1st International Conference on Molecules, Polymers and Material Physics

Instituto de Física Gleb Wataghin
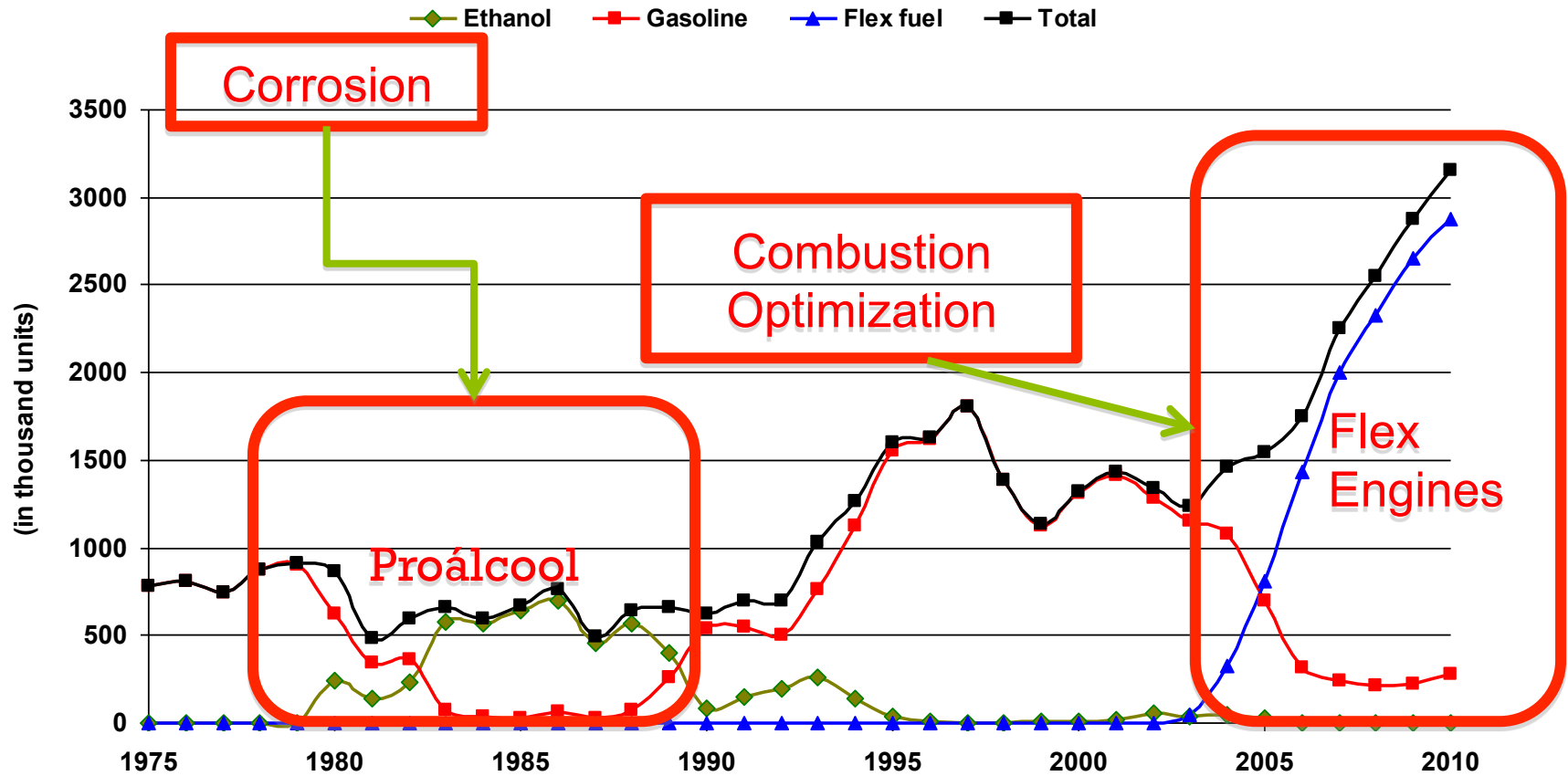UNICAMP
IFGW

Low energy electron scattering data for chemical plasma treatment of biomass

by

Marco A. P. Lima
Unicamp

Motivation I: large scale use of ethanol in engines

Brazilian Sales of light fleet Vehicles (1975-2010)

# Ethanol as Fuel: Plasma Ignition for Vehicle Engines

Theoretical support for an application project working on:

•   Investigation of processes occurring during the ignition of plasma and its consequences in post-discharge for an internal combustion engine;

•   The proper parameters to be applied in cars that operate on "poor mixtures" reducing pollutants released into the atmosphere, especially considering the spark plug discharge.

Low-energy electron scattering from methanol and ethanol

PHYSICAL REVIEW A **77**, 042705 (2008)
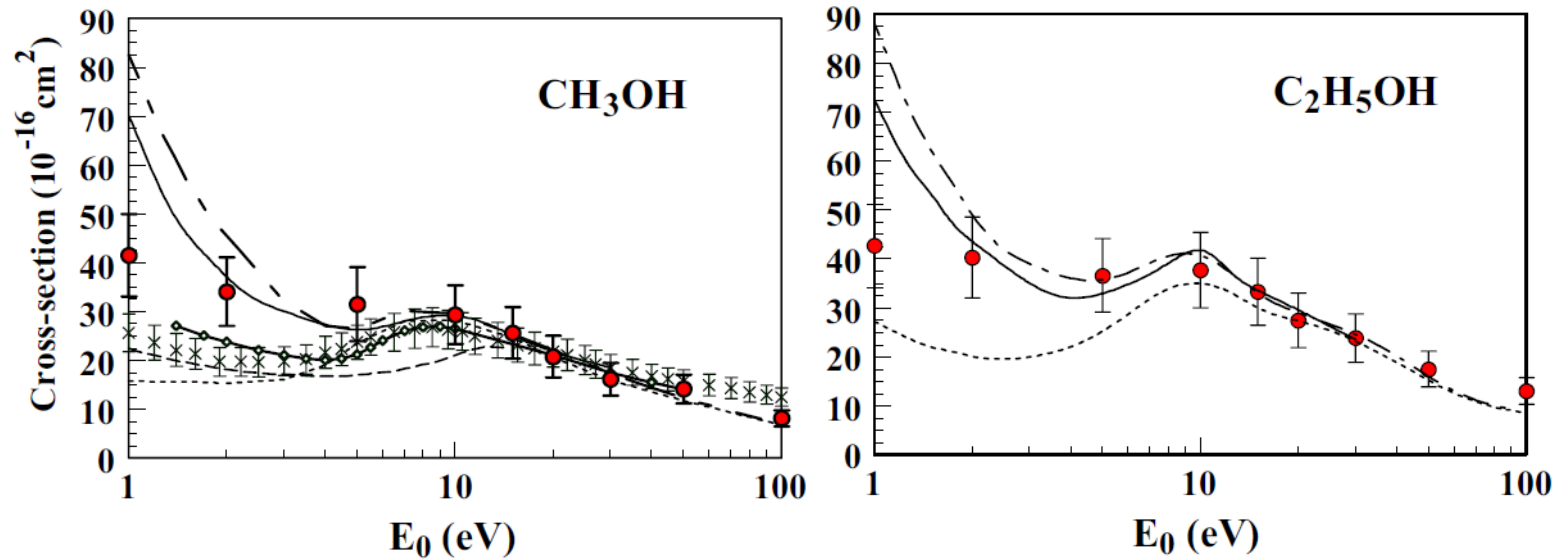
Integral elastic scattering cross sections for CH_3OH. Legend: ●: present experiment; —·—: SMCPP SEP; —: SMC SEP; ---- (short dashes): SMC SE which is similar to SMCPP SE; and ---- (long dashes): *R*-matrix ICSs of Bouchiha *et al.* (without Born correction) [10]. × Total cross section measurements of Szmytkowski and Krzysztofowicz [24] and —◆— of Schmieder [22]. ----- (short dashes) are from the SMCPP SE which is similar to SMC SE.

MAPLima

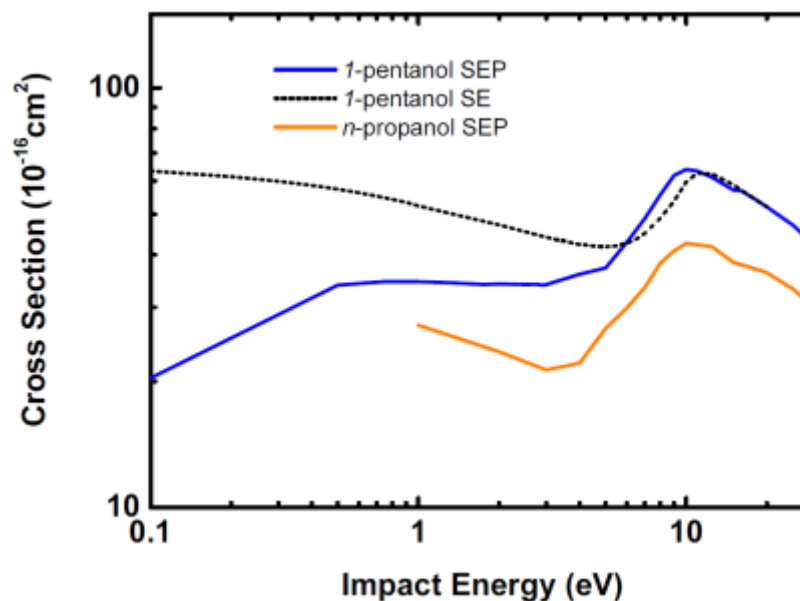# NSF/CNPq project (experiments from Morty Khakoo's group)

Elastic scattering of slow electrons by *n*-propanol and *n*-butanol

PHYSICAL REVIEW A **78**, 062714 (2008)
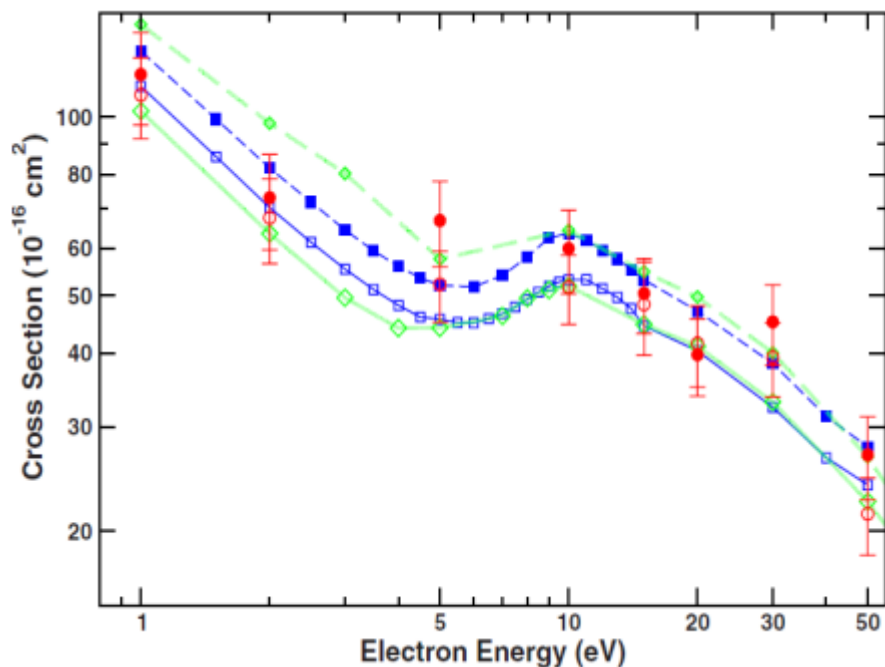
Electron scattering of slow electrons by *1-pentanol (a drop in fuel)*

Integral elastic cross sections for electron collisions with *n*-propanol and *n*-butanol. Red circles are experimental values, thin blue lines with squares results from all-electron calculations, and thick green lines with diamonds results from pseudopotential calculations. Open symbols and solid lines are propanol data; solid symbols and dashed lines are butanol data.

NSF/CNPq project (experiments from Morty Khakoo's group)

Motivation II: large scale production of ethanol

A sugarcane industry of Sugar/Ethanol/Bioeletricity

Motivation II: large scale production of ethanol

Biomass: a source of energy and carbon

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Motivation II: large scale production of ethanol

Biomass: a source of energy and carbon

Motivation II: large scale production of ethanol

First generation ethanol: crushing the cane for the juice

Motivation II: large scale production of ethanol

Bagasse piles at the mill.

2nd generation ethanol? Other high value bioproducts?
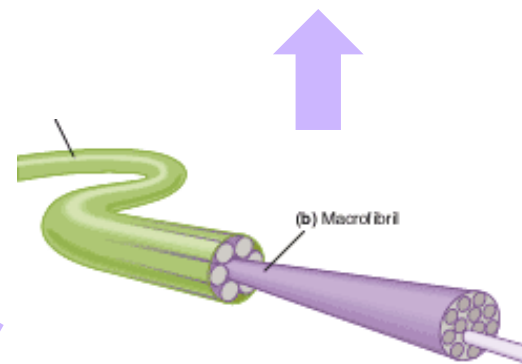
Biomass: a source of energy and carbon
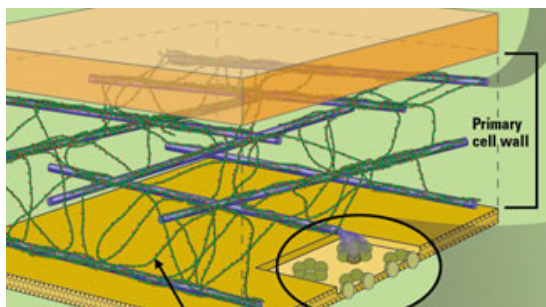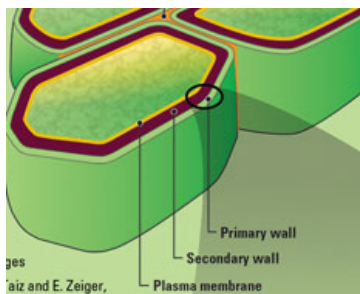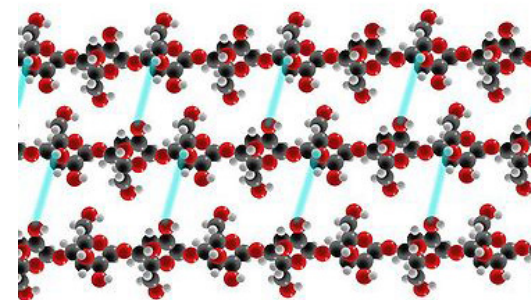
Biomass is Made Up with Fermentable Sugars
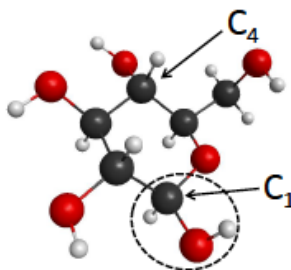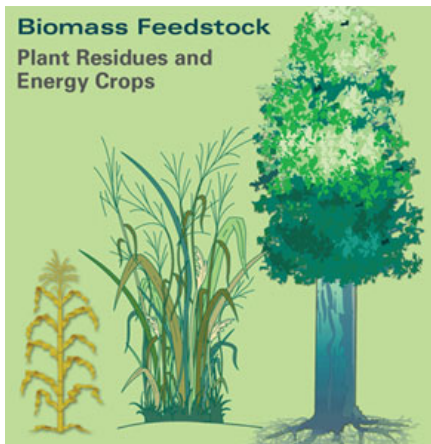
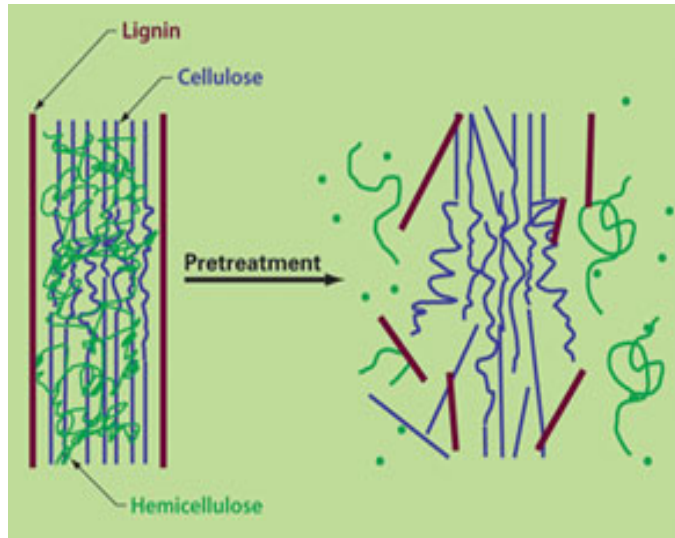β-D-glucose
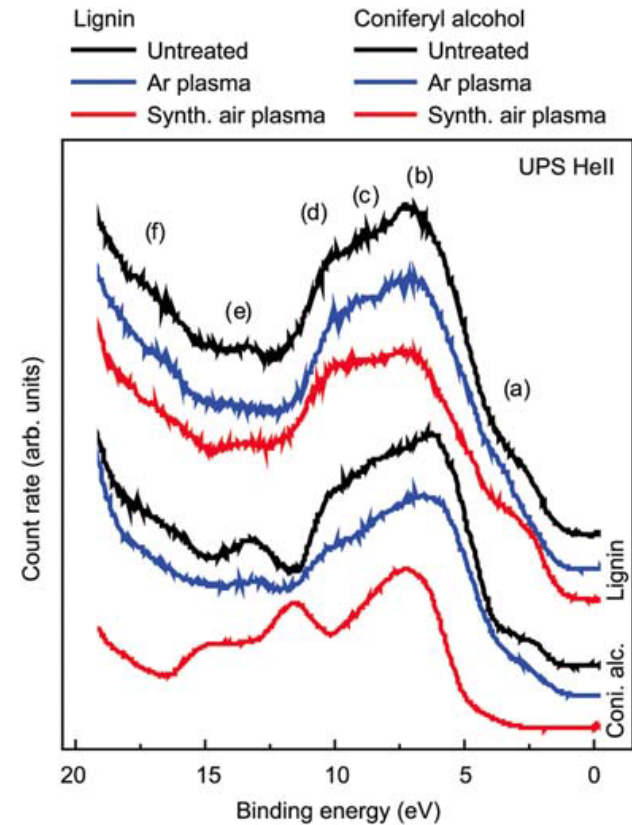
cellobiose

Biomass Feedstock
Plant Residues and
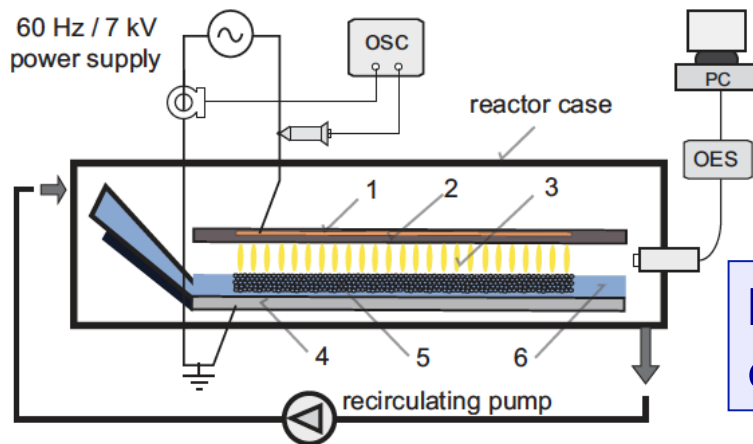Energy Crops
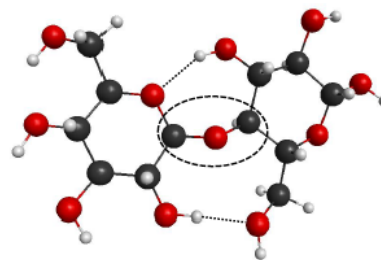
Lignocellulose is Resistant to Hydrolysis

