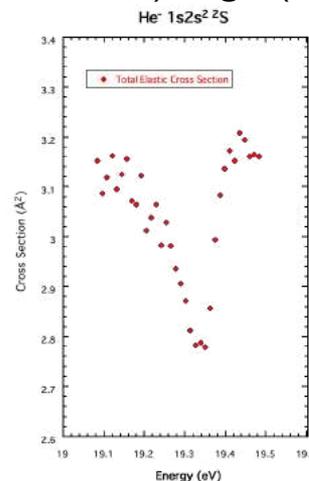
Marler & Surko 2005



A (not so) new development – an electron trap

- The buffer gas (Surko) trap technique has much to offer low energy electron collision measurements -
 - High resolution, high efficiency, high flux source of electrons - e.g. the huge $^2\Pi$ vibrational resonance cross section in N_2 which offers new channels for trapping and cooling
 - The technique enables DIRECT, absolute measurement of integral inelastic cross sections – no need for angular measurements and subsequent integration, as is the norm in current electron work, which also suffers from not accessing the full angular range (unless a magnet is used !)
 - Could resolve some outstanding discrepancies, and fill some gaps in the current literature - N_2 , NO , H_2O , C_6H_6 , biomolecules, For both vibrational and electronic excitation
- At ANU we have installed a simple, retractable, thermionic electron source in one of our positron trap beamlines to enable a high resolution (~ 35 meV), high (tunable) flux, pulsed source of electrons for such studies.
- Measurements are underway !

Demonstrated energy resolution and cross section measurement for the He^- $1s\ 2s^2\ ^2S$ resonance at 19.365 eV (Machacek and Buckman July 2021)



Message from Prof. Jimena Gorfinkiel

Theory: R-Matrix

R-matrix method:

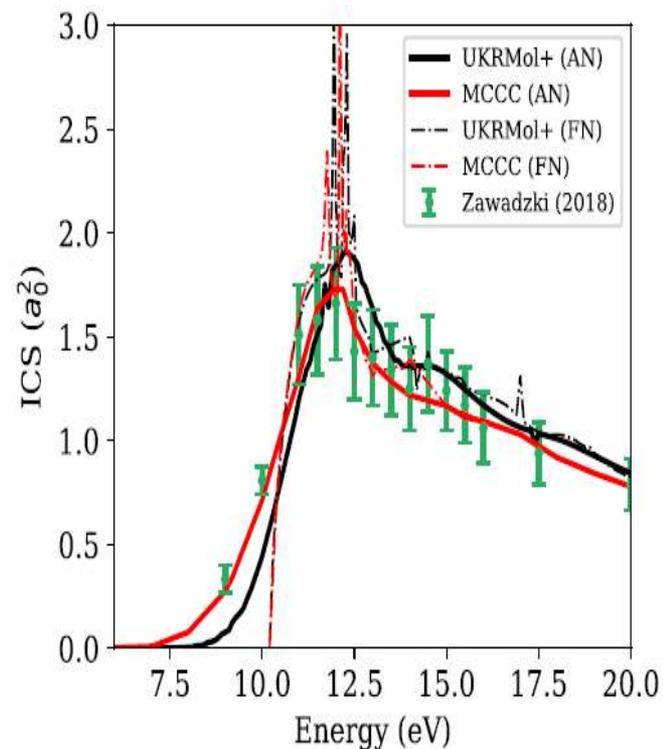
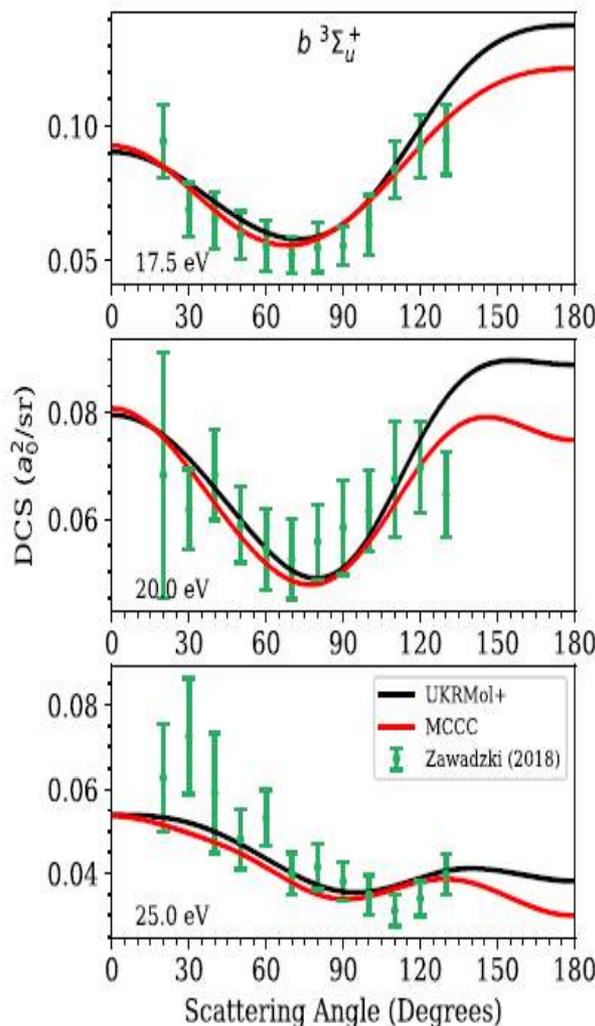
- ❑ Redevelopment of UKRmol+ suite to treat: electron and positron (without Ps formation) scattering, photoionization, etc. has enabled higher quality calculations and better use of HPC Mašin et al, CPC, **249**, 107092 (2020),
- ❑ Current software generates some of the data necessary for many scientific areas of applied relevance
- ❑ Strengths:
 - ❑ Relative low cost of calculating for many scattering energies
 - ❑ Electronic excitation and core-excited resonances well described (if target states well described)
- ❑ Weakness:
 - ❑ description of highly polarizable molecules
 - ❑ Some lack of flexibility in the computational chemistry approaches
 - ❑ inclusion of nuclear motion: only bound states of diatomics

H₂

- Elastic and inelastic scattering
- High quality calculations available and fairly converged

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

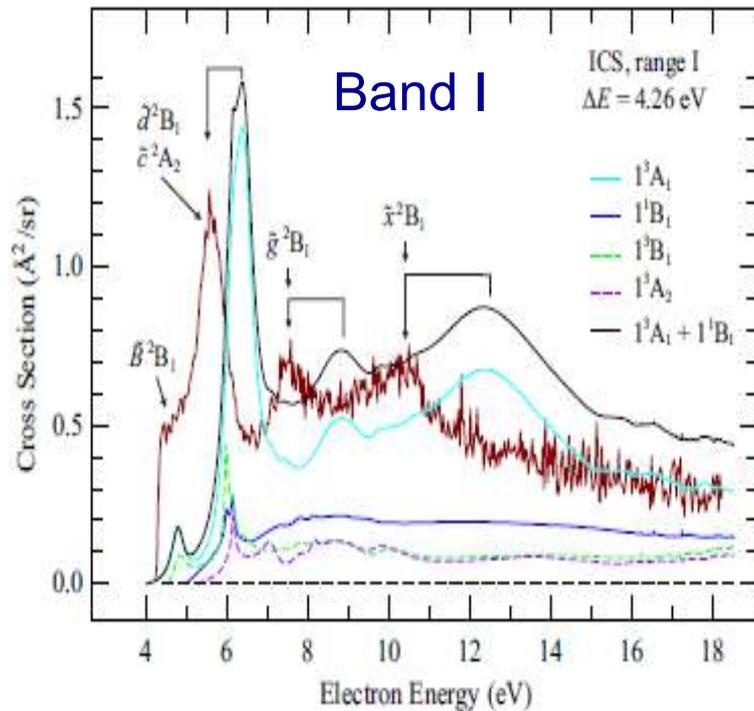
Meltzer et al, JPB **53** (2020)
145204



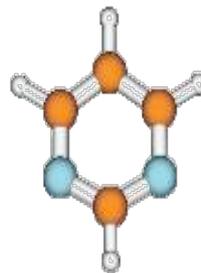
Excellent agreement between theoretical methods: UKRmol+ (R-matrix) and MCCC (molecular convergent close-coupling) for electronic excitation into some states

Electronic Excitation:

Excellent agreement for state-to-state cross section for specific angles and core excited resonances



Excellent agreement for bands of states (angle integral) and 7 core-excited resonances



Pyrimidine

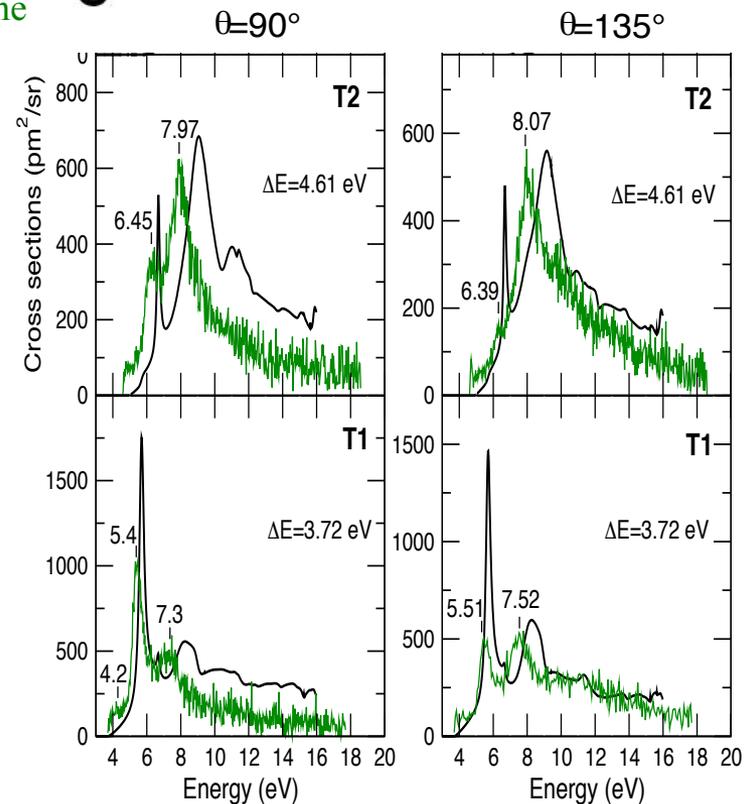
Regeta et al, JCP **144** (2016)



Thiophene

T1: first triplet state
T2: second triplet state

— Electron Energy Loss
— R-matrix



Loupas, et al, JPCA, 2018, **122**, 1146

R-matrix outlook:

❑ Challenges

- ❑ Inclusion of environment effects
- ❑ Provision of data for studies involving nuclear motion (e.g. associative detachment, etc.)
- ❑ Scattering from excited states
- ❑ Positron scattering: inclusion of Ps formation

❑ Plans

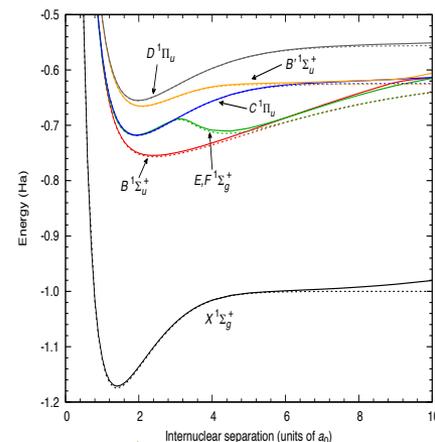
- ❑ Further optimization of codes to enable bigger calculations
- ❑ Implementation of additional QM methodologies (i.e. inclusion of effective core potentials)
- ❑ Improve user-friendliness to enable non-experts to use codes to address data needs (e.g. AMPGateway: <https://ampgateway.org/>)

Message from Prof. Igor Bray, Prof. Dmitry Fursa and Liam Scarlett Theory: MCCC

MCCC method: fixed-nuclei (FN) & adiabatic nuclei (AN) approaches

- Born-Oppenheimer approximation \longrightarrow Solve for the electronic wave function $\langle \phi_f | H_T | \phi_i \rangle = \varepsilon_f \delta_{fi}$
- Fixed-nuclei approximation, $R = \text{fixed}$
- Diagonalization of the target Hamiltonian H_T \longrightarrow modeling of *infinite* number of bound & continuum states with a *finite* number of pseudostates in a Sturmian (Laguerre) basis

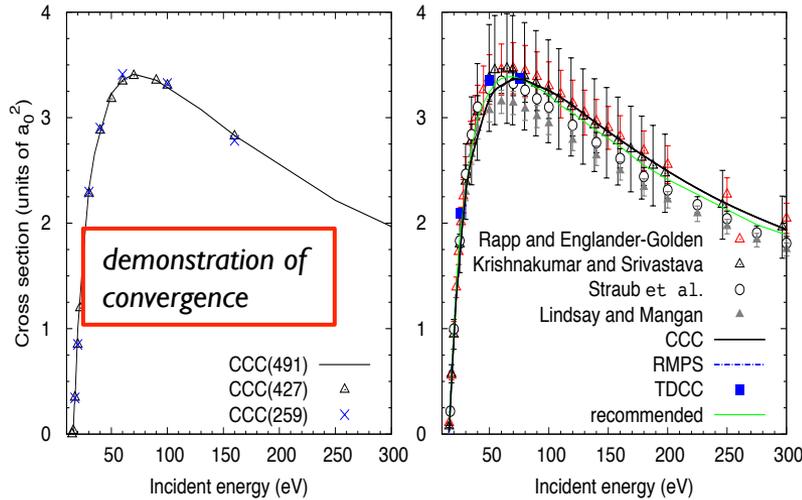
- N -state multi-channel expansion $\Psi_i^{(+)}(\mathbf{x}_p, \mathbf{x}_t) = \mathcal{A} \sum_{n=1}^N F_n(\mathbf{x}_p) \phi_n(\mathbf{x}_t)$
- Solve integral LS equation for the T matrix $T_{fi}(\vec{k}_f, \vec{k}_i) = V_{fi}(\vec{k}_f, \vec{k}_i) + \sum_{n=1}^N \int d^3k \frac{V_{fn}(\vec{k}_f, \vec{k}) T_{ni}(\vec{k}, \vec{k}_i)}{E + i0 - \varepsilon_n - k^2/2}$
- Adiabatic nuclei T matrix \longrightarrow
- $\varphi_{n\mu}(R)$ are vibrational wave functions $T_{f\mu,iv}(E) = \int dR \varphi_{f\mu}(R) T_{fi}(E; R) \varphi_{iv}(R)$
- vibrationally-resolved cross sections $\sigma_{f\mu,iv}(E) \propto |T_{f\mu,iv}(E)|^2$



- Advantages of MCCC: {
- Spheroidal-coordinate formulation- natural for diatomics \rightarrow accurate wave functions to large R
 - Computationally efficient code, OpenMP + MPI parallelization, GPU – to be implemented soon convergence of the collision data is established
- Limitations of MCCC: {
- the code is available only for H_2^+ , H_2 and isotopologues (so far)