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

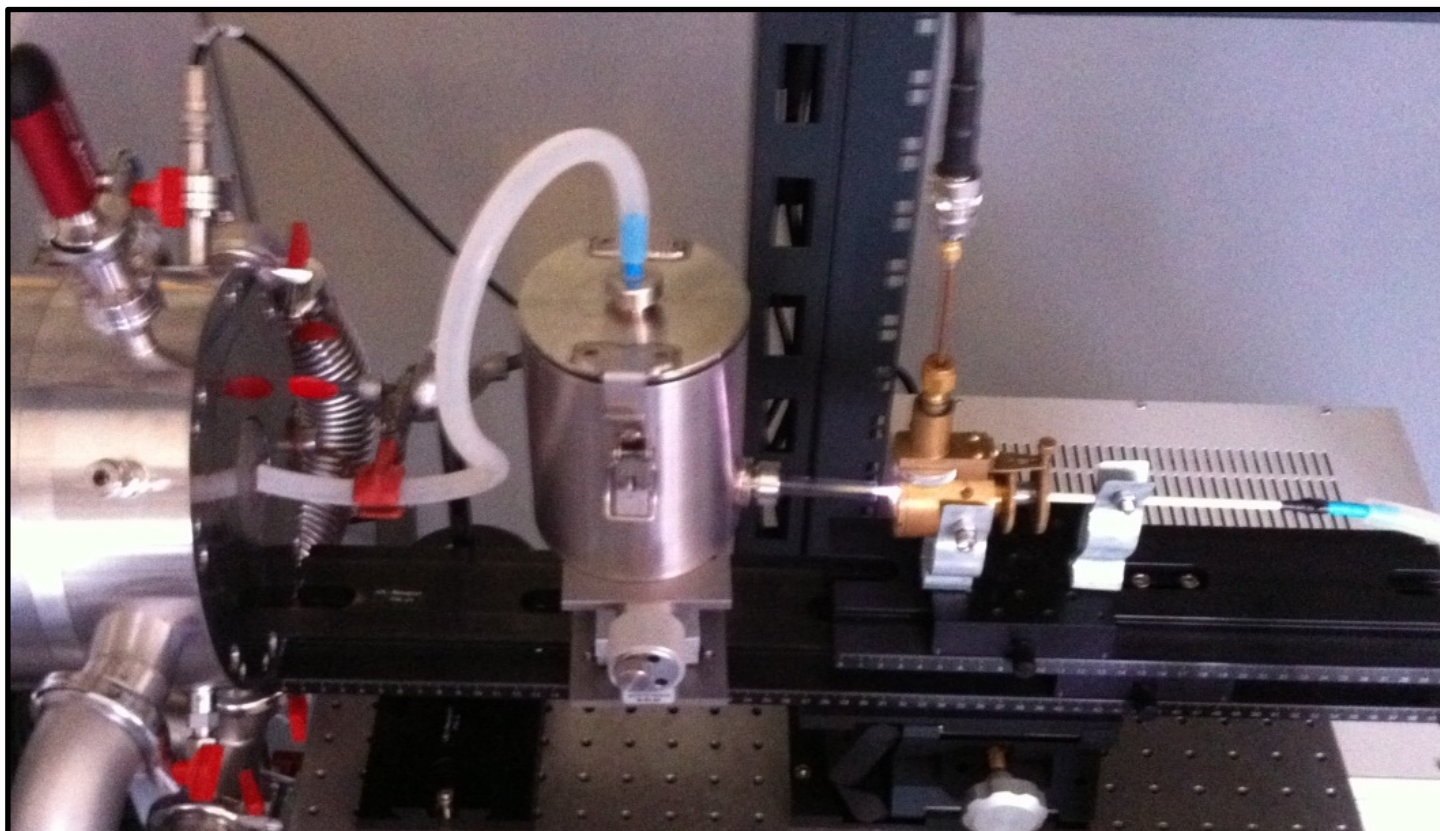Lothar Klarhöfer[1], Wolfgang Viöl[2,3,*] and Wolfgang Maus-Friedrichs[1]

Dielectric Barrier Discharge (DBD): electron flux on substrate ~10^8 cm^{-2} s^{-1}

Sugarcane Bagasse Plasma Pretreatment

Treatment conditions

- ~ 25 g of dry sugarcane bagasse (50% moisture) – milled at $500\mu m$
- Gas flow Mixture: 95% Ar (1.9 SLM) and 5% O_2 (0.1 SML)
- $\Delta t_{treatment}$ = 3h

Biomass Chemical Analysis

Lignin concentration (%) of raw bagasse and samples related to plasma torch treatment and washing procedure by water and NaOH 1% solution at room temperature.

| Samples	Soluble Lignin (%)	Insoluble Lignin (%)	Total of Lignin remaining (%)
raw bagasse	1.58 ±0.01	20.3 ± 0.1	21.9 ± 0.1
Washed by H_2O	2.4 ± 0.9	21.4 ± 0.9	23.8 ± 0.9
Washed by NaOH 1%	**1.3 ± 0.9**	**12.6 ± 0.9**	**13.9 ± 0.9**

About 40% of original lignin was removed!!!

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
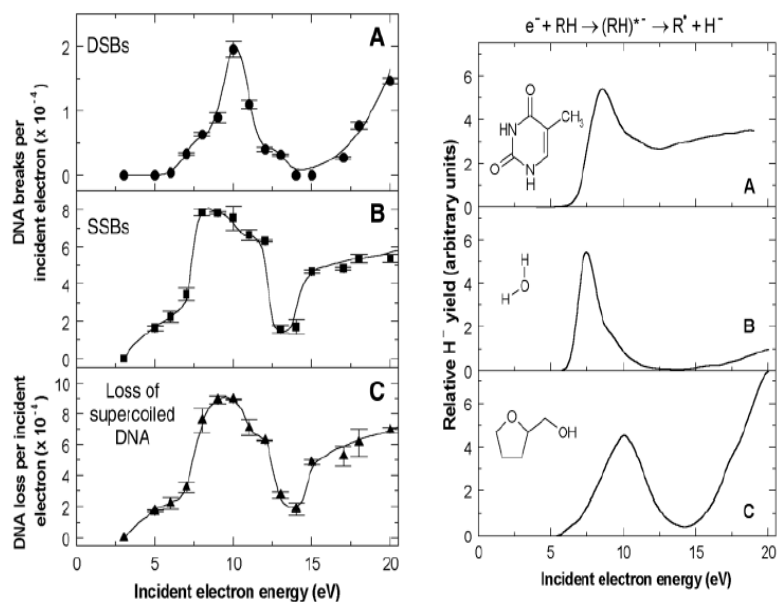
Science, **287** 1658 (2000)

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.
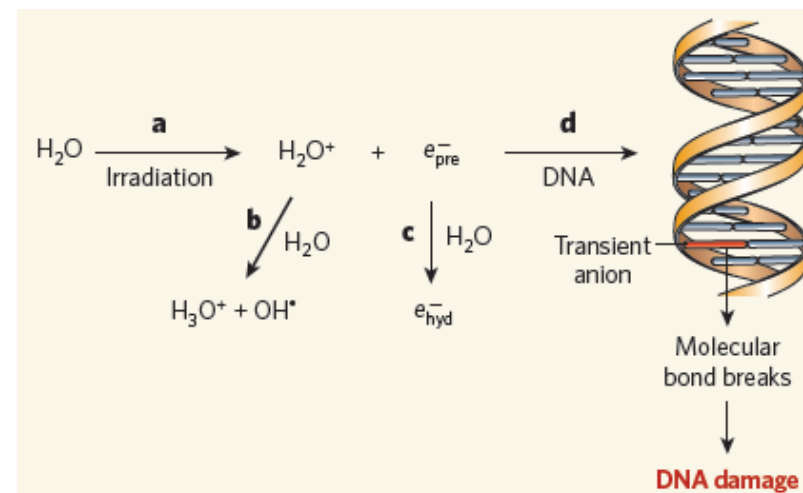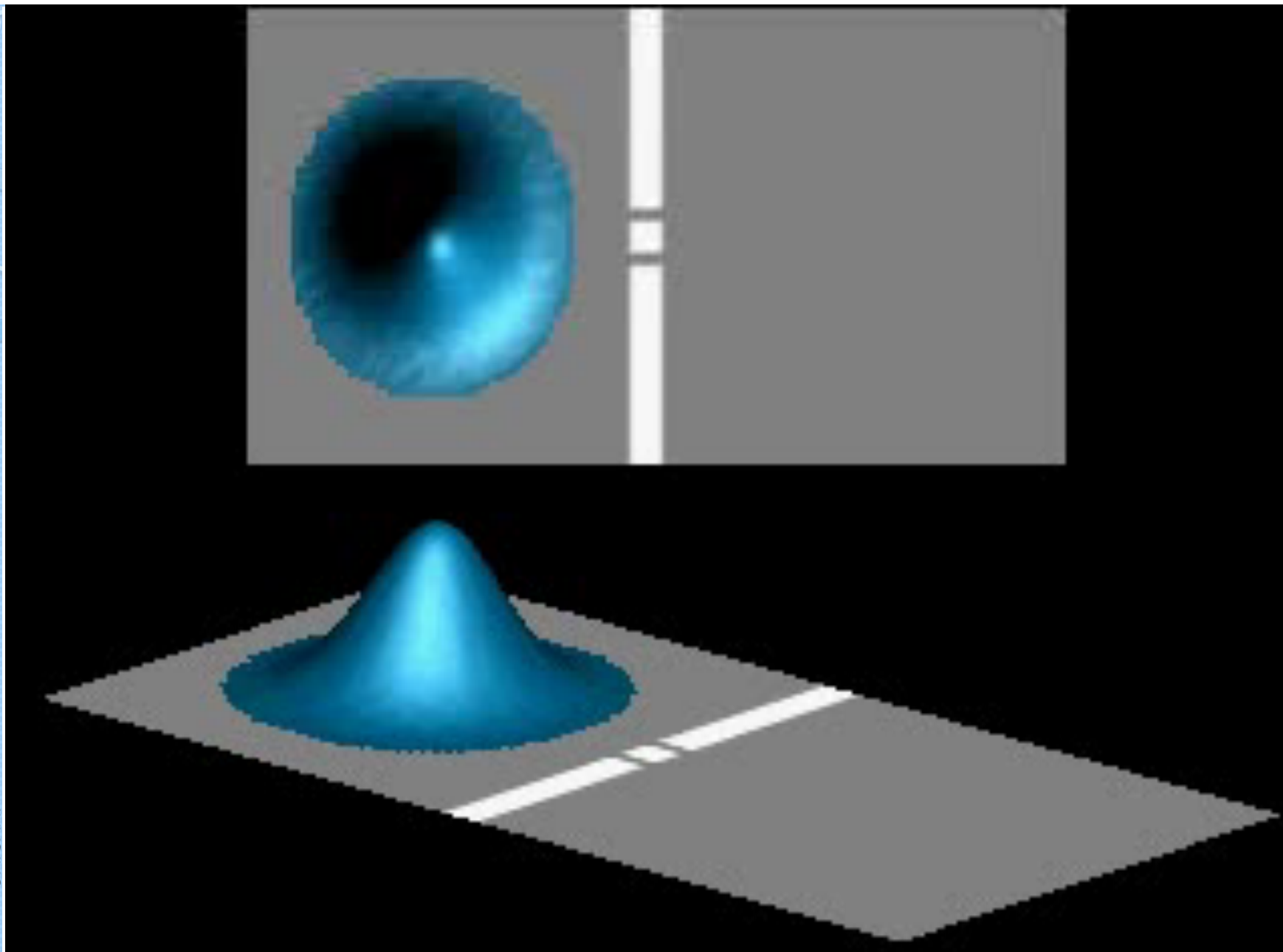

Sanche, Nature **461**, 358 (2009)

J|A|C|S
COMMUNICATIONS

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

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

Two slits interference

To see this animations, visit: **http://www.embd.be/quantummechanics/**

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Scattering theory

Theoretical background

Schrödinger equation

$$H\Psi_{\vec{k}_m}^{(\pm)}(\vec{r}_1,\cdots,\vec{r}_{N+1}) = E\Psi_{\vec{k}_m}^{(\pm)}(\vec{r}_1,\cdots,\vec{r}_{N+1})$$

Asymptotic condition

$$\Psi_{\vec{k}_i}^{(\pm)}(\vec{r}_1,\cdots,\vec{r}_{N+1}) \xrightarrow{r_{N+1}\to\infty} S_{\vec{k}_i} + \sum_f^{\text{open}} f_{i\to f}^B(\vec{k}_i,\vec{k}_f)\Phi_f \frac{e^{\pm ik_f r_{N+1}}}{r_{N+1}}$$

$$S_{\vec{k}_i} = \Phi_i e^{i\vec{k}_i\bullet\vec{r}_{N+1}}$$

Differential cross section

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

Scattering theory

Schrödinger differential equation

$$H\Psi_{\vec{k}_m}^{(\pm)} = \left[H_N + T_{N+1} + V \right] \Psi_{\vec{k}_m}^{(\pm)} = E\Psi_{\vec{k}_m}^{(\pm)}$$

Lippmann-Schwinger integral equation

$$\Psi_{\vec{k}_m}^{(\pm)} = S_{\vec{k}_m} + G_o^{(\pm)} V \Psi_{\vec{k}_m}^{(\pm)}$$

$$S_{\vec{k}_m} = \Phi_m e^{i\vec{k}_m \cdot \vec{r}_{N+1}}$$

Free-particle Green's function   (Source of uncertainty – controllable)

$$G_o^{(\pm)} = \frac{1}{E - T_{N+1} - H_N \pm i\varepsilon} = \lim_{\varepsilon \to 0} \sum_m \int d^3k \, \frac{|\Phi_m \vec{k}\rangle\langle\vec{k}\Phi_m|}{\dfrac{k_m^2}{2} - \dfrac{k^2}{2} \pm i\varepsilon}$$

Schwinger Variational Principle

The Schwinger Variational method serves to get a scattering amplitude free of first order errors for a scattering process that respect the equations

$$A^{(\pm)}|\Psi_{\mathbf{k}}^{(\pm)}\rangle = V|S_{\mathbf{k}}\rangle \text{ and } \begin{cases} f_{\mathbf{k_f},\mathbf{k_i}} = \langle S_{\mathbf{k_f}}|V|\Psi_{\mathbf{k_i}}^{(+)}\rangle \\[2mm] f_{\mathbf{k_f},\mathbf{k_i}} = \langle \Psi_{\mathbf{k_f}}^{(-)}|V|S_{\mathbf{k_i}}\rangle \qquad \text{and } A^{(\pm)} = V - VG_0^{(\pm)}V \\[2mm] f_{\mathbf{k_f},\mathbf{k_i}} = \langle \Psi_{\mathbf{k_f}}^{(-)}|A^{(+)}|\Psi_{\mathbf{k_i}}^{(+)}\rangle \end{cases}$$

The bilinear form of the variational principle for the scattering amplitude is

$[f_{\mathbf{k_f},\mathbf{k_i}}] = \langle S_{\mathbf{k_f}}|V|\Psi_{\mathbf{k_i}}^{(+)}\rangle + \langle \Psi_{\mathbf{k_f}}^{(-)}|V|S_{\mathbf{k_i}}\rangle - \langle \Psi_{\mathbf{k_f}}^{(-)}|A^{(+)}|\Psi_{\mathbf{k_i}}^{(+)}\rangle$ where arbitrary and

independent variations with respect to $\begin{cases} \langle \delta\Psi_{\mathbf{k_f}}^{(-)}|(V|S_{\mathbf{k_i}}\rangle - A^{(+)}|\Psi_{\mathbf{k_i}}^{(+)}\rangle) = 0 \\ (\langle S_{\mathbf{k_f}}|V - \langle \Psi_{\mathbf{k_f}}^{(-)}|A^{(+)})|\delta\Psi_{\mathbf{k_i}}^{(+)}\rangle = 0 \end{cases}$

lead to $\begin{cases} V|S_{\mathbf{k_i}}\rangle - A^{(+)}|\Psi_{\mathbf{k_i}}^{(+)}\rangle = 0 \Rightarrow A^{(+)}|\Psi_{\mathbf{k_i}}^{(+)}\rangle = V|S_{\mathbf{k_i}}\rangle \\ \langle S_{\mathbf{k_f}}|V - \langle \Psi_{\mathbf{k_f}}^{(-)}|A^{(+)} = 0 \Rightarrow A^{(-)}|\Psi_{\mathbf{k_f}}^{(-)}\rangle = V|S_{\mathbf{k_f}}\rangle \text{ with } A^{(+)\dagger} = A^{(-)} \end{cases}$

$A^{(\pm)}|\Psi_{\mathbf{k}}^{(\pm)}\rangle = V|S_{\mathbf{k}}\rangle$ *must be equivalent to* $H|\Psi_{\mathbf{k}}^{(\pm)}\rangle = E|\Psi_{\mathbf{k}}^{(\pm)}\rangle$ *with*

proper boundary conditions

Schwinger Multichannel Method for electron scattering

In this formalism the operator $A^{(+)}$ was redefined as:

$$A^{(+)} = \frac{1}{2}(PV + VP) - VG_P^{(+)}V + \frac{1}{N+1}\left[\hat{H} - \frac{N+1}{2}(\hat{H}P + P\hat{H})\right]$$

where $\quad P \equiv \sum_{\ell=1}^{open} |\Phi_\ell\rangle\langle\Phi_\ell| \quad$ and $\quad \hat{H} = E - H$

(Channel coupling: source of uncertainty – uncontrollable)

All electrons are identical. So, an expansion of the scattering wave function must be done in a basis $\{\chi_\mu\}$ of anti-symmetric functions (Slater determinants):

$$|\Psi_{\vec{k}_m}^{(\pm)}\rangle = \sum_\mu a_\mu^{(\pm)}(\vec{k}_m)|\chi_\mu\rangle \quad \text{where} \quad \{|\chi_\mu\rangle\} = \{a_{N+1}|\Phi_i\rangle\otimes|\varphi_j\rangle\}$$

(N+1 wave-function expansion: source of uncertainty – controllable)

The final form of the scattering amplitude is equal to the one of the Schwinger Variational principle

$$f_{\vec{k}_i,\vec{k}_f} = -\frac{1}{2\Pi}\sum_{mn}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle$$

with $\quad d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle \quad$ and $\quad S_{\vec{K}_i} \equiv \Phi_i(\vec{r}_1,...,\vec{r}_N)\,e^{i\vec{K}_i\cdot\vec{r}_{N+1}}$

Coupling level

R. F. da Costa, F. J. da Paixão and M.A. P. Lima,
J. Phys. B **38**, 4363 (2005)

➡ Elastic scattering with and without polarization effects

❶ Open channel Projector has only one state

$$P = | \Phi_o \rangle \langle \Phi_o |$$

➡ Φ_o is molecular target ground state obtained in Hartree-Fock approximation

(Target description: source of uncertainty – program limitation)

❷ Configuration space is made of

(N+1 wave-function expansion: source of uncertainty – controllable)

$$| \chi_\mu \rangle = \begin{cases} a_{N+1} | \Phi_o \rangle \otimes | \varphi_i \rangle \\ a_{N+1} | \Phi_j \rangle \otimes | \varphi_k \rangle, j \geq 2 \end{cases}$$

➡ Doublet states made of products of target triplet and singlet states by φ_k

➡ Φ_j, $j \geq 2$ are virtual states obtained from single excitations of the molecular target