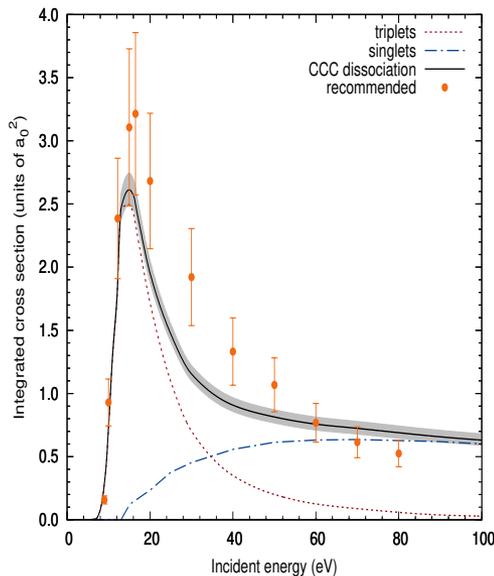
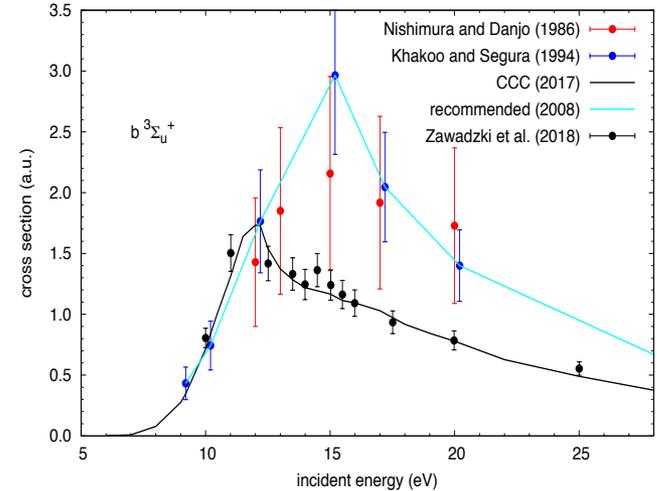
e^-H_2 total ionization cross section

Zammit, Savage, Fursa & Bray,
Phys. Rev. Lett. **116** (2016) 233201
Phys. Rev. A **95** (2017) 022708



Cross sections for the $b^3\Sigma_u^+$ state

Zawadzki *et al.*,
Phys. Rev. A **97** (2018) 050702(R);
Phys. Rev. A **98** (2018) 062704

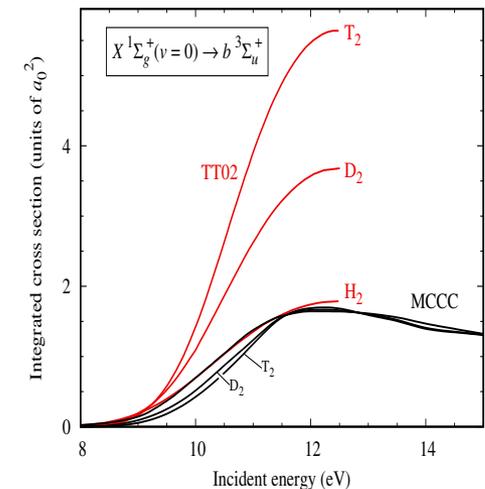


Electron-impact dissociation of H_2 to neutral fragments

Scarlett *et al.*, Eur. Phys. J. D **72** (2018) 34

Isotopic and vibrational-level dependence of H_2 dissociation by electron impact

Scarlett *et al.*, Phys. Rev. A **103** (2018) 34



MCCC fully vibrationally resolved cross sections

Calculations have been performed for over 58,000 transitions in H₂ and its 5 isotopologues includes dissociation cross sections

Scarlett et al., Atomic Data and Nuclear Data Tables, **137** (2021) 101361, **139** (2021) 101403

Scattering on all bound levels of the state

Data files per transition:

MCCC-el-H2-

B1Su_vf=10.X1Sg_vi=0.txt

Analytic fits
$$\sigma(x) = \left(\frac{x-1}{x}\right) \left(\frac{A_0^2 \ln(x)}{x} + \frac{A_1}{x} + \frac{A_2}{x^2} + \frac{A_3}{x^3} + \frac{A_4}{x^4} + \frac{A_5}{x^5}\right)$$

In collaboration with Yu. Ralchenko (NIST)

Number of bound vibrational levels

State	Molecule					
	H ₂	HD	HT	D ₂	DT	T ₂
<i>X</i> ¹ Σ _g ⁺	15	18	19	21	24	26
<i>B</i> ¹ Σ _u ⁺	37	43	45	52	57	64
<i>EF</i> ¹ Σ _g ⁺	33	38	40	47	51	57
<i>C</i> ¹ Π _u	14	16	17	19	21	24
<i>B'</i> ¹ Σ _u ⁺	9	11	12	13	15	16
<i>GK</i> ¹ Σ _g ⁺	9	10	11	12	13	15
<i>I</i> ¹ Π _g	4	4	5	5	6	7
<i>J</i> ¹ Δ _g	18	20	22	26	28	31
<i>H</i> ¹ Σ _g ⁺	72	83	88	102	112	125
<i>D</i> ¹ Π _u	18	21	22	25	28	31
<i>b</i> ³ Σ _u ⁺	0 (dissociative)					
<i>a</i> ³ Σ _g ⁺	19	22	23	27	30	34
<i>c</i> ³ Π _u	20	23	25	29	31	35
<i>e</i> ³ Σ _u ⁺	8	9	10	11	12	14
<i>h</i> ³ Σ _g ⁺	4	5	5	6	6	7
<i>d</i> ³ Π _u	20	23	25	29	32	35
<i>g</i> ³ Σ _g ⁺	19	22	23	27	30	33
<i>i</i> ³ Π _g	4	4	5	5	6	7
<i>j</i> ³ Δ _g	18	21	22	26	28	32

Initial states

Final states

All cross sections and fits available online

- Atom. Data Nucl. Data Tables supplementary materials
- IAEA hcdb: Atomic and Molecular Data for Fusion Energy Research
- <https://db-amdis.org/hcdb/>
- MCCC Database – mccc-db.org ← the latest and most comprehensive dataset

Further applications

- **Vibrationally-resolved cross sections** for scattering on excited states of H₂ and isotopologues.
- Extension to more complex diatomics: beginning with HeH⁺
 - will require implementation of GPU acceleration to be computationally feasible.
 - Eventual aim of studying arbitrary quasi- one- and two-electron diatomics.
- **Beyond the adiabatic-nuclei approximation: electronic and vibrational close coupling**
 - Allows accurate studies of low-energy and resonant scattering processes
 - Currently in progress – first results to be published soon.
- **Dissociative attachment: will follow directly from electronic-vibrational close-coupling method with some additional development.** This process is an important source of negative ions – applications in fusion and astrophysics.
- Rotationally-resolved calculations (in progress now): **cross sections fully resolved in electronic, vibrational, and rotational levels.** Also allows studies of polarisation (e.g. Fulcher- α emission).

Message from Prof. Bill McCurdy & other leaders Theory: Complex Kohn Method

Complex Kohn Method



Ann Orel



Tom Rescigno



Cynthia Trevisan



Robert Lucchese



Bill McCurdy



U.S. DEPARTMENT OF
ENERGY

Short status report from C.W. McCurdy, R. R. Lucchese, A. E. Orel
and T. N. Rescigno on Complex Kohn Method

Two main thrusts in current Complex Kohn approach to electron scattering and photoionization:

Basis Set Kohn – Legacy codes based on variational expansion of continuum wave functions in combination of multi-centered Gaussians and numerical continuum basis functions. Allows coupled channels with multireference CI correlated target states.

Grid-Based Kohn – New technology based on iterative convergence of T-matrix on purely numerical grids- complex Kohn with numerical Schwinger technology. Convergence with respect to partial wave expansions accelerated by use of overset grids.

Basis Set Kohn

Advantages:

- Fast, runs on single processor platforms.
- Offers great flexibility in choice of correlated target and channel wavefunctions and inclusion of correlation and polarization effects with *ab initio* optical potentials.

Limitations:

- Reliance on basis sets and separable expansions.
- Difficult to gauge systematic convergence.
- Limited to relatively small target molecules and continuum electron energies less than 50 eV.

Grid-based Kohn

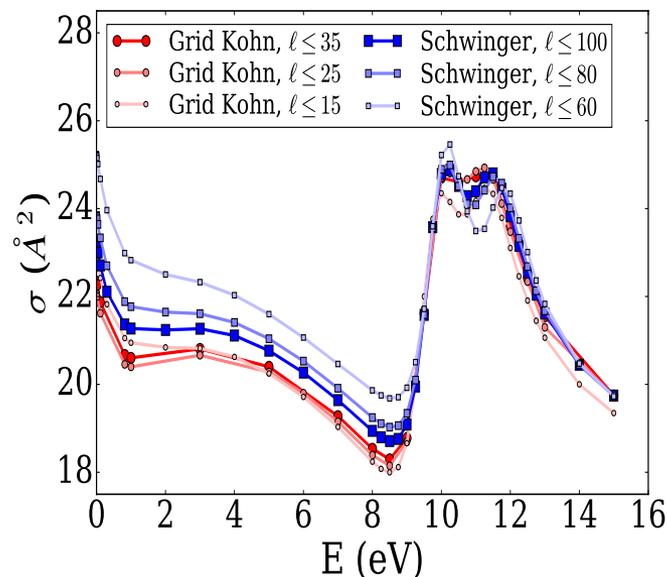
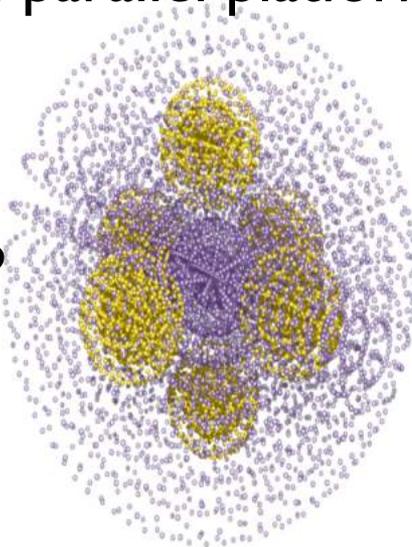
Advantages:

- Eliminates dependence on basis sets in computing scattering wavefunctions.
- Use of overset grids to accelerate convergence with partial wave expansions in each subgrid
- Runs on parallel platforms. Scalable to large molecules.

Overset

Grids:

Subgrids on atoms overlap a central grid of DVR functions



Convergence of partial wave expansions for overset grids is much faster than a single center expansion

Limitations:

- Currently limited to single configuration target and channel wave functions. Multichannel implementation under development.

Examples

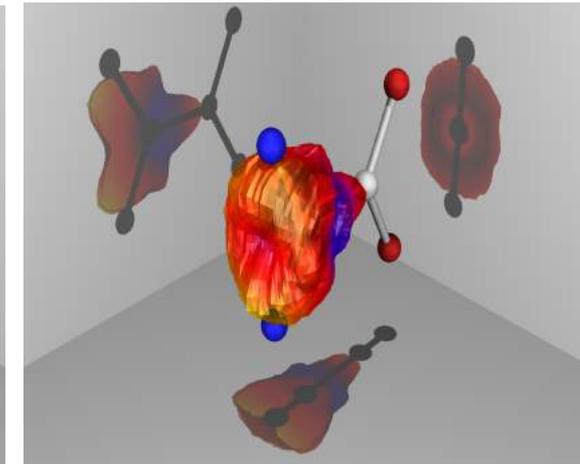
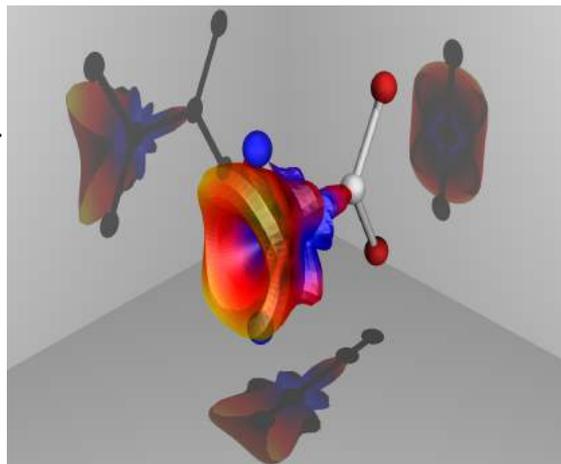
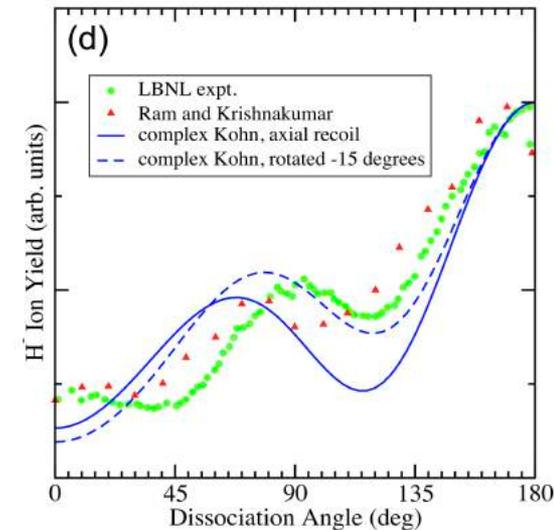
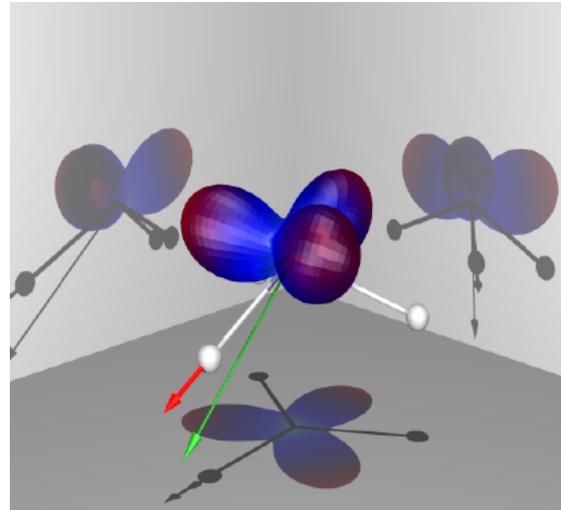
Dissociative attachment with basis set Kohn – use complex Kohn to locate DEA resonances and multi-channel analysis of S-matrix to calculate entrance amplitudes and angular distributions.

- **H⁻/NH₃ from DEA at 10 eV**

Comparison of theory and experiment for the body-frame angular dependence of electron attachment

- **Inner-shell ionization and hole-localization – photoionization in the body frame**

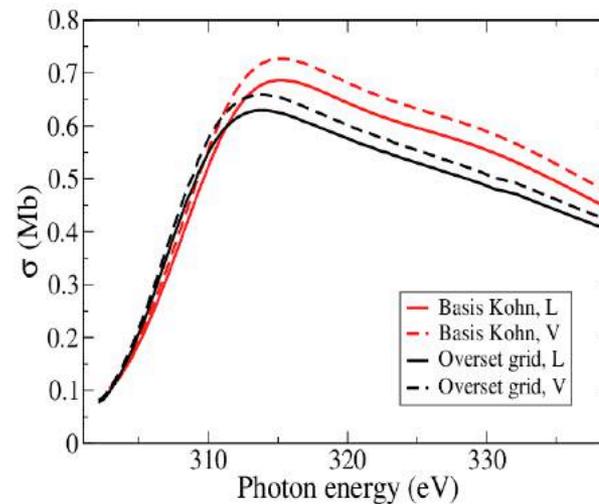
Comparison of computed (left) and measured (right) C(-1s) MFPADs for C₂H₂F₂. The carbon being ionized is on the H₂ side. Photoelectrons are preferentially ejected toward the hydrogens and away from the fluorines.