➡ φ_i are one-particle wave functions (square integrable molecular orbitals) used in description of the continuum

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Coupling level

➡️ Inelastic scattering with and without polarization

❶ Open channel projector contains channels of our choice (truncation means approximation)

$$P = \sum_{\ell}^{open} |\Phi_{\ell}\rangle\langle\Phi_{\ell}|$$

➡️ $|\Phi_{\ell}\rangle$ are molecular target states obtained with single configuration interaction

❷ Again the configuration space is made of

$$|\chi_{\mu}\rangle = \begin{cases} a_{N+1} |\Phi_o\rangle \otimes |\varphi_i\rangle \\ a_{N+1} |\Phi_j\rangle \otimes |\varphi_k\rangle, j \geq 2 \end{cases}$$

➡️ Doublet states made of products of target triplet and singlet states by φ_k

➡️ Polarization effects are included with j greater than the number of open channels

MAPLima

Electron scattering by large molecules

Pseudopotential formalism
(source of uncertainty – optional for light molecules)

[D. R. Hamann, M. Schlüter and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979)]

❶ The pseudo-state energy is equal to the real eigenvalue for a given configuration;

❷ The pseudopotential is equal to the real potential beyond a certain core radius r_c, and it is soft at the origin;

❸ The normalized pseudo wave function is equal to the real one beyond the core radius r_c and it is soft and without nodes

❹ The integrals from 0 to r of the real and pseudo functions agree for $r > r_c$ for each valence state:

$$-\frac{1}{2}\left[(r\Psi)^2 \frac{d}{dE}\frac{d}{dr}\ln\Psi\right]_{r>r_c} = \int_0^{r>r_c} \Psi^2 r^2 dr$$

"Norm Conservation"

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Theoretical co-authors

Eliane M. de Oliveira (posdoc)
Alexandra Natalense
Marco A. P. Lima

Sergio d'A. Sanchez
Márcio H. F. Bettega

Romarly F. da Costa

Márcio T. do N. Varella (coordinator)

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Shape resonances are related to angular momentum traps
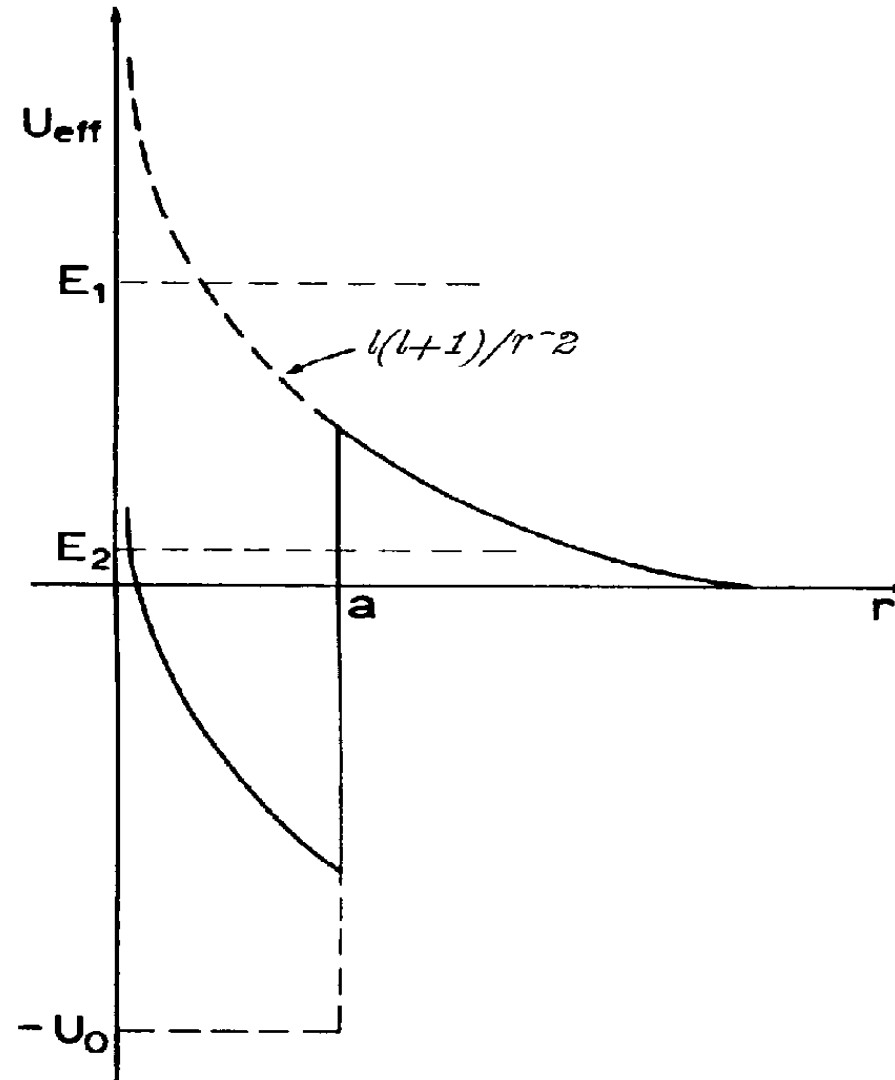
Low energy elastic electron scattering from pirrole

- There are π^* (ring) and σ^* (N–H) shape resonances in pyrrole. Nice prototype!

Pyrrole
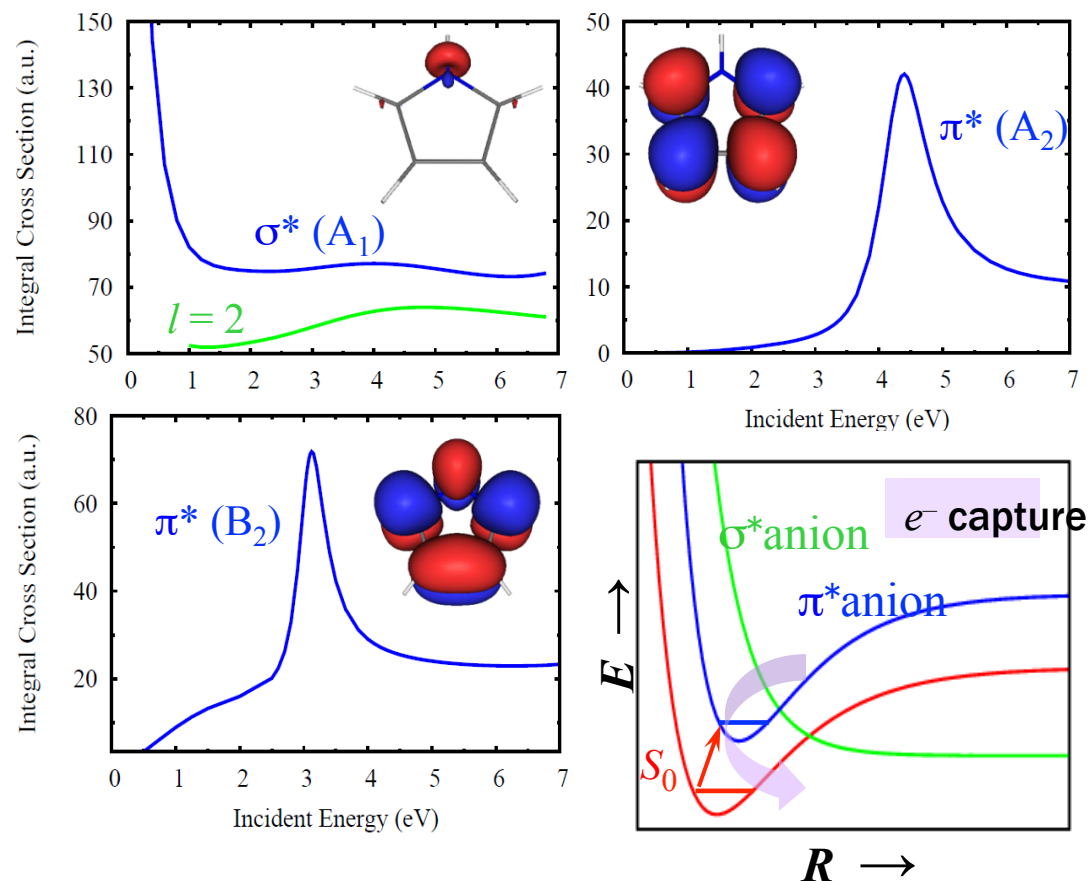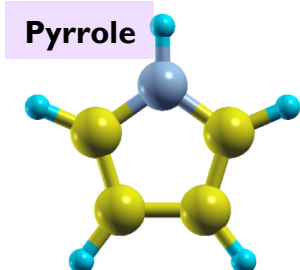
de Oliveira EM, Lima MAP, Bettega MHF, Sanchez SD, da Costa RF, and Varella MTD, J. Chem. Phys. **132**, 204301 (2010)

Lignin Subunits

Phenol   **Guaiacol**   **Syringol**

MetOH   **MetOH**
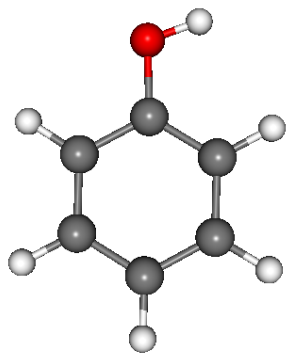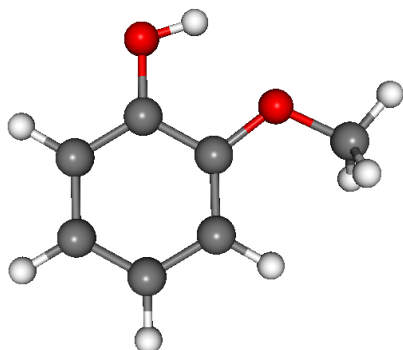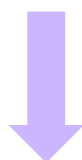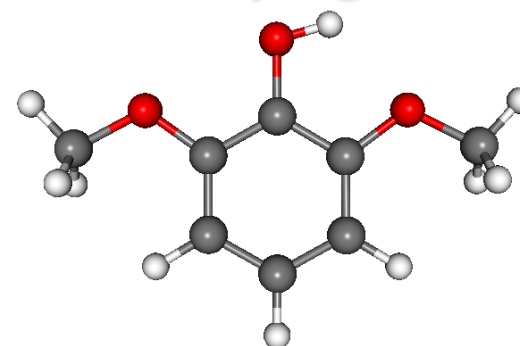
PropenylOH   **PropenylOH**   **PropenylOH**
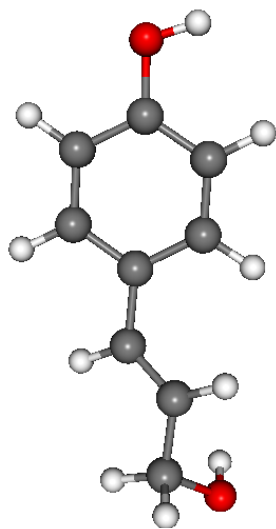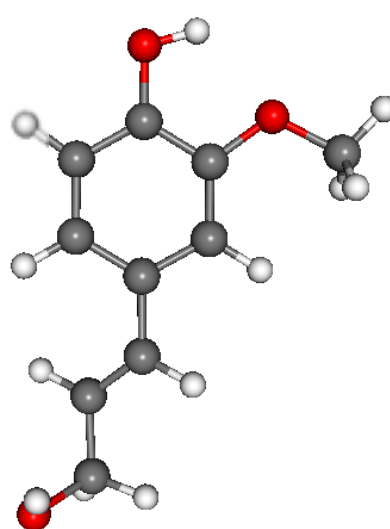
p-coumaryl alcohol   coniferyl alcohol   sinapyl alcohol
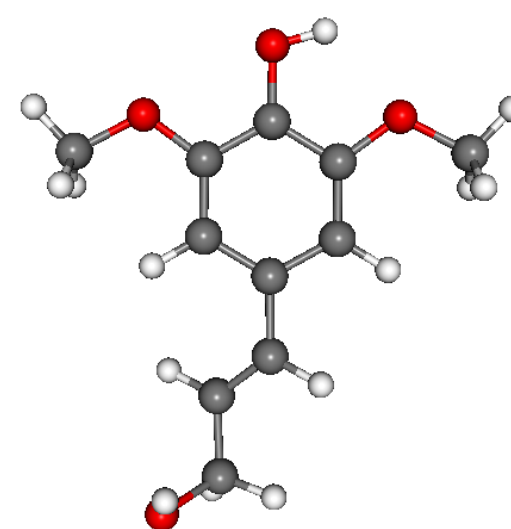
Shape resonance spectra of lignin subunits

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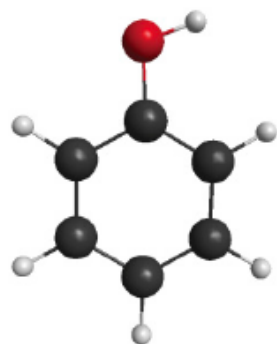
phenol

—— SEP

---- SE

guaiacol

—— SEP

---- SE

---- SE

p-coumaryl alcohol

p-Cu (LUMO)

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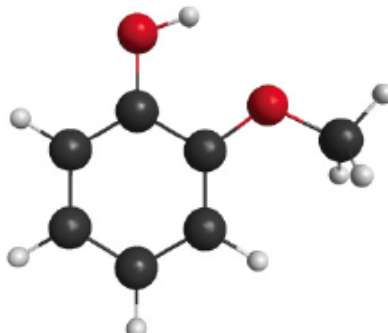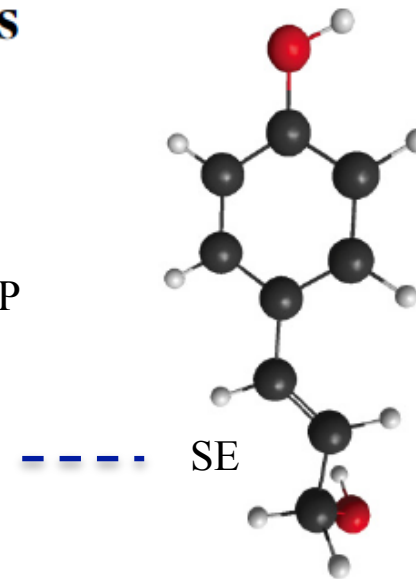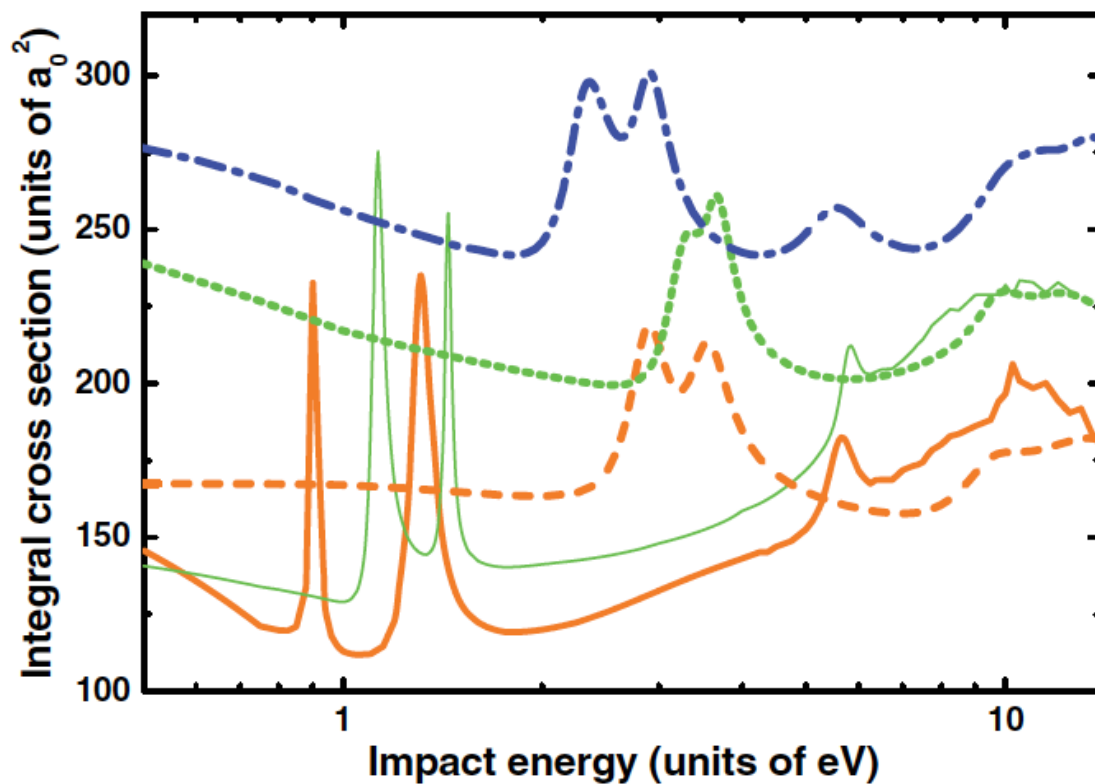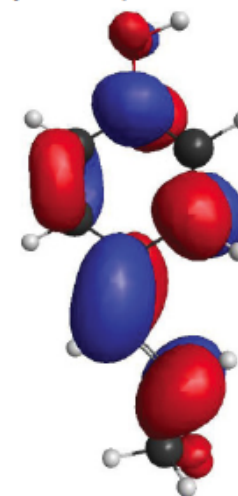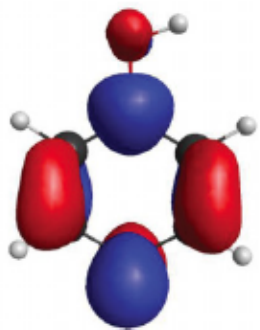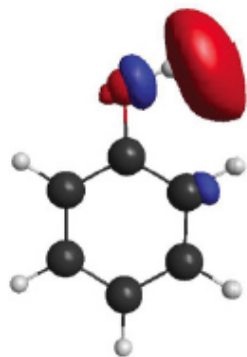
π^* (LUMO+1)

σ^* (LUMO+2)

Phenol: Calculations, ET spectra and DEA data indicate H elimination from π^*/σ^* coupling.
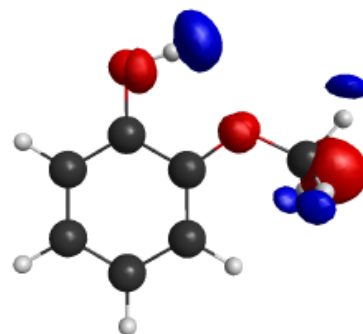

π^* (LUMO)
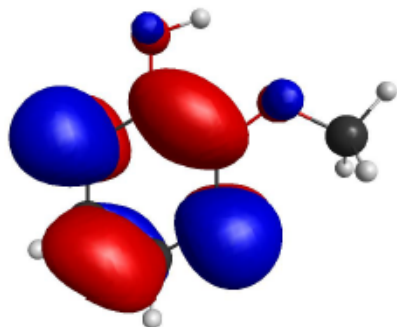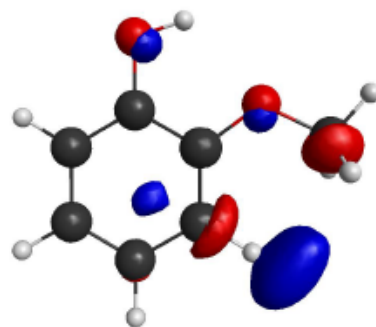
σ^* (LUMO+2)

π^* (LUMO+1)

σ^* (LUMO+3)

Guaiacol: Methoxilation is expected to give rise to other dissociation channels. H elimination should be also observed.
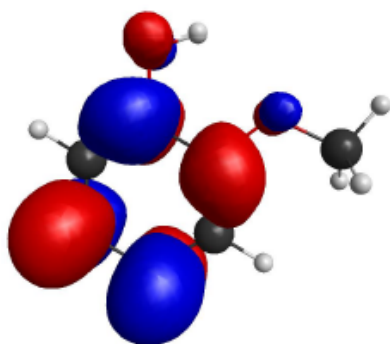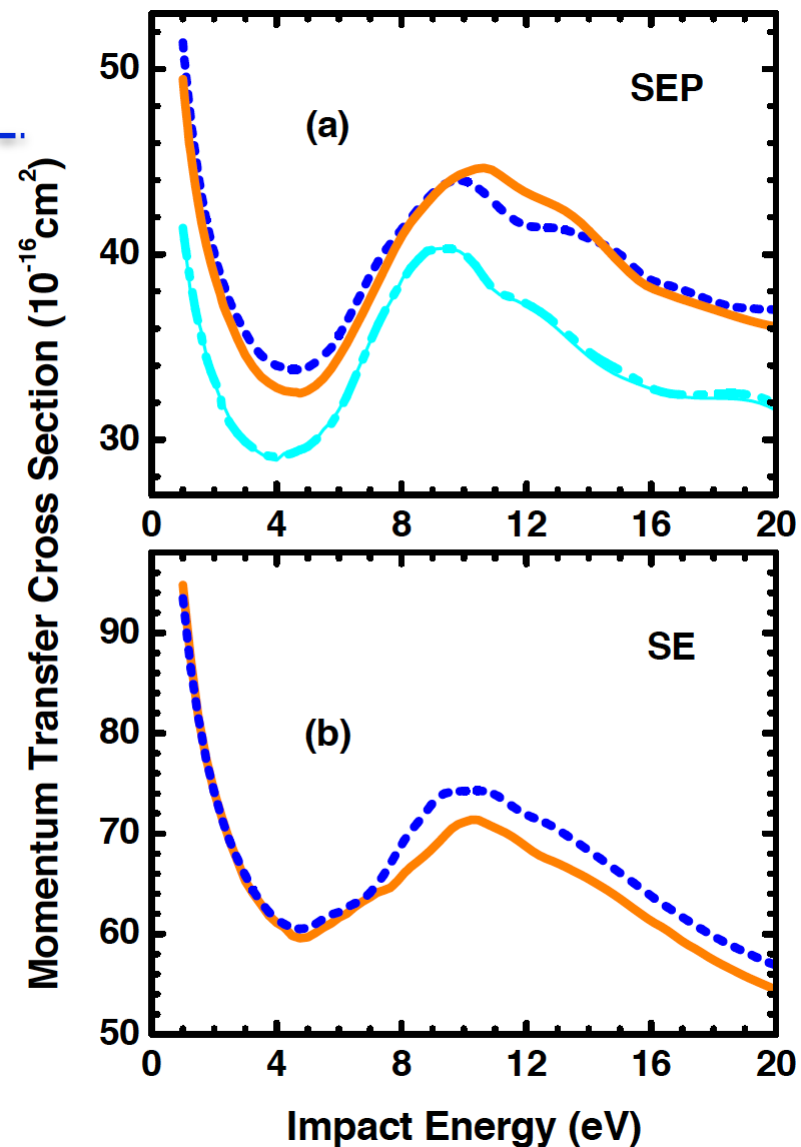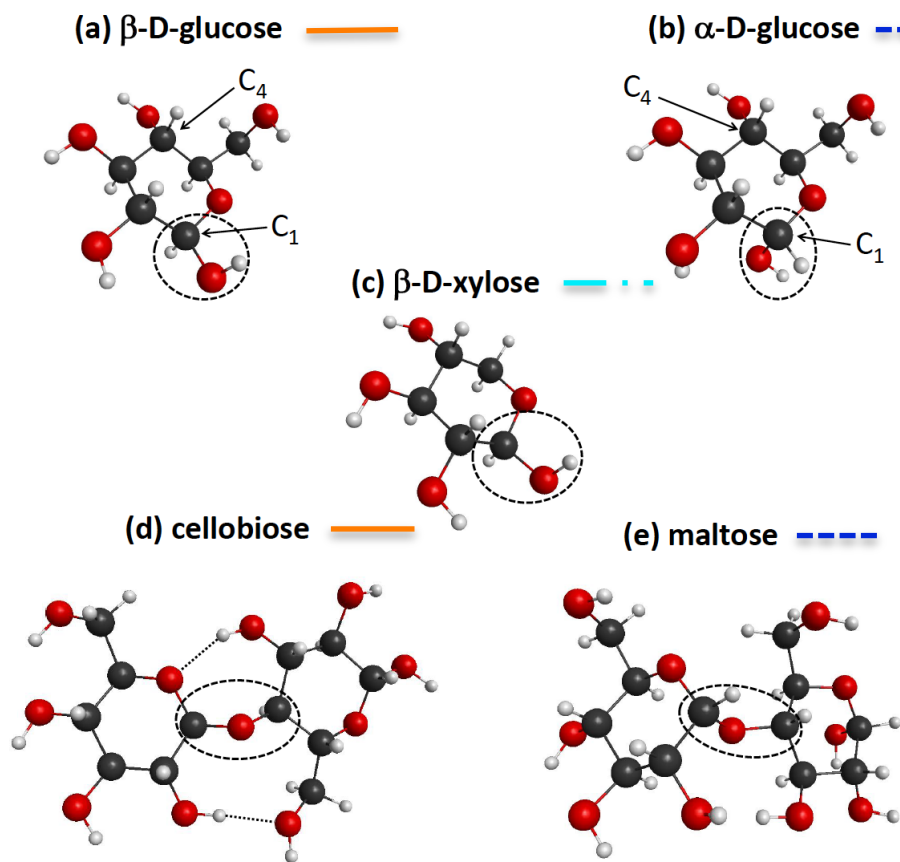
Low-energy electron scattering by cellulose and Hemicellulose components

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

(a) β-D-glucose

(b) α-D-glucose

(c) β-D-xylose

(d) cellobiose

(e) maltose

Theoretical team on electron-scattering of microsolvated molecules

Sylvio Canuto (microsolvation)
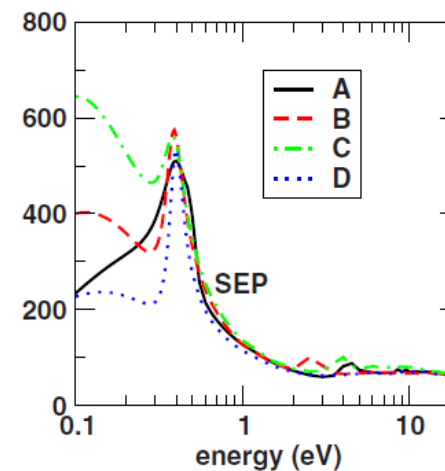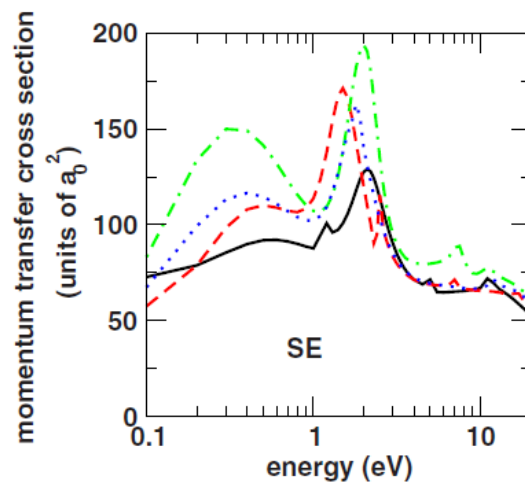Kaline Coutinho (microsolvation)
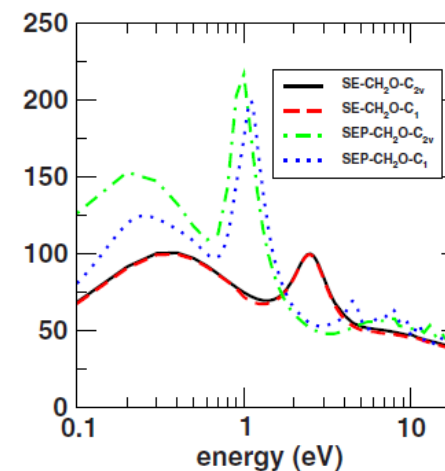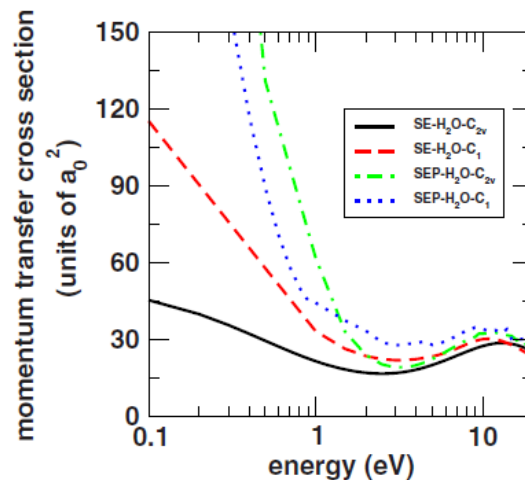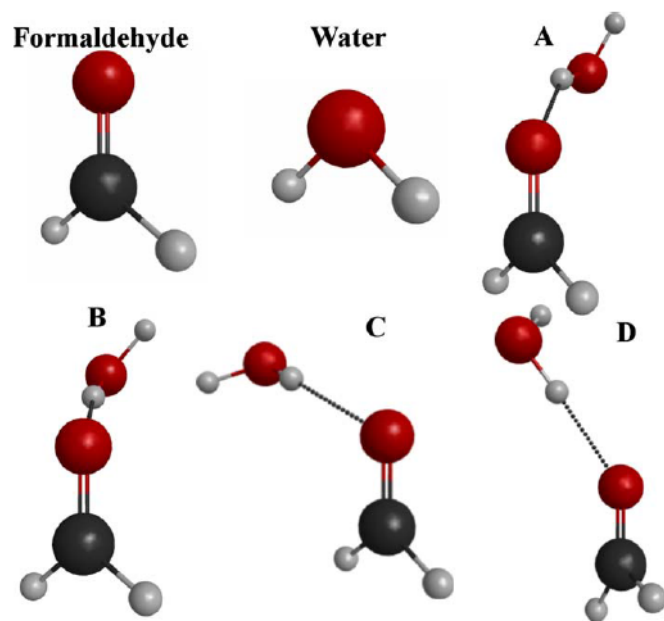Márcio T. do N. Varella

Eliane M. de Oliveira (scattering of solvated phenol)
Marco A. P. Lima

Thiago C. Freitas (his Ph.D. Thesis)
Márcio H. F. Bettega (coordinator)

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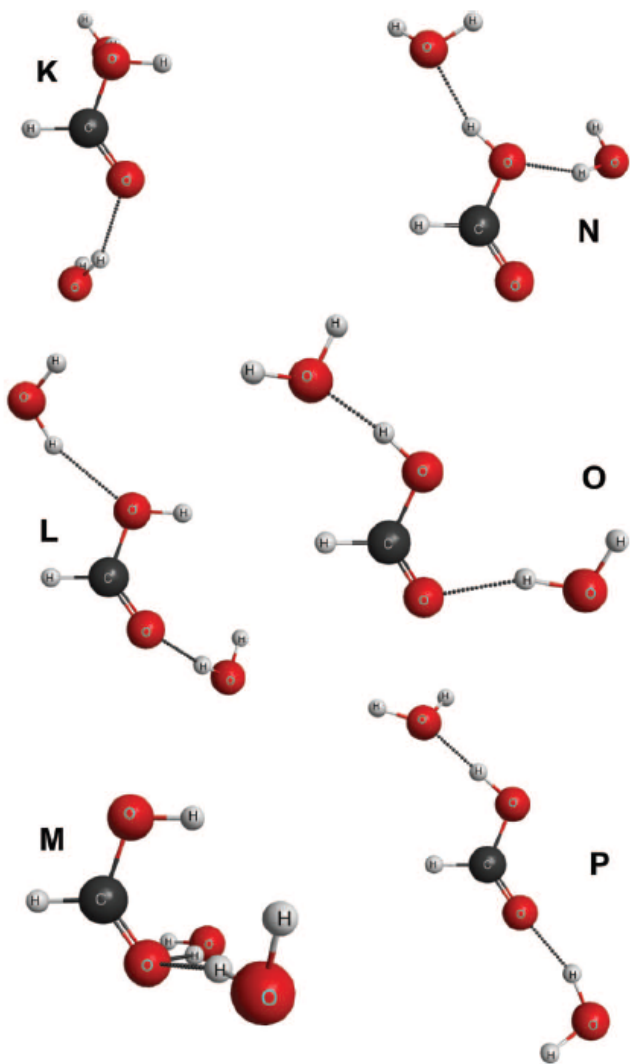
Electron Collisions with the CH$_2$O-H$_2$O complex
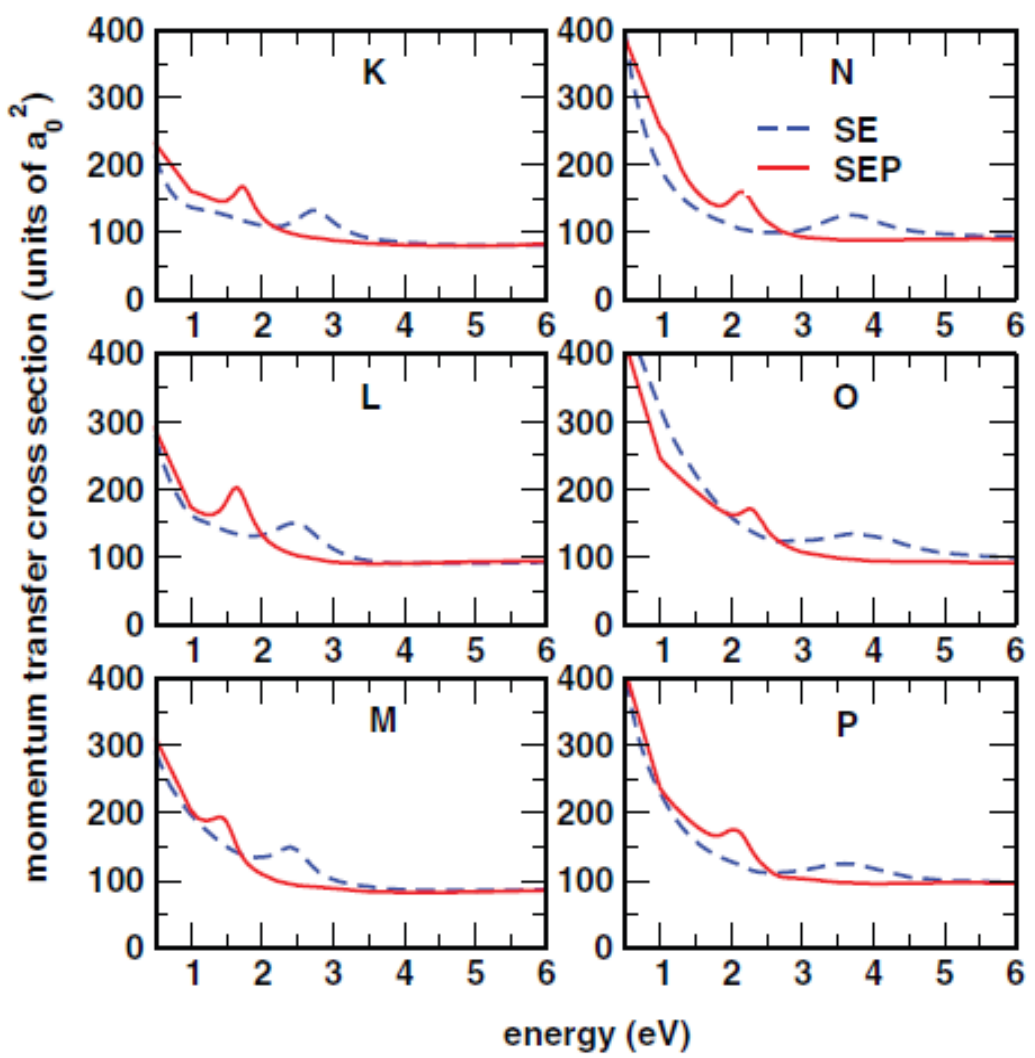
PHYSICAL REVIEW A 80, 062710 (2009)