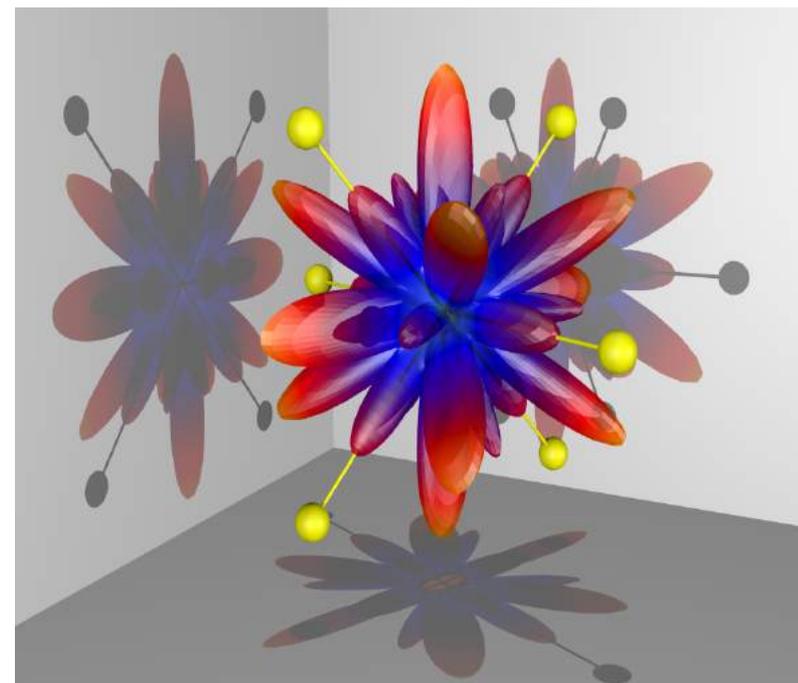
Examples (cont'd)

- Benchmarking Basis set Kohn against fully converged Grid-based Kohn
- Photoionization of large molecules with grid-based Kohn

Body frame angular distribution for ionization of SF₆ averaged over polarization direction at a shape resonance 50 eV above threshold.



Carbon 1s⁻¹ photoionization of CF₄



Complex Kohn Variational Approach to the Electronic Continuum

Today there are few groups measuring electron scattering cross sections of any kind and interest in plasma processing and other applications is waning.

So is electron scattering “over”?

No! The ultrafast revolution relies on the electronic continuum.

- Bandwidth of a 100 attosecond laser pulse is 18 eV.
- High harmonic generation is reaching 100s of eV with subfemtosecond pulses.
- Almost every ultrafast laser experiment and all free-electron laser experiments involve the ionization continuum.

Message from SMCPP leaders

SMCPP: Schwinger Multichannel Method with Pseudopotentials

Schwinger Multichannel Method with Pseudopotentials



Márcio H. F. Bettega
UFPR



Romarly F. da Costa
UFABC



Márcio T. do N. Varella
USP



Marco A. P. Lima
Unicamp



Fábris Kossoski
Toulouse University



Brazilian
National
Agency for
research

Schwinger Multichannel Method

Advantages:

- L^2 method, applicable to molecules of any geometry, taking into account polarization and electronic excitation processes.
- It allows all electron and pseudopotential (norm-conserving) calculations. Therefore, it deals with molecular targets constructed with all (any) atoms of the periodical table.
- Parallel processing. Efficient computational code, allowing very large multichannel calculations.

Limitations:

- Restricted to single excitation configuration interaction target description. Poor interface with bound states codes.
- Restricted to closed-shell molecular targets.
- L^2 method, difficulty to deal with long-range potentials.
- It produces cross sections very sensible to electronic thresholds.
- Ionization is not explicitly taken into account.

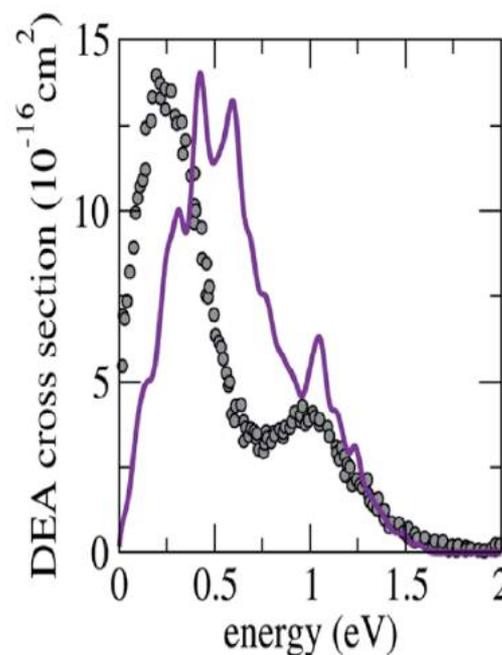
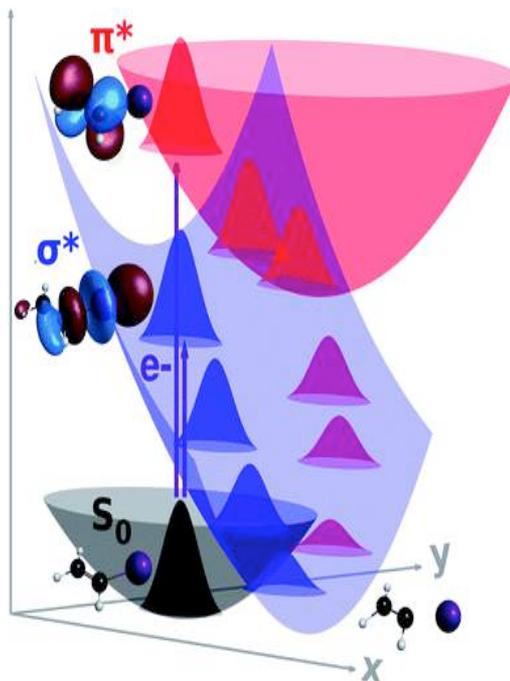
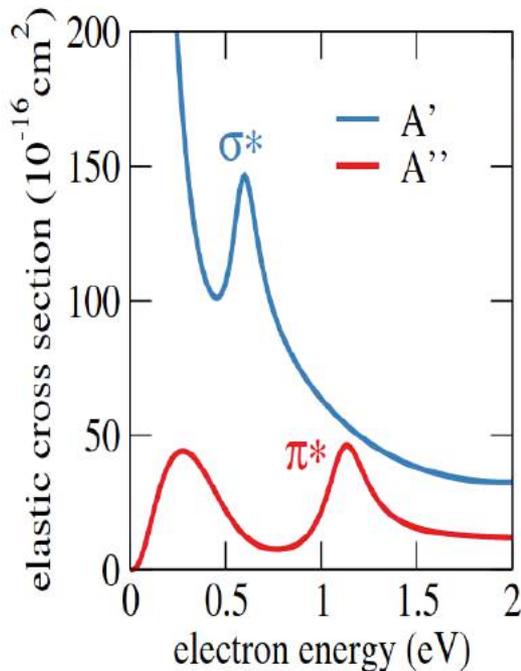
SMC provides widths to simulate dynamics of transient anions

Chloroethane (I shape resonance):

F. Kossoski, M. T. do N. Varella, M. Barbatti, *J. Chem. Phys.* **151**, 224104 (2019).

Iodoethene (2 shape resonances):