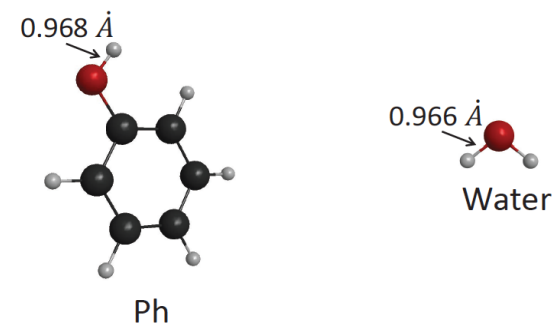# Electron collisions with the HCOOH...(H₂O)n complexes (n=1, 2) in liquid phase: The influence of microsolvation on the π* resonance of formic acid
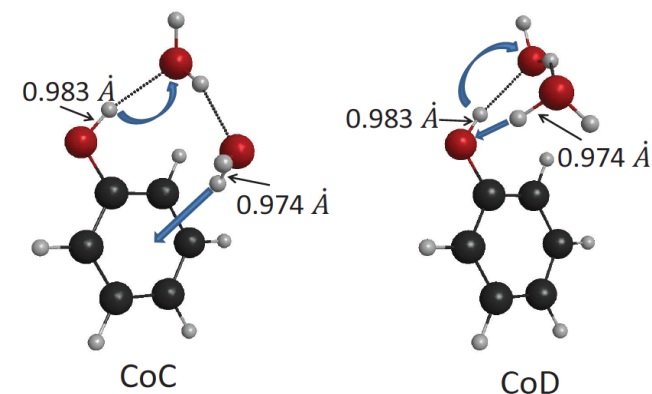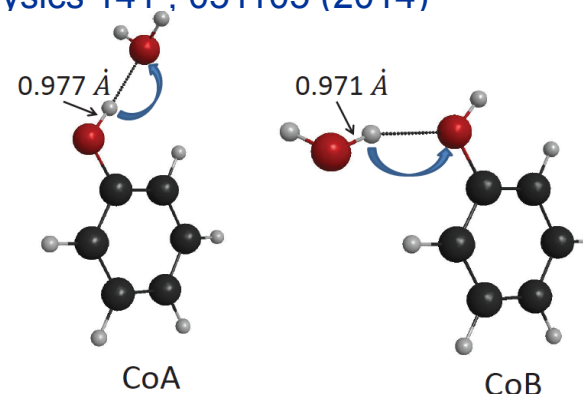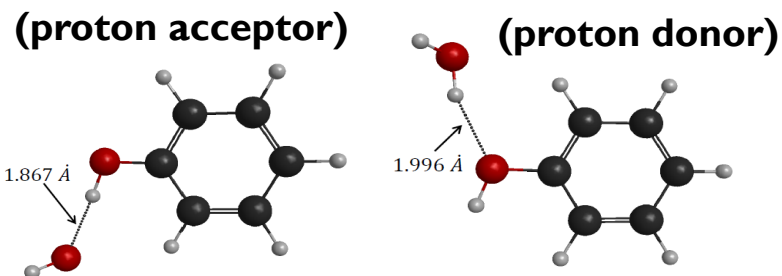
π* shape resonance for HCOOH at around 1.9 eV.
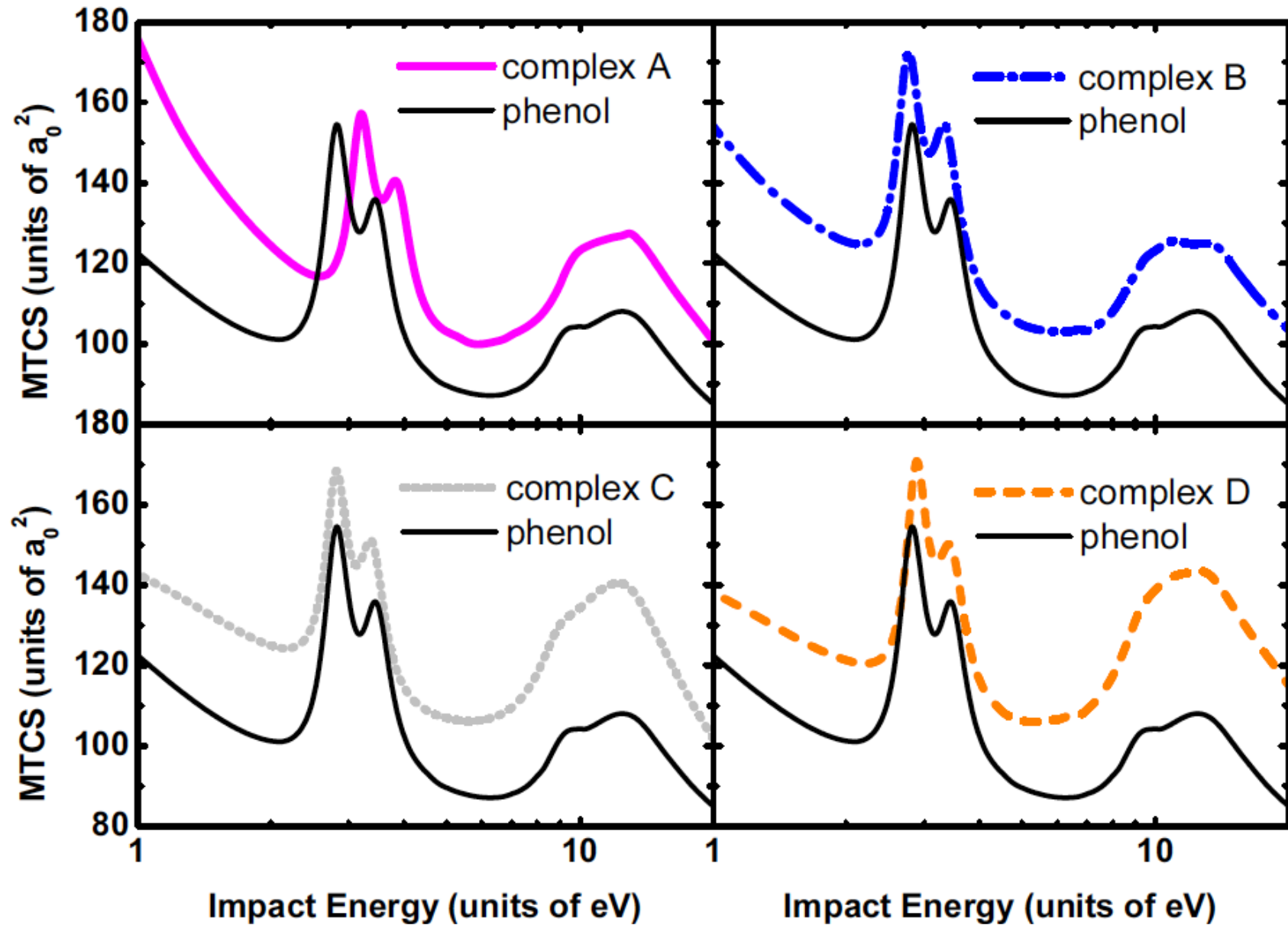
Electron Collisions with Phenol...H$_2$O

E. M. de Oliveira, T. C. Freitas , K. Coutinho , M. T. do N. Varella , S. Canuto , M. A. P. Lima and M.H.F Bettega, The Journal of Chemical Physics 141 , 051105 (2014)

(proton acceptor)   **(proton donor)**

1.867 Å   1.996 Å

0.977 Å   0.971 Å

CoA   CoB

0.983 Å   0.983 Å   0.974 Å
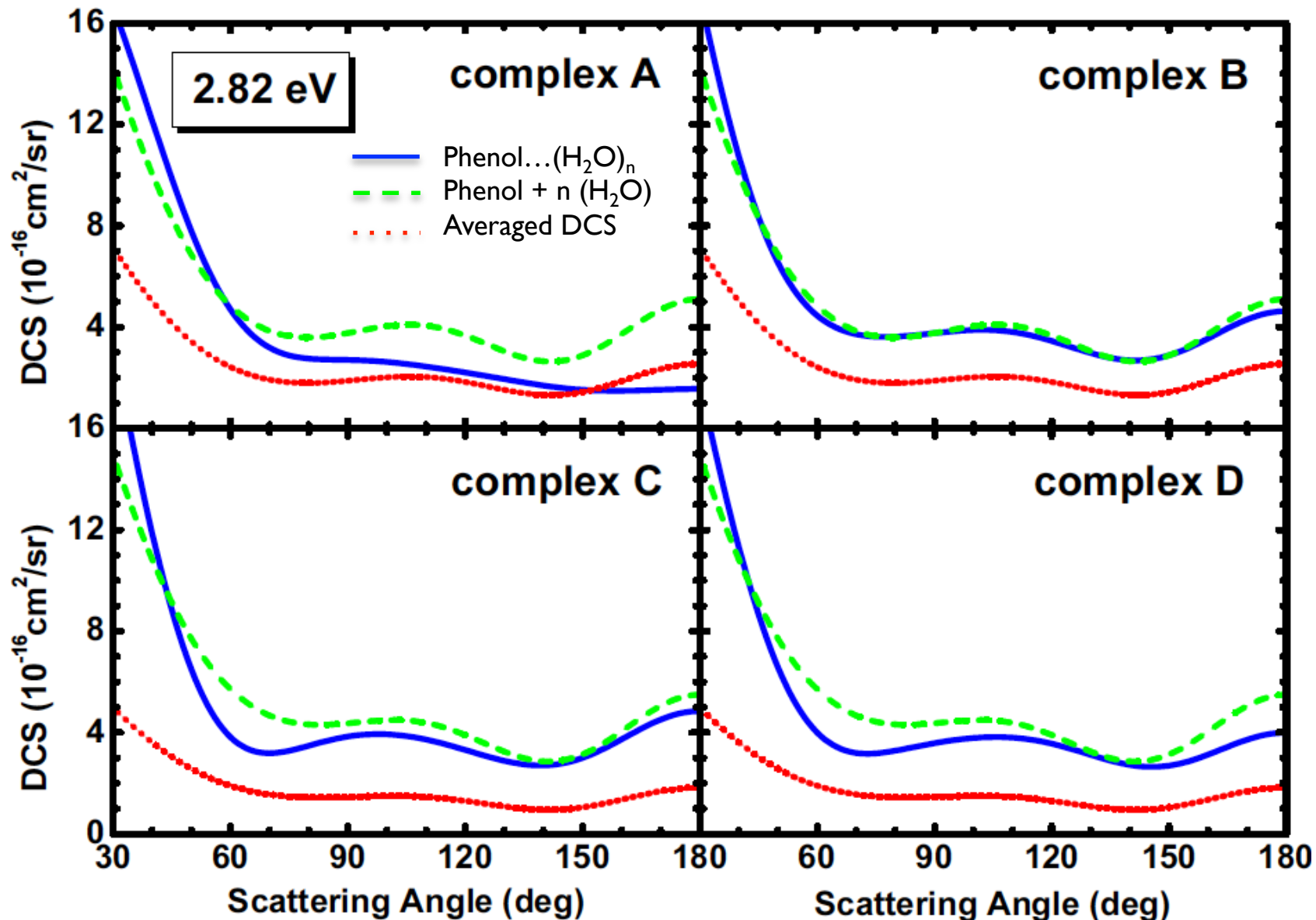
0.974 Å

CoC   CoD

0.968 Å

0.966 Å

Ph   Water

We have studied the microsolvation of Phenol using 4 complexes.

- In Complex A, the water molecule is a proton acceptor.
- In the Complex B, the water is a proton donor.
- Complexes C and D have both situations (one water molecule as acceptor and the other as proton donor).
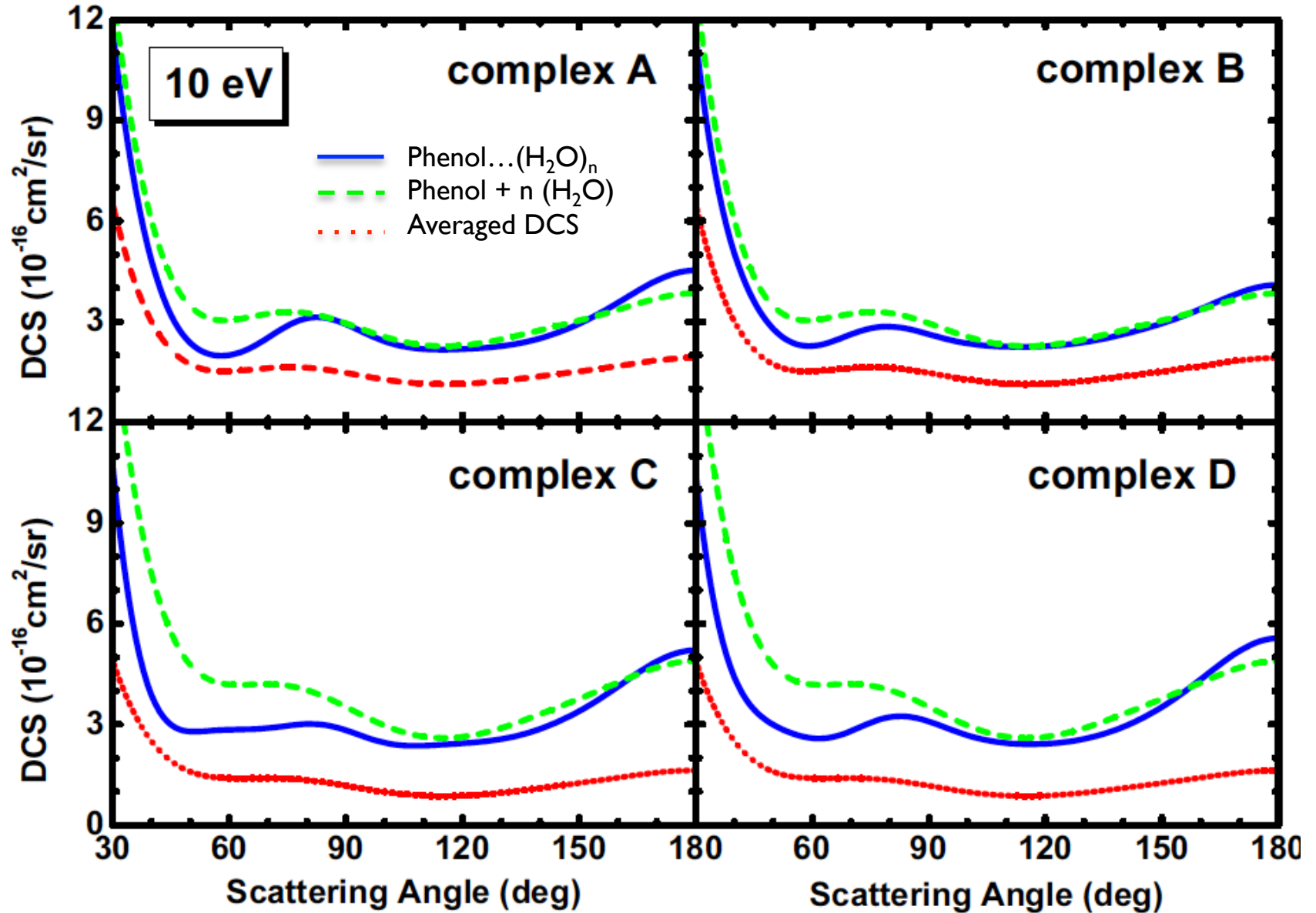
Electron Collisions with Phenol...$(H_2O)_n$: n=1,2

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Electron Collisions with Phenol...(H₂O)ₙ: search for microsolvation signatures in the DCS
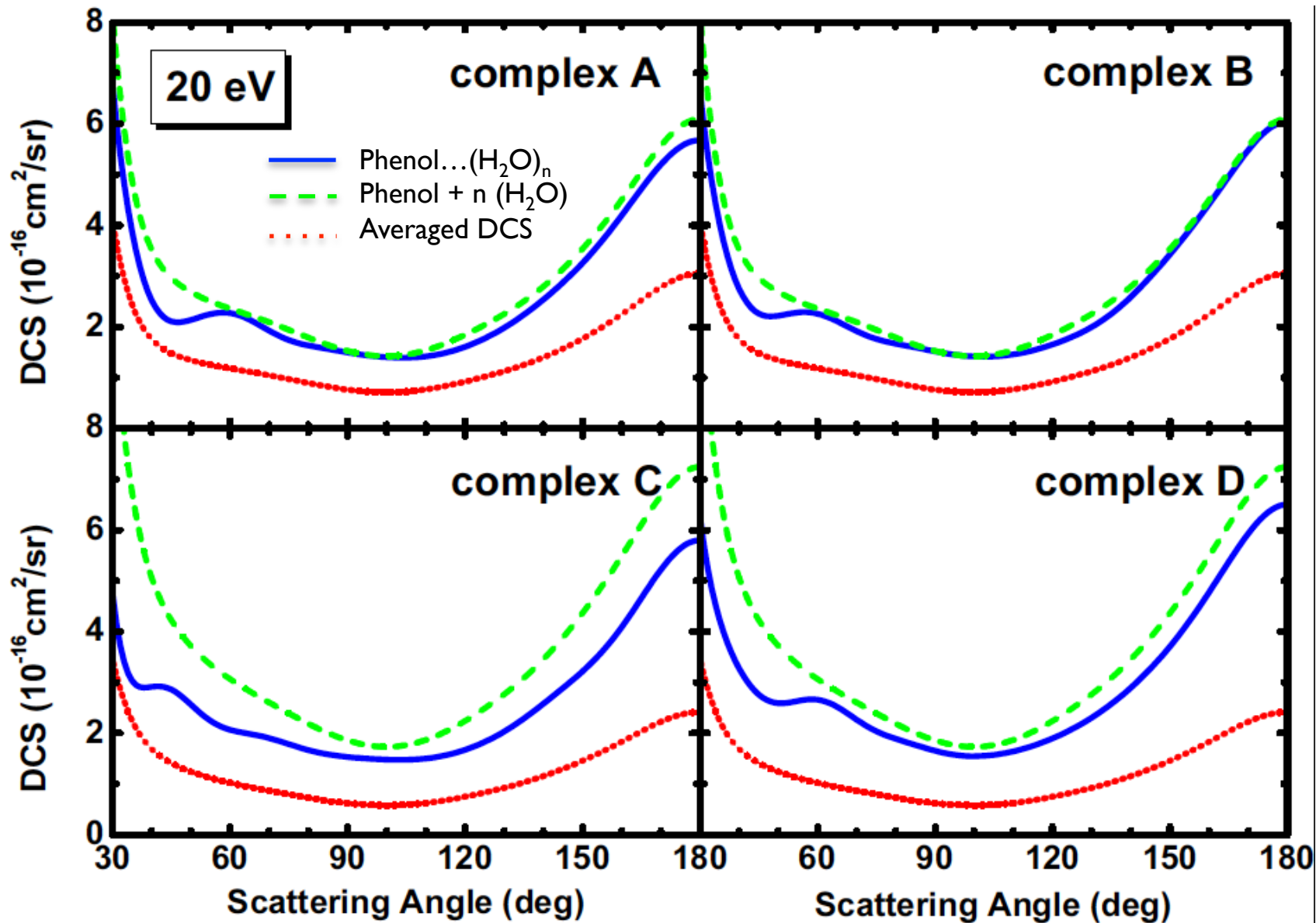
Electron Collisions with Phenol...(H$_2$O)$_n$: search for microsolvation signatures in the DCS

Electron Collisions with Phenol...$(H_2O)_n$: search for microsolvation signatures in the DCS

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ELECTRONIC EXCITATION

Theoretical co-authors

Eliane M. de Oliveira (posdoc)
Marco A. P. Lima

Márcio H. F. Bettega

Márcio T. do N. Varella

Romarly F. da Costa (coordinator)

Electronic excitation of H_2 by electron impact
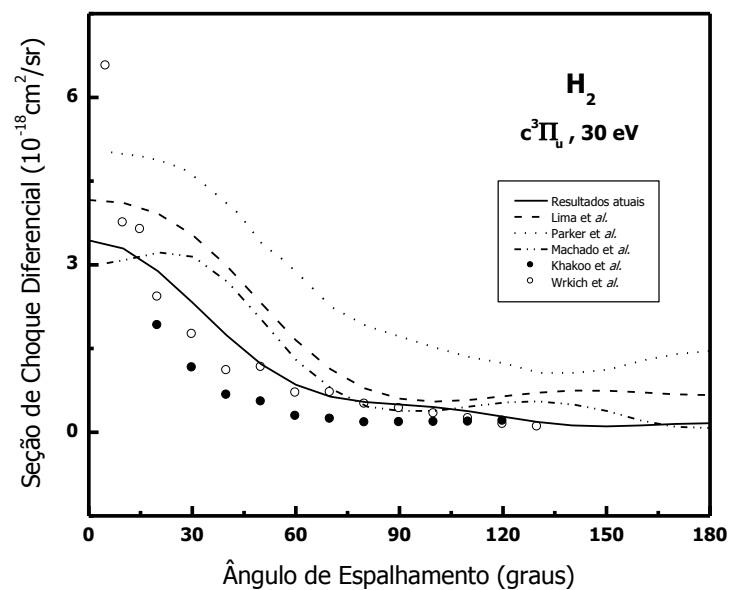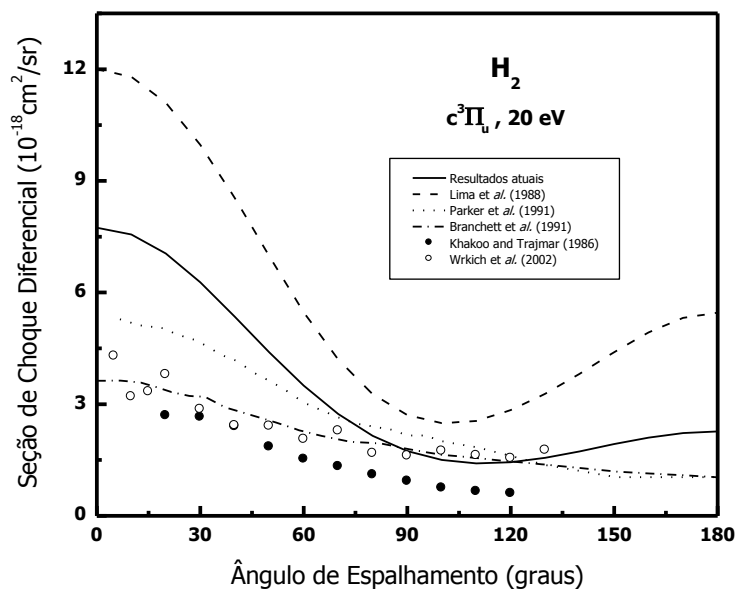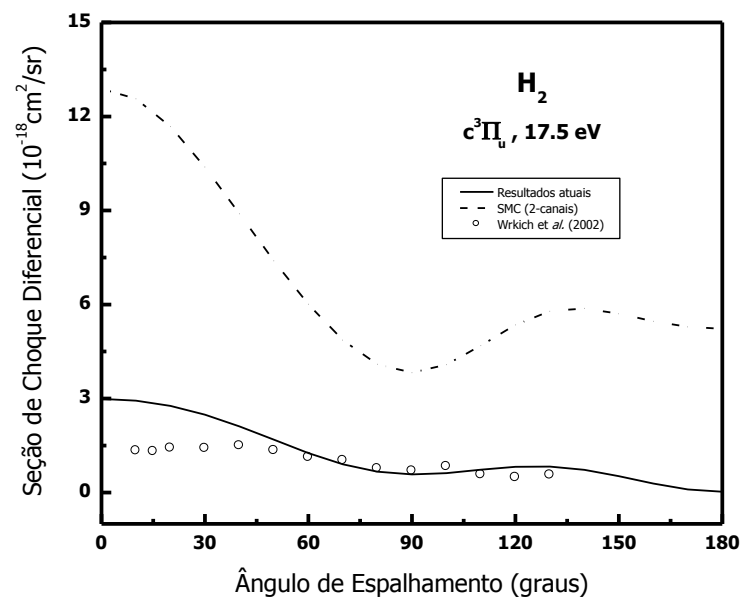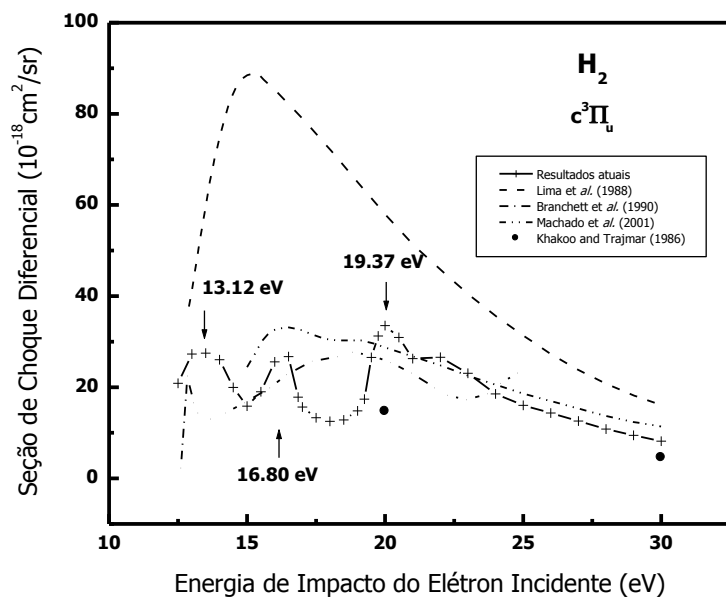
Electronic transition $X\ ^1\Sigma_g \rightarrow A\ ^3\Sigma_u^+$ of N_2 by electron impact
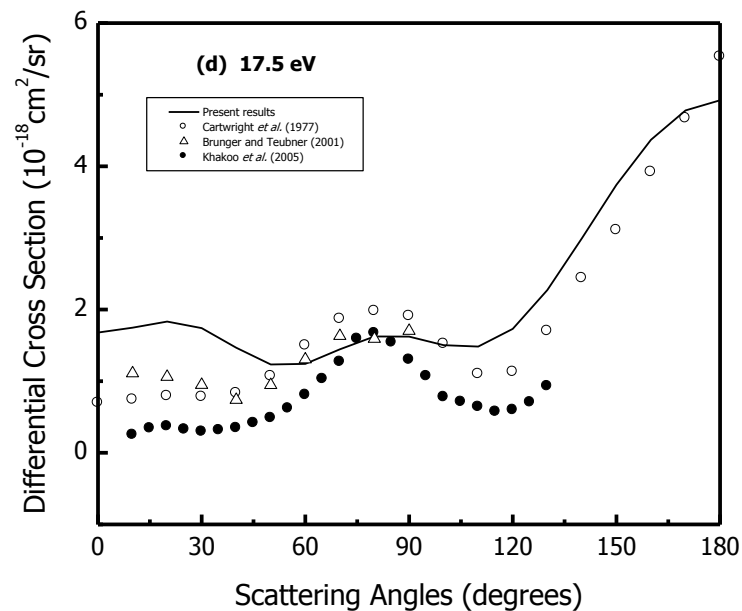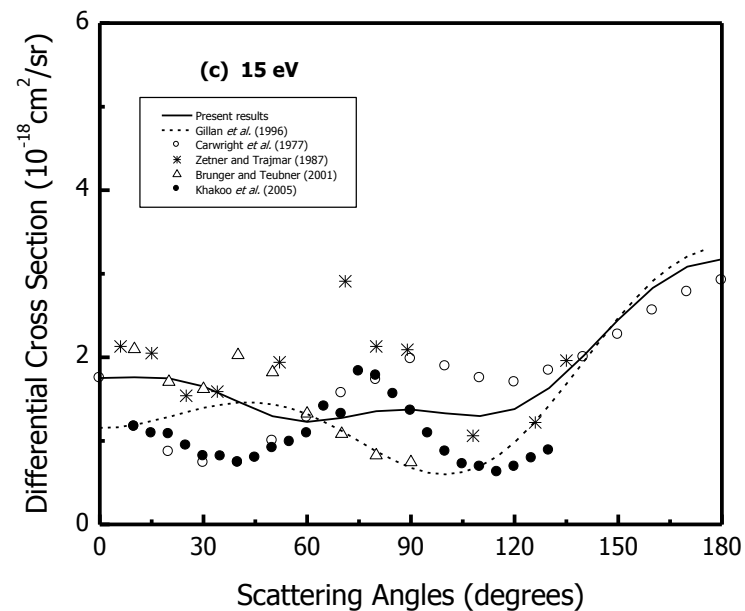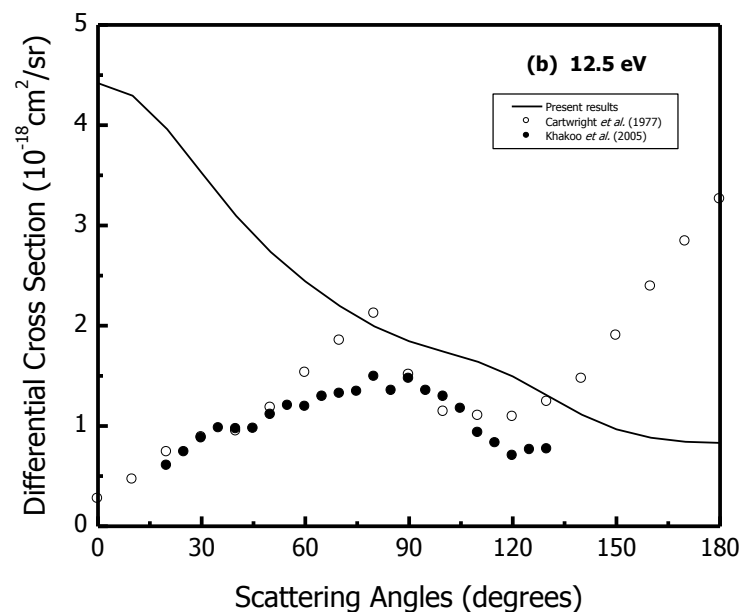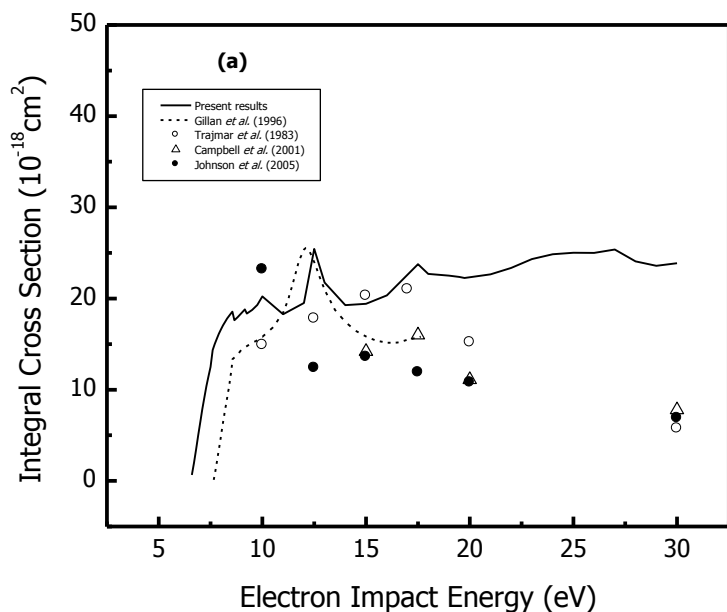
Electronic transition $X\ ^1\Sigma_g^+ \rightarrow a'\ ^1\Sigma_u^-$ of N_2 by electron impact

R.F. da Costa and M.A. P. Lima, Phys. Rev. A **75**, 022705 (2007)

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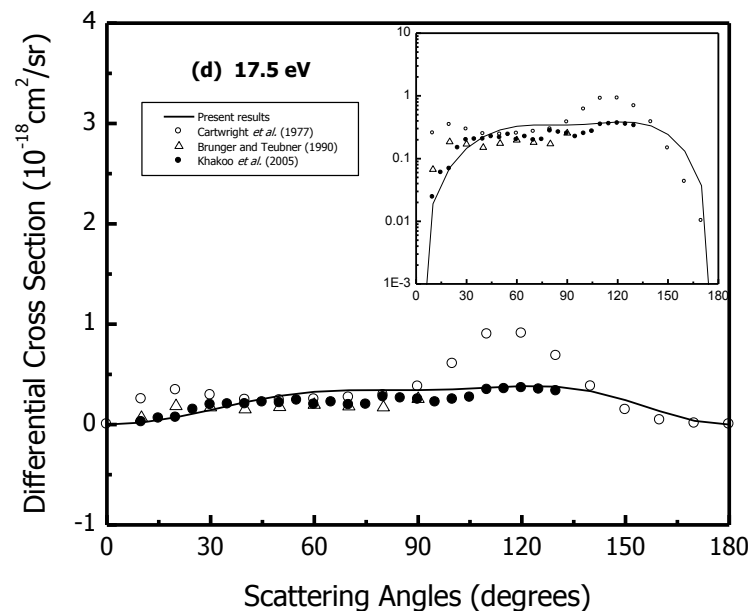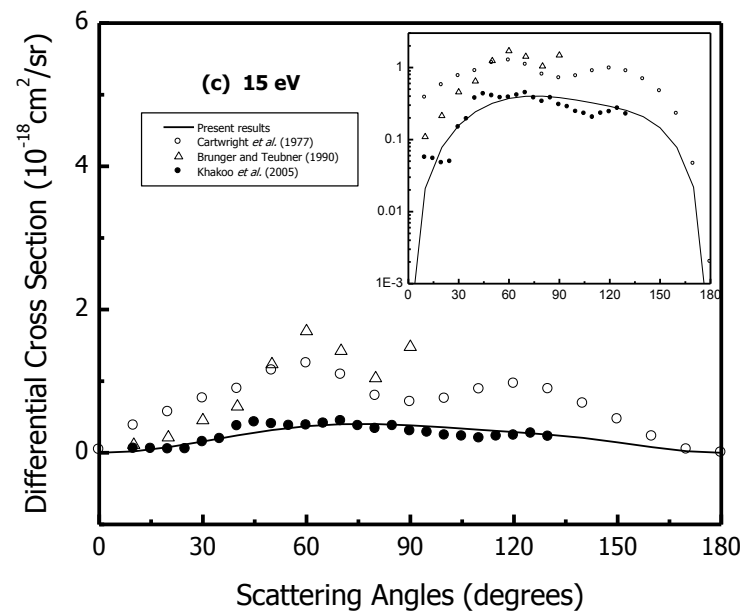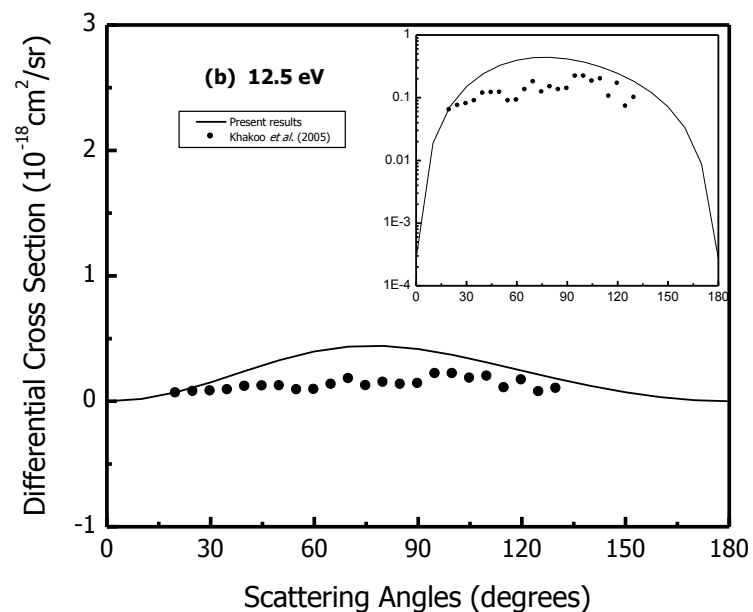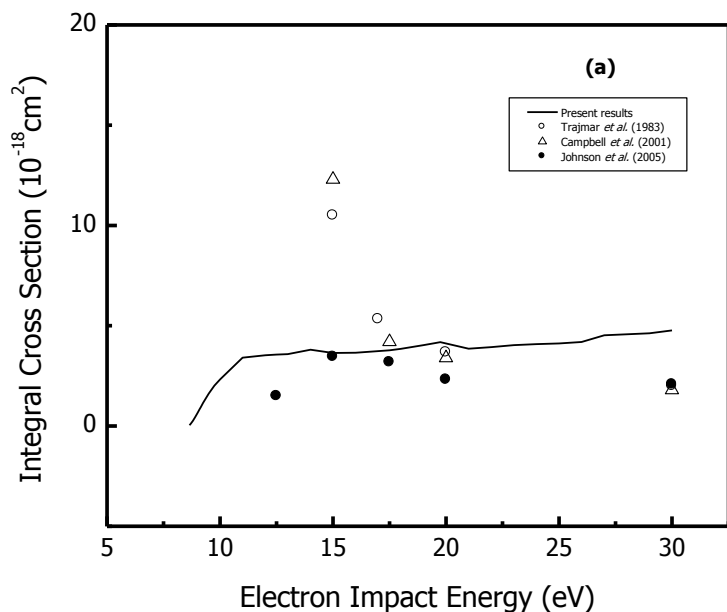
Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact
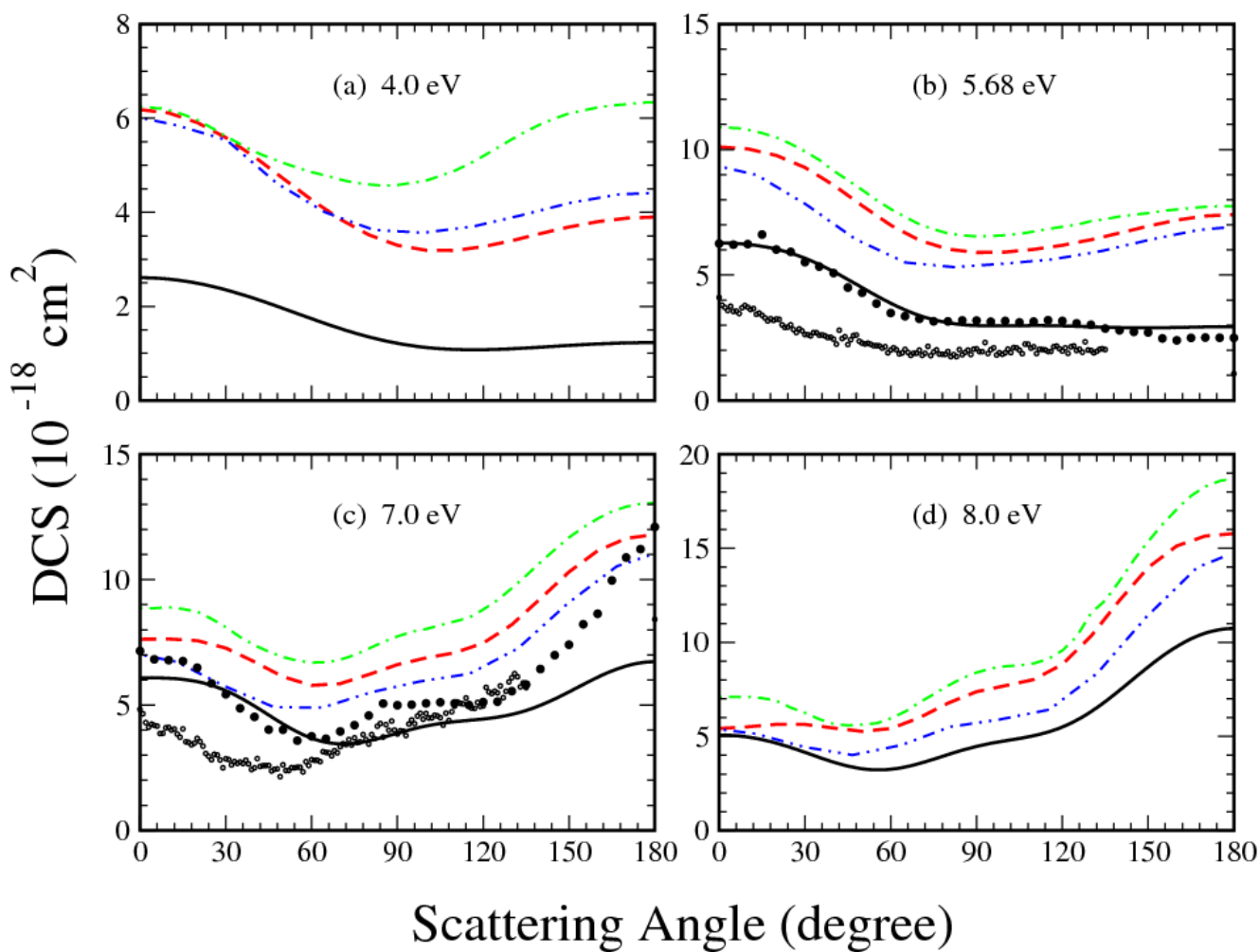
Color lines are
Close-coupling
Calculations
and
bullets are
M. Allan´s
data