F. Kossoski, M. Barbatti, *Chem. Sci.* **11**, 9827 (2020).



SMC scattering calculations provide resonance energies and widths

A model for the widths is employed during on-the-fly dynamics simulations

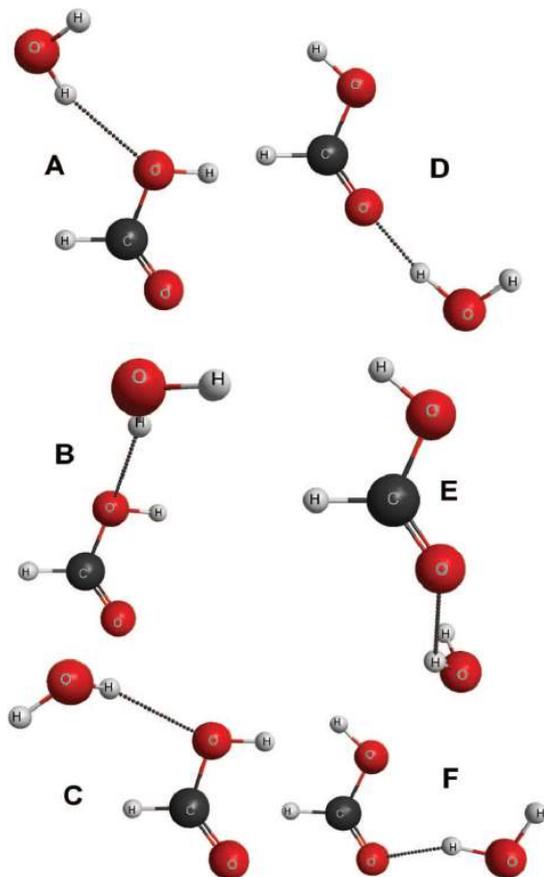
Computed absolute DEA cross sections (purple) and relative experimental data (gray)

Micro-solvation in elastic scattering

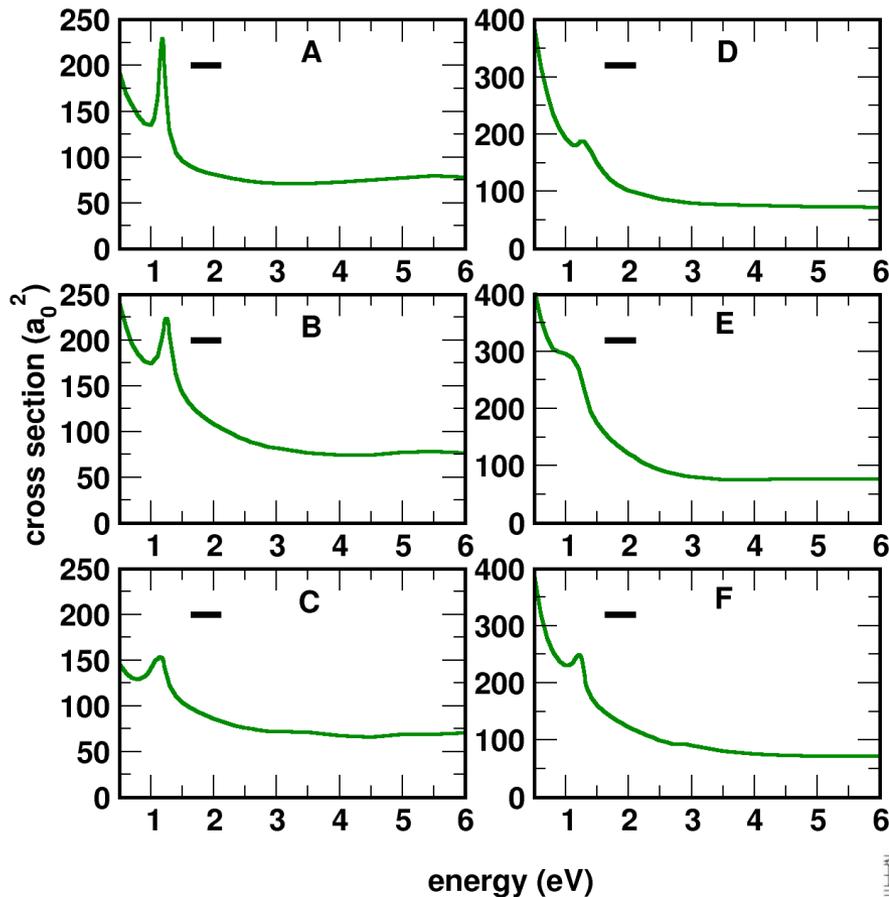
Simple first step towards more realistic situations

Electron collisions with the HCOOH...(H₂O)_n complexes (n=1, 2) in liquid phase: The influence of microsolvation on the π^* resonance of formic acid

THE JOURNAL OF CHEMICAL PHYSICS 138, 174307 (2013)



π^* shape resonance for HCOOH at around 1.9 eV.

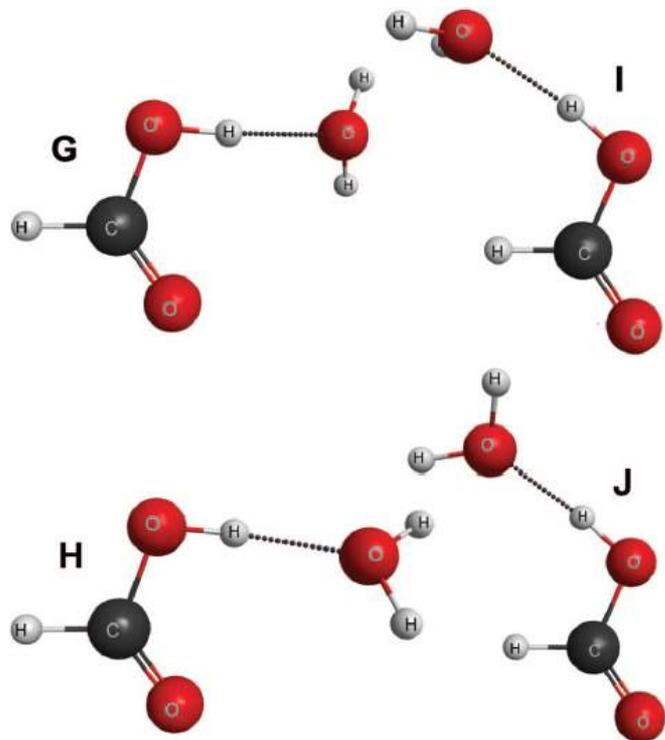


A to F: 1W **proton donor**.
A to C: *trans*; D to F: *cis*

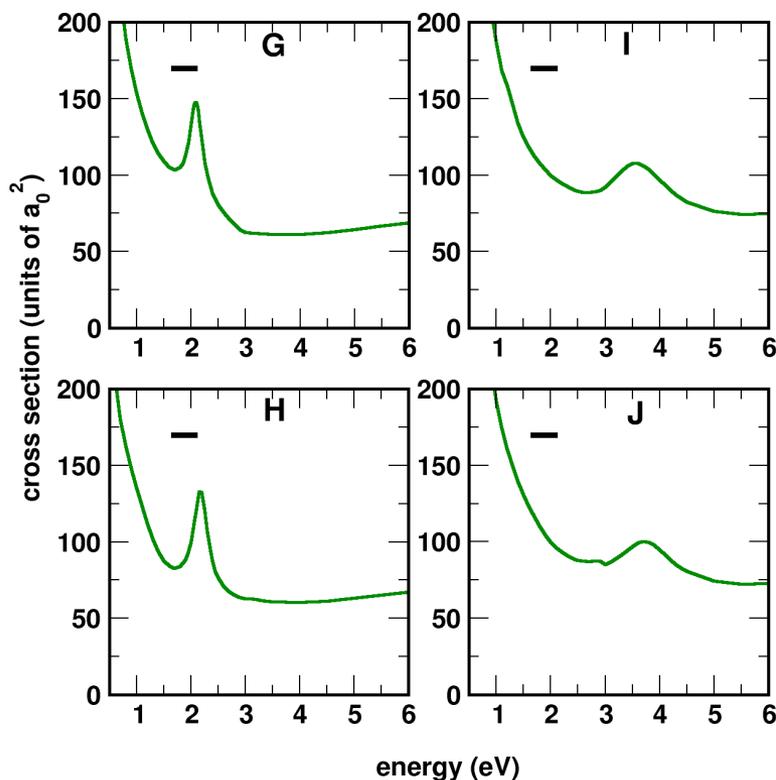
Electron collisions with the HCOOH...(H₂O)_n complexes (n=1, 2) in liquid phase: The influence of microsolvation on the π^* resonance of formic acid