Surprisingly, at higher energies the agreement is not good!!
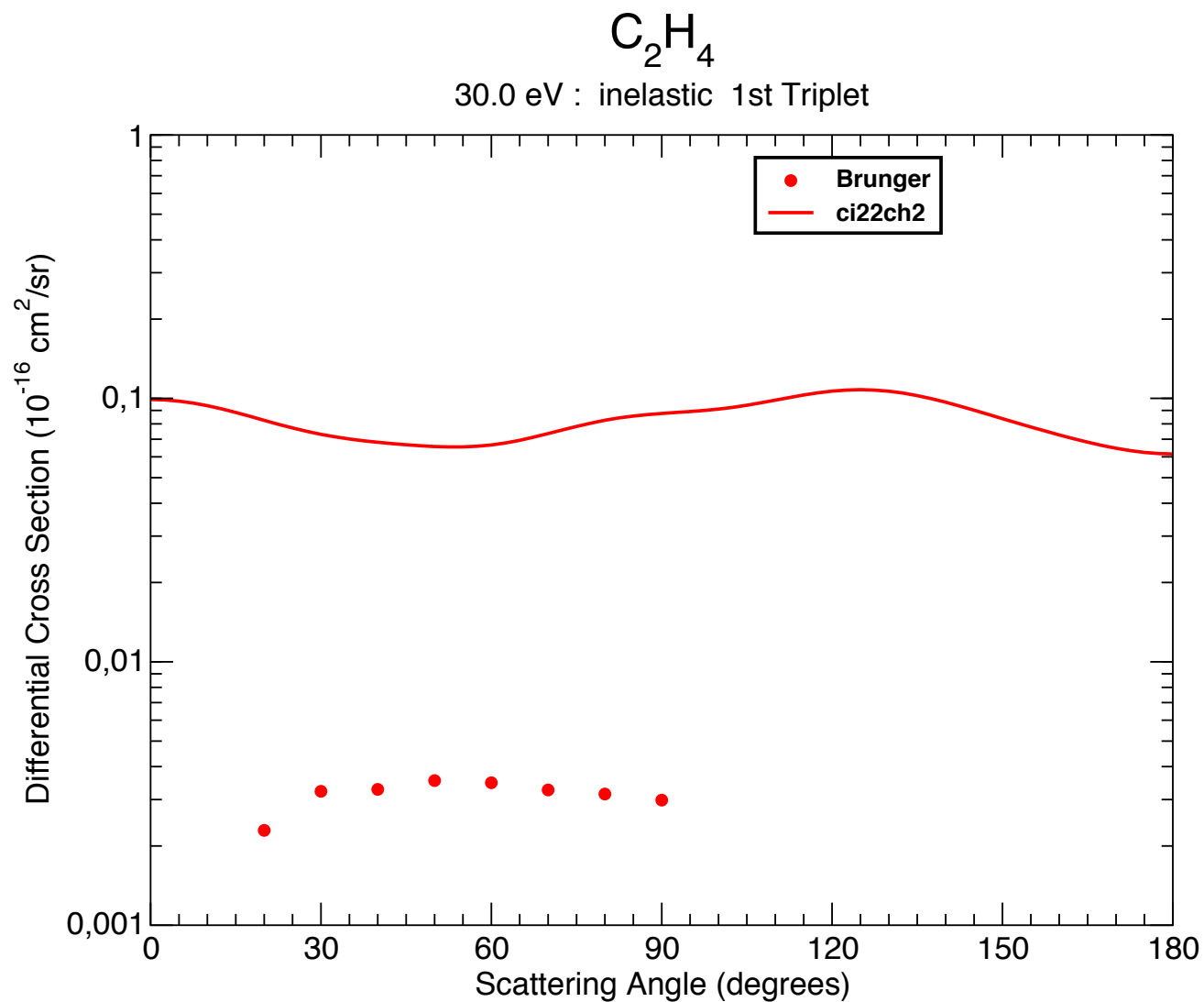
C_2H_4

30.0 eV : inelastic 1st Triplet

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

exp. 1 (singlets) / exp. 1 (triplets)
exp. 2 (singlets) / exp. 2 (triplets)
Full SCI (singlets) / Full SCI (triplets)
MOBSCI (singlets) / MOBSCI (triplets)

2 states

2 states

3   4   5   6   7   8   9   10

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TABLE I. Calculated and experimental excitation energies for ethylene. Up to 20, 30 and 50 eV, the FSCI spectrum is composed by 138, 260 and 402 electronically excited states, respectively. The MOBSCI calculations at these energies were performed with 45 excited states, where 17 of them are physical excited singlets or triplets states and the others are pseudostates.

	Energy (eV)		
	FSCI	MOBSCI	Expt.
TRIPLET	3.56	3.60	4.36[a]
	6.90	6.92	6.98[a]
	7.73	7.75	7.79[a]
	8.48	8.83	8.15[b]
	8.80	9.08	8.57[b]
	9.06	9.19	
	9.42	9.58	
	9.48	9.73	
	9.54	9.74	
SINGLET	7.11	7.13	7.11[b]
	7.83	7.85	7.80[b]
	7.88	8.55	7.90[b]
	8.99	9.28	8.28[a]
	9.24	9.37	8.62[b]
	9.25	9.54	8.90[a,b]
	9.63	9.71	9.10[a]
			9.33[a]
			9.51[a,c]
			9.62[a]

[a] Experimental data from Ballard *et al.* [24].

[b] Experimental data from Do *et al.* [16].

[c] For this energy were found two states.

Multichannel effects on the elastic process of e⁻-C₂H₄ scattering

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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C_2H_4

10 eV : elastic 1 --> 1

Multichannel effects on the elastic process of e⁻-C_2H_4 scattering

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
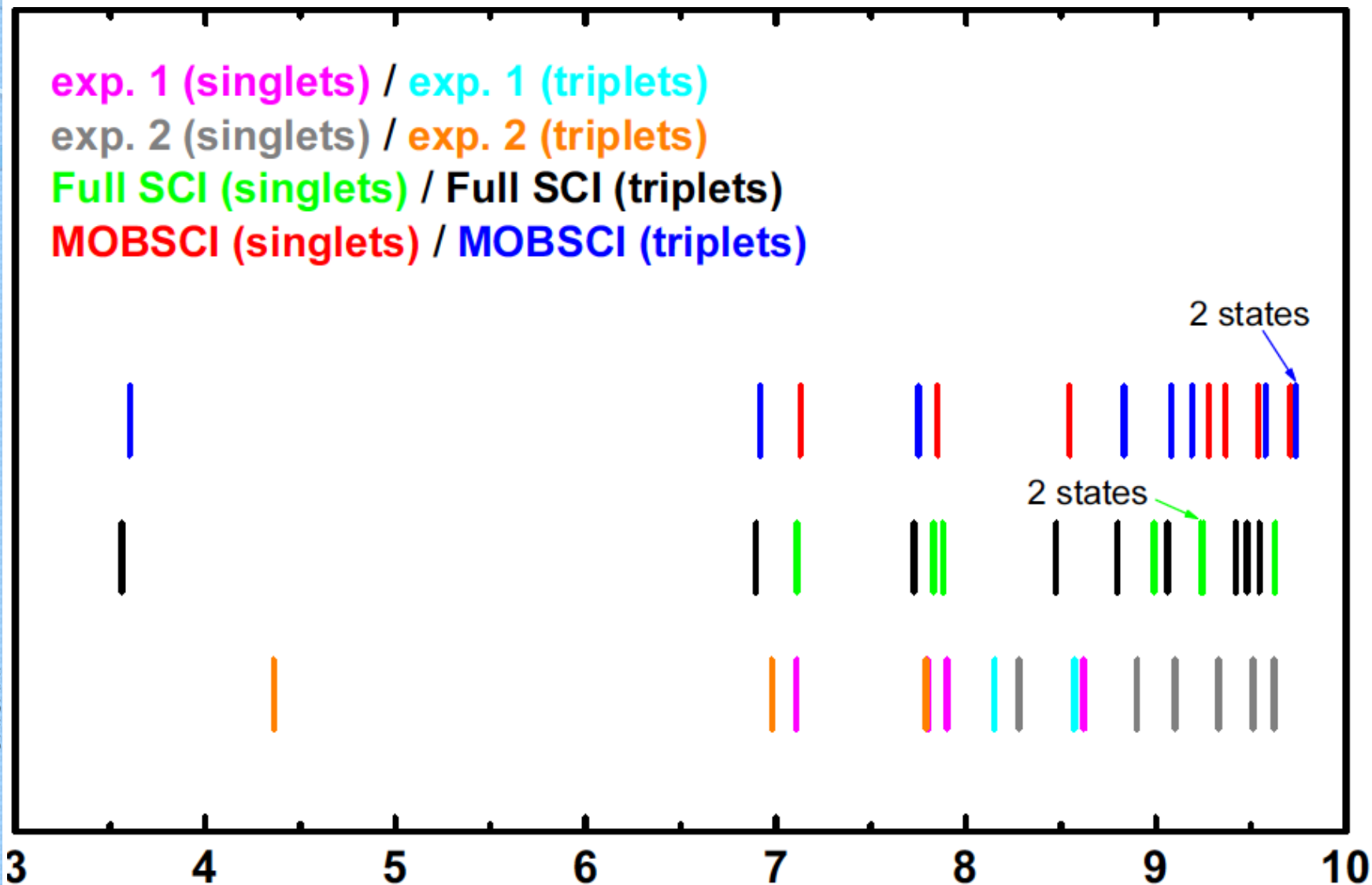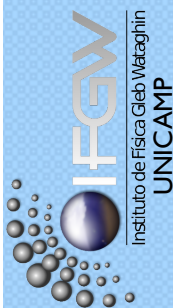*Phys. Rev. A*, in preparation (2014)

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C_2H_4

15 eV : elastic 1 --> 1

Multichannel effects on the elastic process of e⁻-C₂H₄ scattering

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

C_2H_4

20 eV : elastic 1 --> 1

Multichannel effects on the elastic process of e⁻-C₂H₄ scattering

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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C_2H_4

30 eV : elastic 1 --> 1

Legend:
- Khakoo
- Tanaka
- ci22-ch1
- ci22-ch2
- ci14-ch17
- ci22-ch45

Y-axis: Differential Cross Section (10^{-16} cm²/sr)

X-axis: Scattering Angle (degrees)

Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

C_2H_4

5.7 eV : inelastic 1st Triplet

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Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

C_2H_4

7.0 eV : inelastic 1st Triplet

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Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
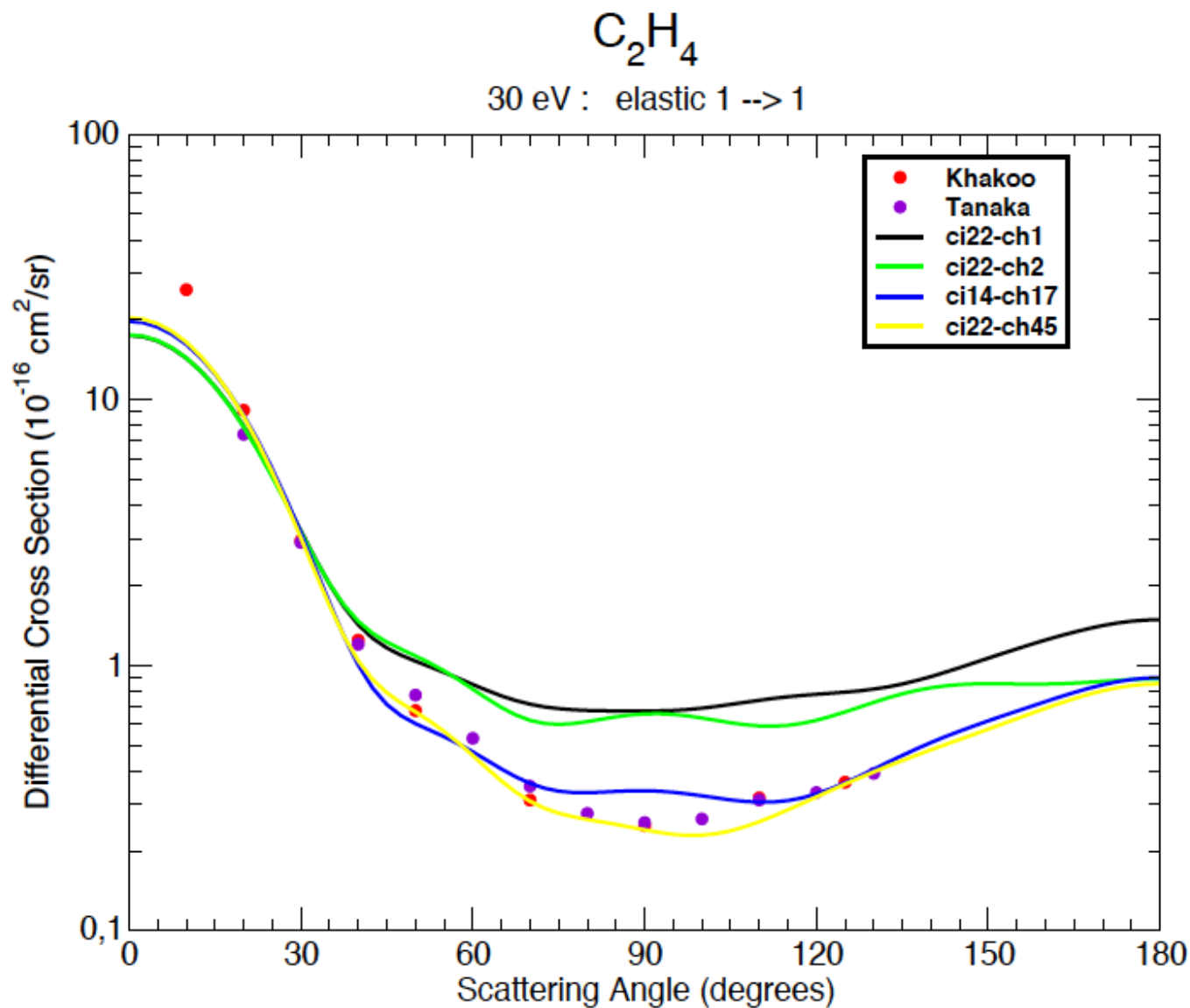E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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C_2H_4

11.0 eV : inelastic 1st Triplet

Legend:
- Brunger (red dot)
- Allan (black dot)
- ci22ch2 (green line)
- ci22ch17 (blue line)

Y-axis: Differential Cross Section (10^{-16} cm^2/sr)
X-axis: Scattering Angle (degrees)

Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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C_2H_4

15.0 eV : inelastic 1st Triplet

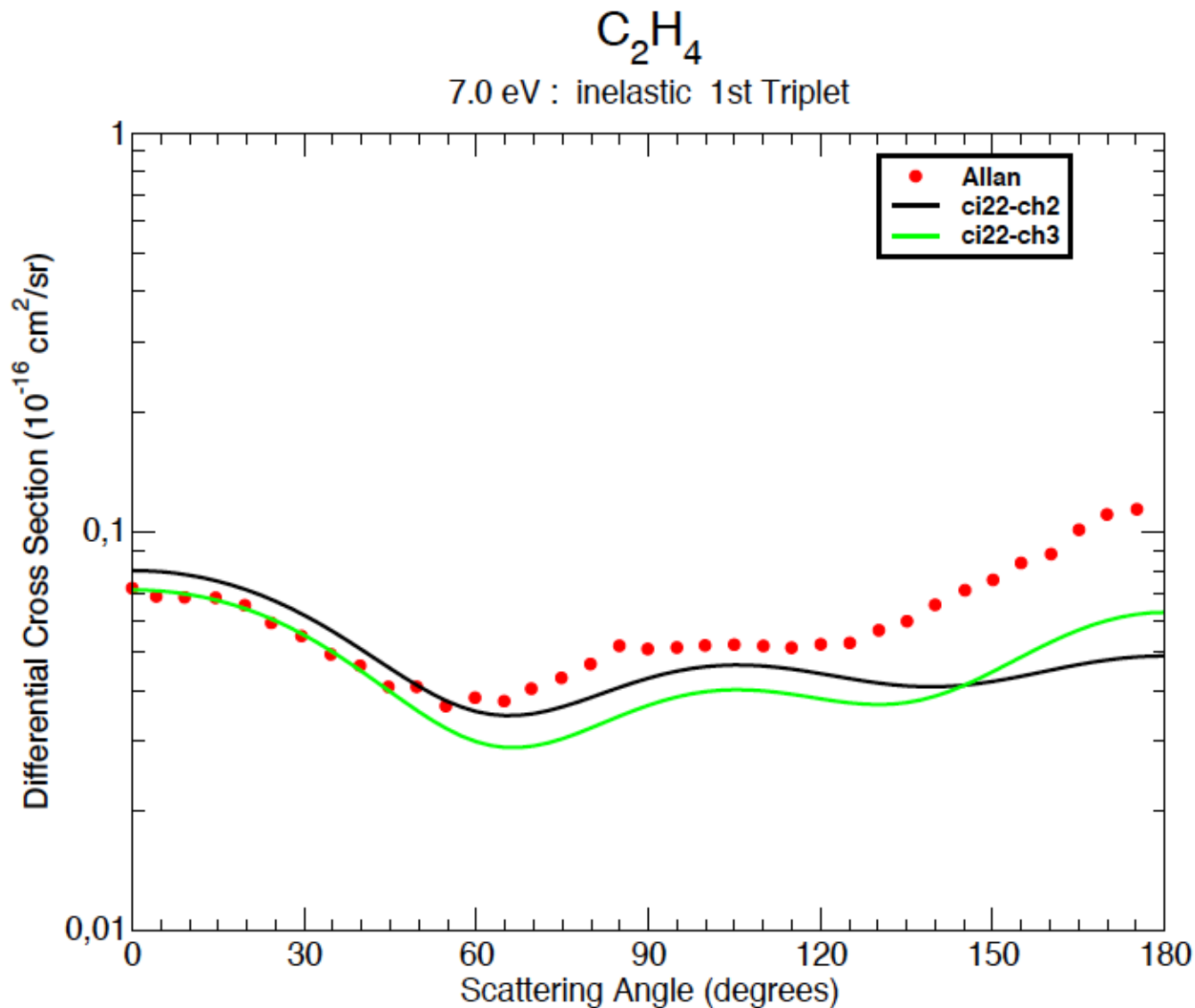# Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