THE JOURNAL OF CHEMICAL PHYSICS 138, 174307 (2013)

π^* shape resonance for HCOOH at around 1.9 eV.



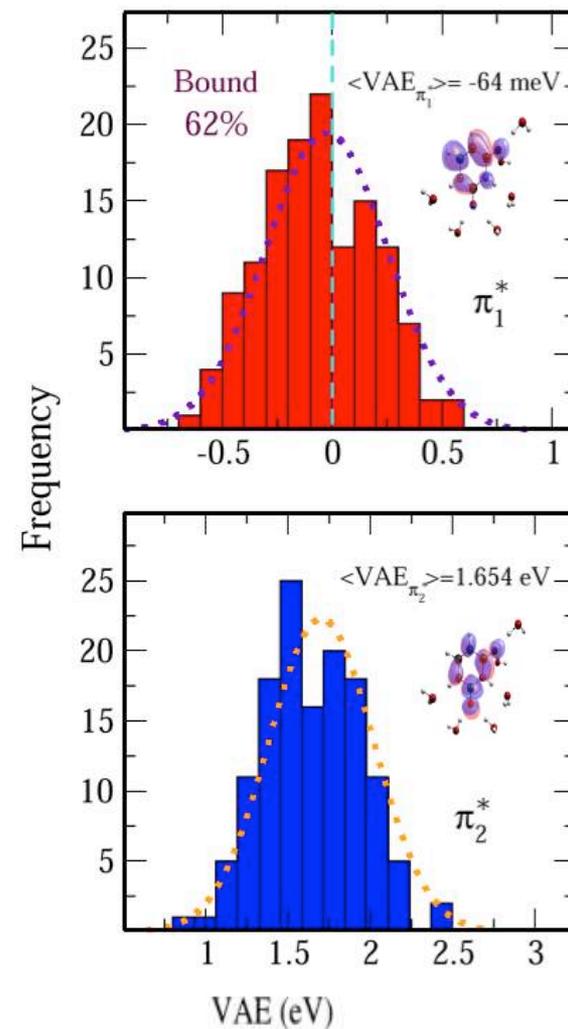
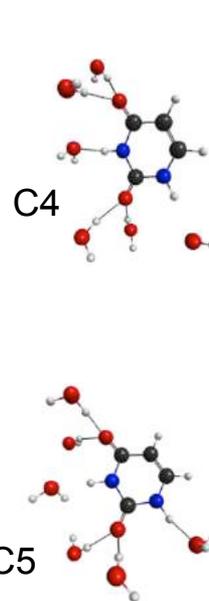
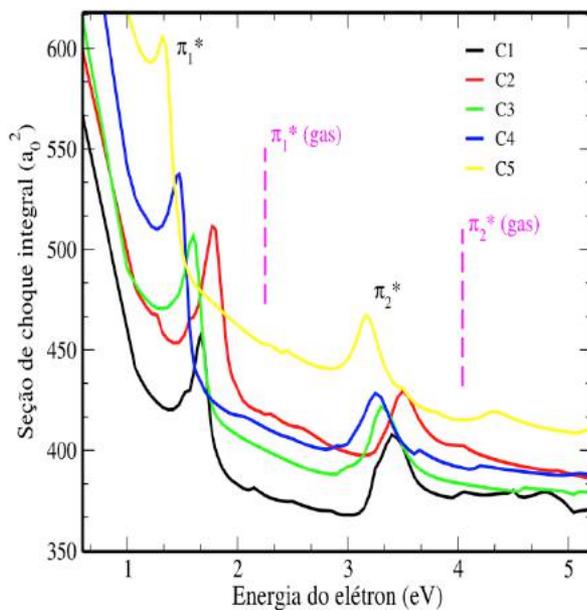
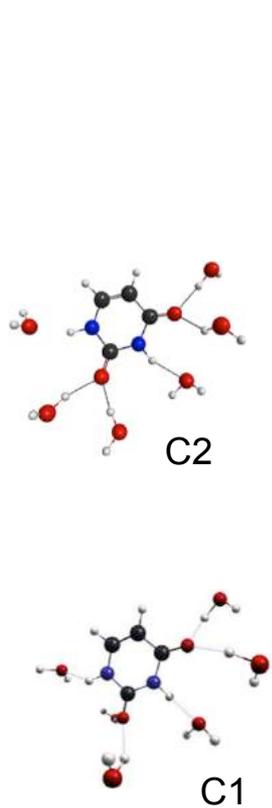
G to J: 1W **proton acceptor**.
G and H: *trans*; I and J: *cis*



Solvent Effects on the shape resonances π^* of uracil

THE JOURNAL OF CHEMICAL PHYSICS 152, 084301 (2020)

- Combining scattering techniques with classical Monte Carlo simulations.
- Liquid phase.
- Characterizing anions in microsolvation environment.
- s-QM/MM - Statistics of the solvent effect.

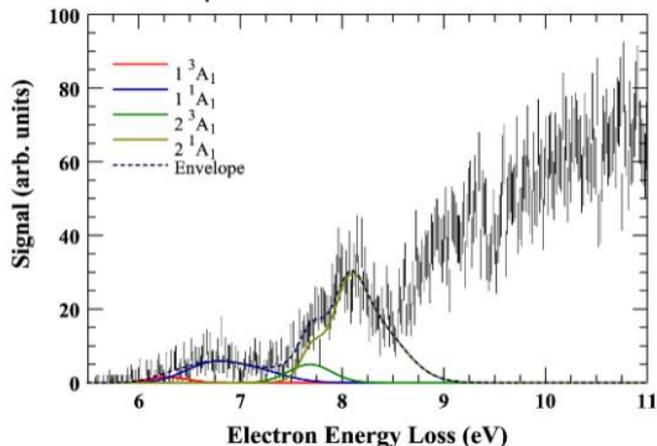


Electronic excitation Cross Sections

Very large close-coupling calculations

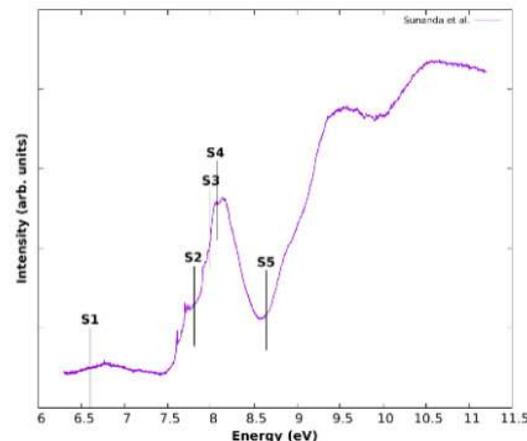
Ethanol case (trans): 431 energetically open electronic states

Hargreaves *et al.*, singlets in the band 2: ($S_2 + S_3$)
from EELS experiment



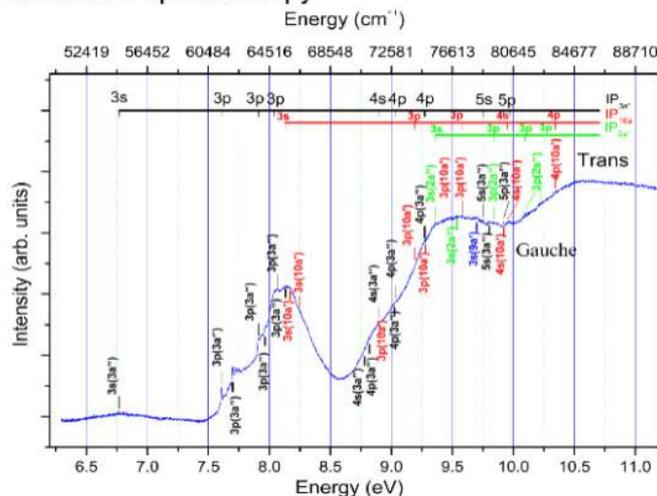
L. R. Hargreaves, M. A. Khakoo, C. Winstead, V. McKoy. *J. Phys. B: At. Mol. Opt. Phys.*, 49, 185201 (2016).

Falkowski *et al.*, singlets in the band 2: ($S_2 + S_3 + S_4$)
from EOM-CCSD calculations

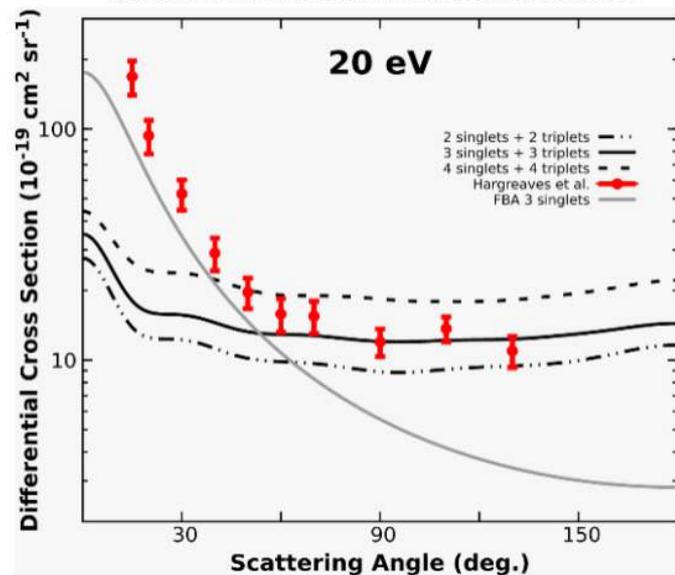


A. G. Falkowski, M. A. P. Lima, F. Kossoski, *J. Chem. Phys.* 152, 244302 (2020).

Sunanda *et al.*, singlets in the band 2 ($S_2 + S_3 + S_4 + S_5$)
from VUV spectroscopy



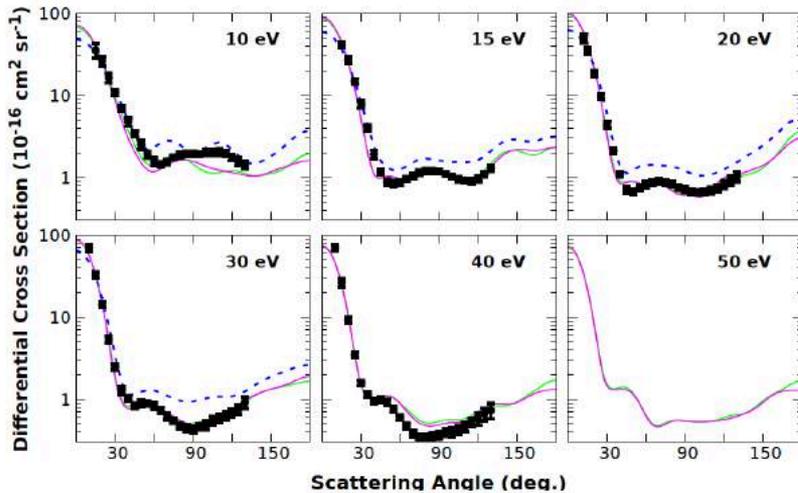
K. Sunanda, A. K. Das, and B. Rajasekhar, *J. Quant. Spectrosc. Radiat. Transf.* 237, 106609 (2019).



Experimental and theoretical efforts to define the spectral composition of the bands are needed in the interpretation of the results!

Benzene: elastic

Current: 117 CH, 305 CH, Bettega: 1 CH, Cho *et al.*: ● experimental



H. Cho, R. J. Gulley, K. Sunohara, M. Kitajima, L. J. Uhlmann, H. Tanaka, and S. J. Buckman, *J. Phys. B: At. Mol. Opt. Phys.* **34**, 1019 (2001).

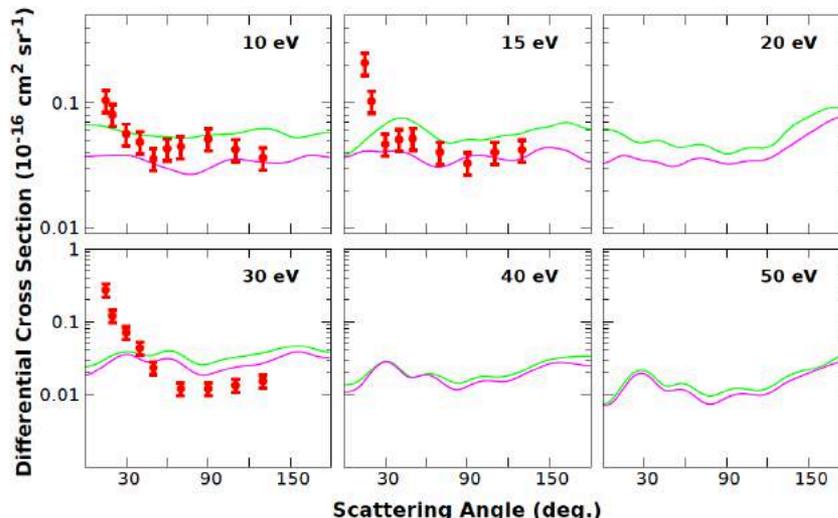
- All electronic channels are below 10 eV.
- Elastic cross sections are pretty much converged.



- Increase from 117 to 305 electronic states still shows some flux competition, but we are very optimistic about convergence.

Benzene: band 2 ($^1B_{1u} + ^3E_{1g}$)

Current: 117 CH, 305 CH, Kato *et al.*: ● experimental



H. Kato, M. Hoshino, H. Tanaka, P. Limão-Vieira, O. Ingólfsson, L. Campbell, and M. J. Brunger, *J. Chem. Phys.* **134**, 134308 (2011).

Conclusions

Theoretical calculations and experimental measurements of cross sections in electron-molecule scattering improved substantially in the last 30 years. New computers, new programs, new experimental techniques can induce an even better scenario in the near future. This raises an important funding question:

how more accurate do they must be?

My opinion (fomenting a discussion)

We, from the basic science community on electron-molecule scattering, justify our research on very important and, in some cases, very profitable applications. We have to work closer to chemical plasma and electron-scattering induced chemistry modelers in order to assess the quality, the accuracy, and the importance of our data for predictions of new applications. Otherwise, the funding agencies may say that we have done enough.

Thank you very much for your attention

A copy of this presentation is at

<http://www.ifi.unicamp.br/~maplima/maplima-EMS2021.pdf>

Special thanks to all the message contributors presented here. They are co-authors of this presentation.