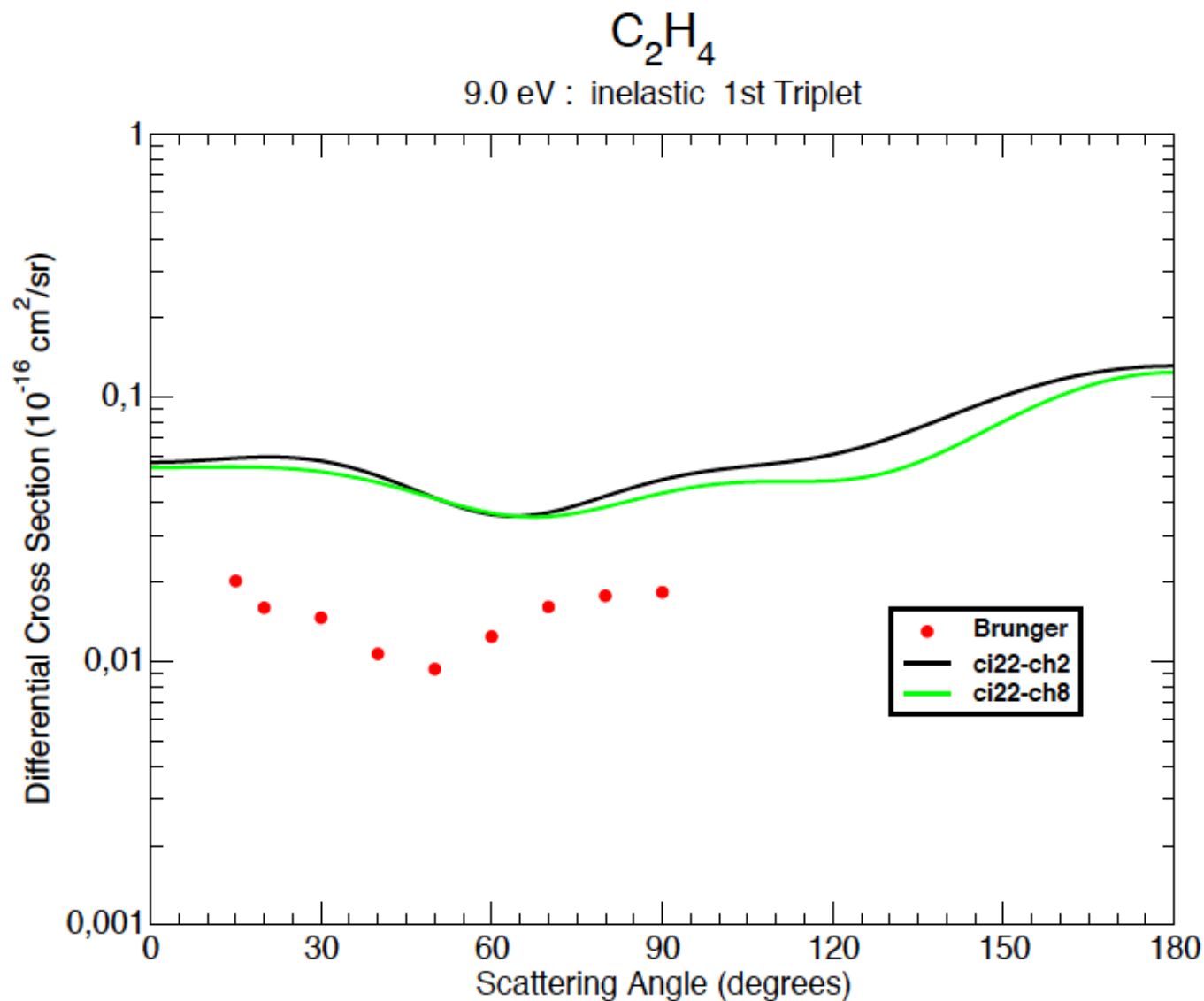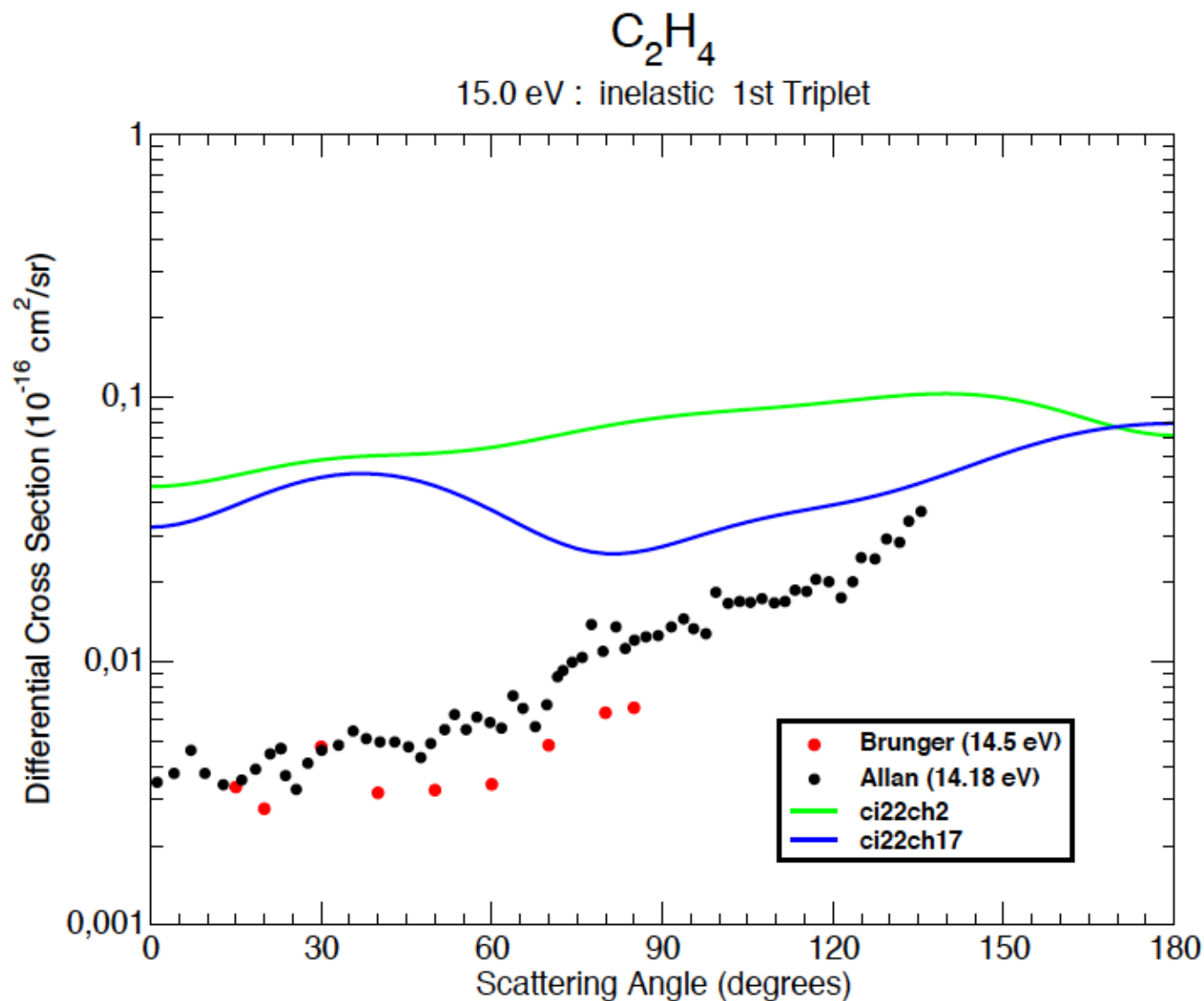# Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

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Multichannel effects on the Electronic excitation of ã $^3B_{1u}$ state of C_2H_4 by electron impact

R. F. da Costa, M. H. F. Bettega, M. T. do N. Varella,
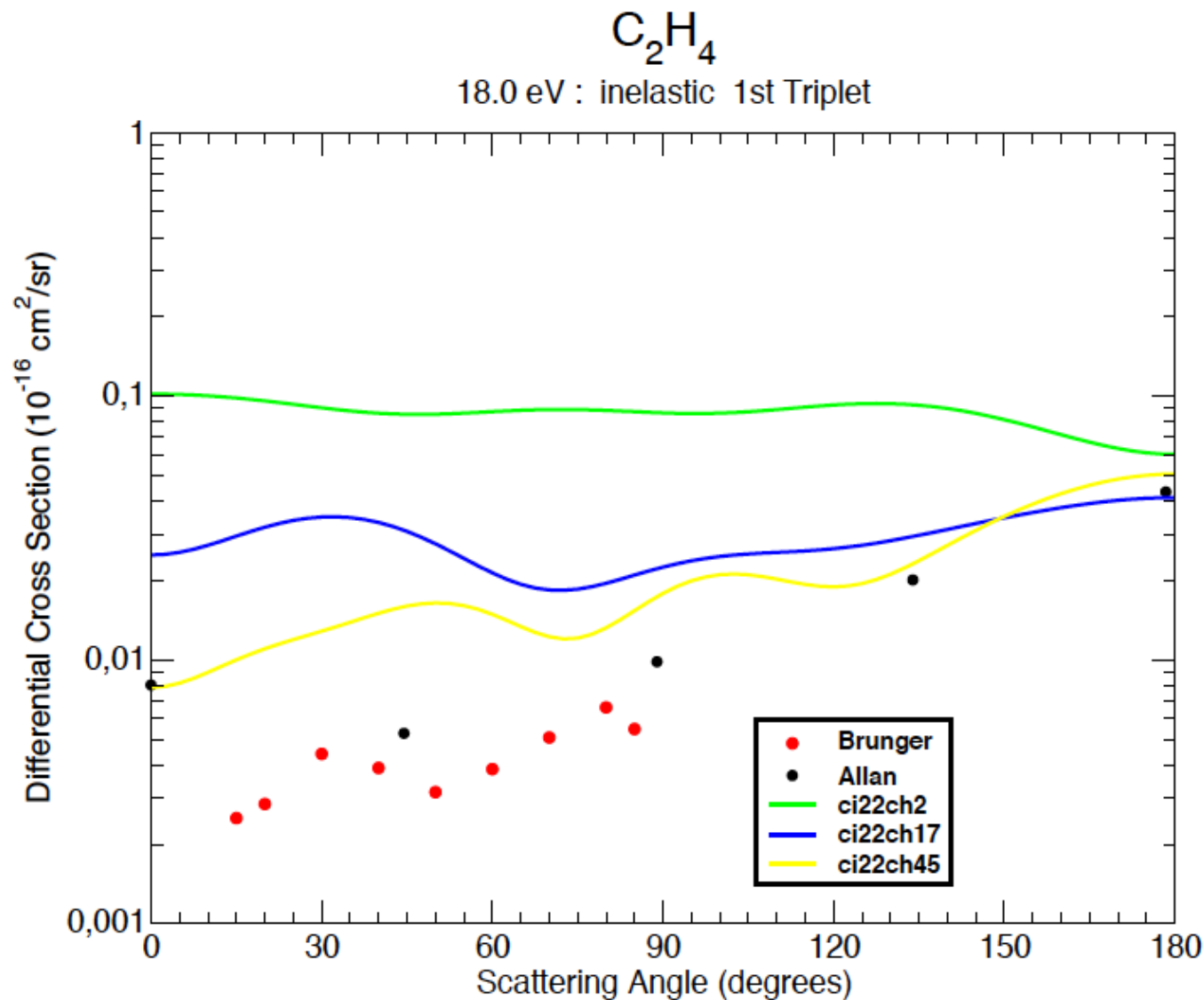E. M. de Oliveira and M. A. P. Lima,
Phys. Rev. A, in preparation (2014)

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C_2H_4

50.0 eV : inelastic 1st Triplet

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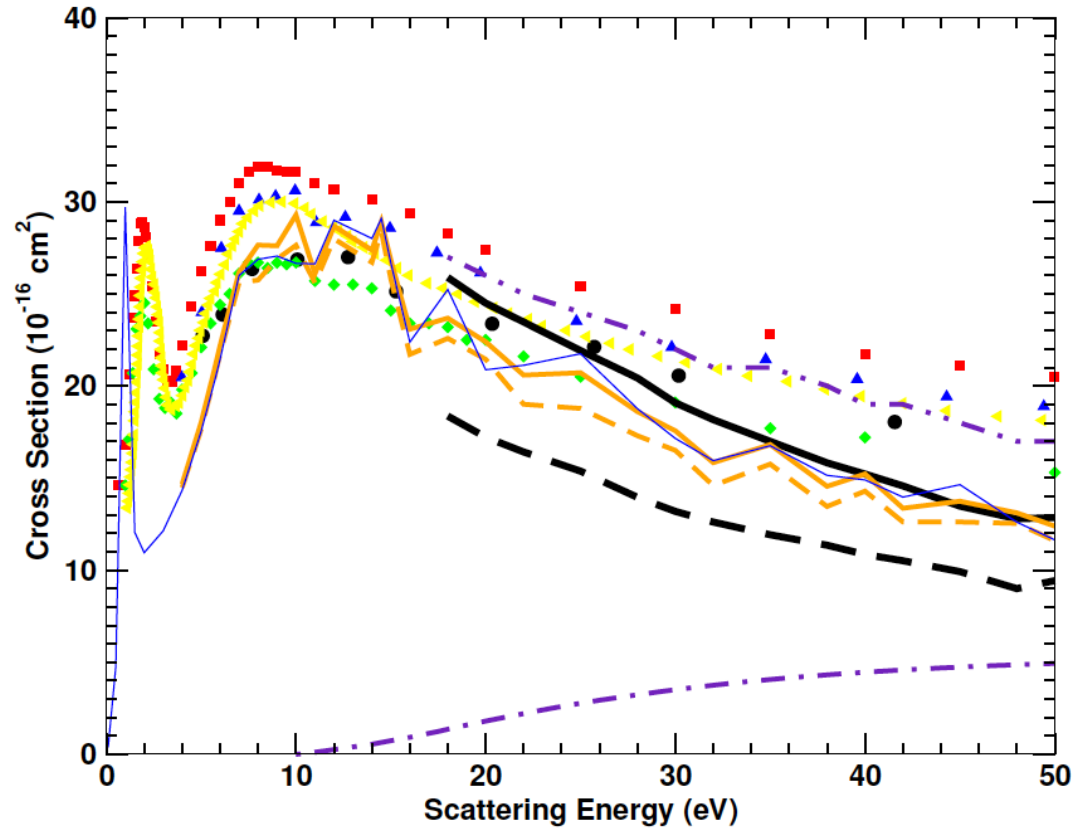UNICAMP

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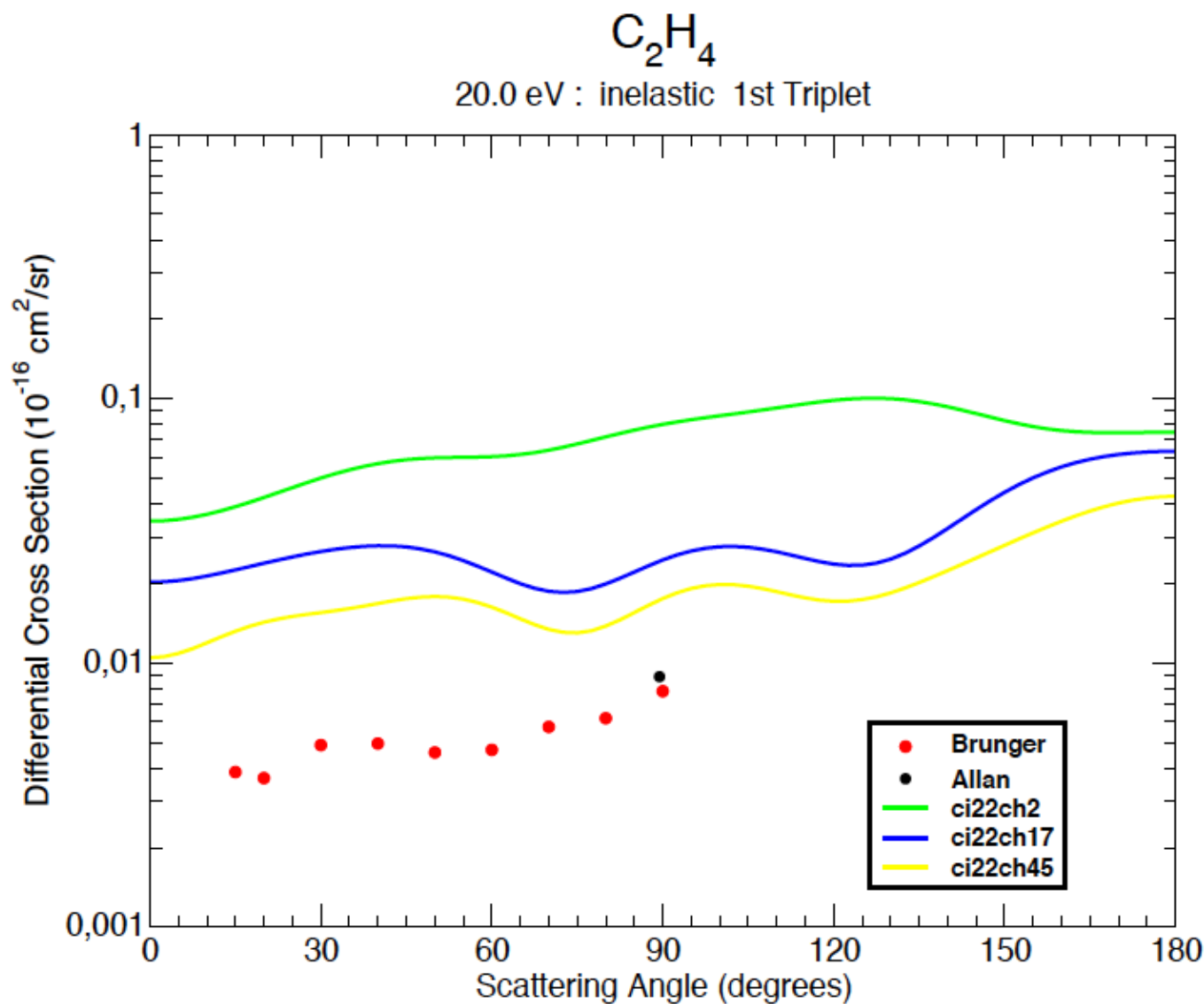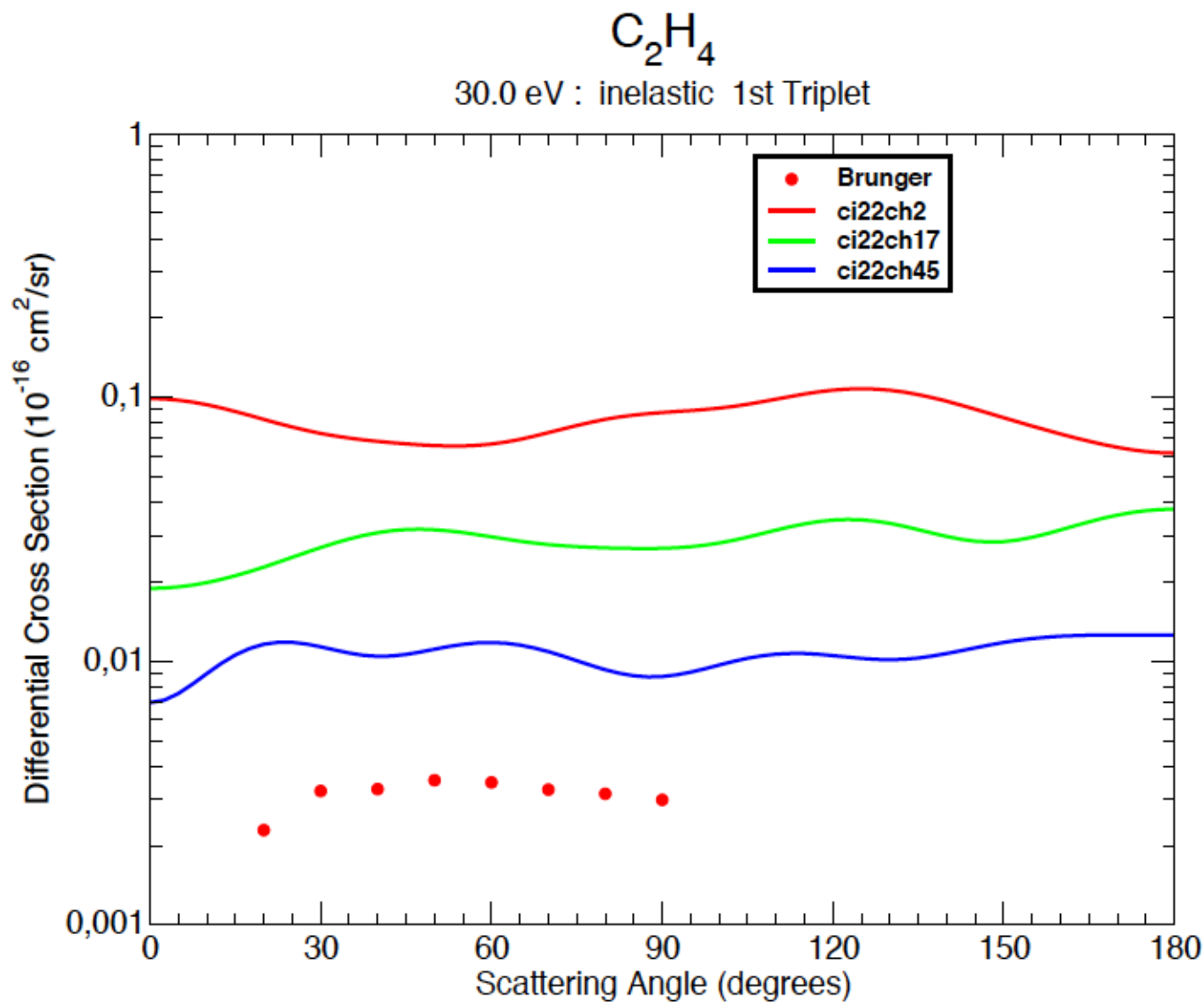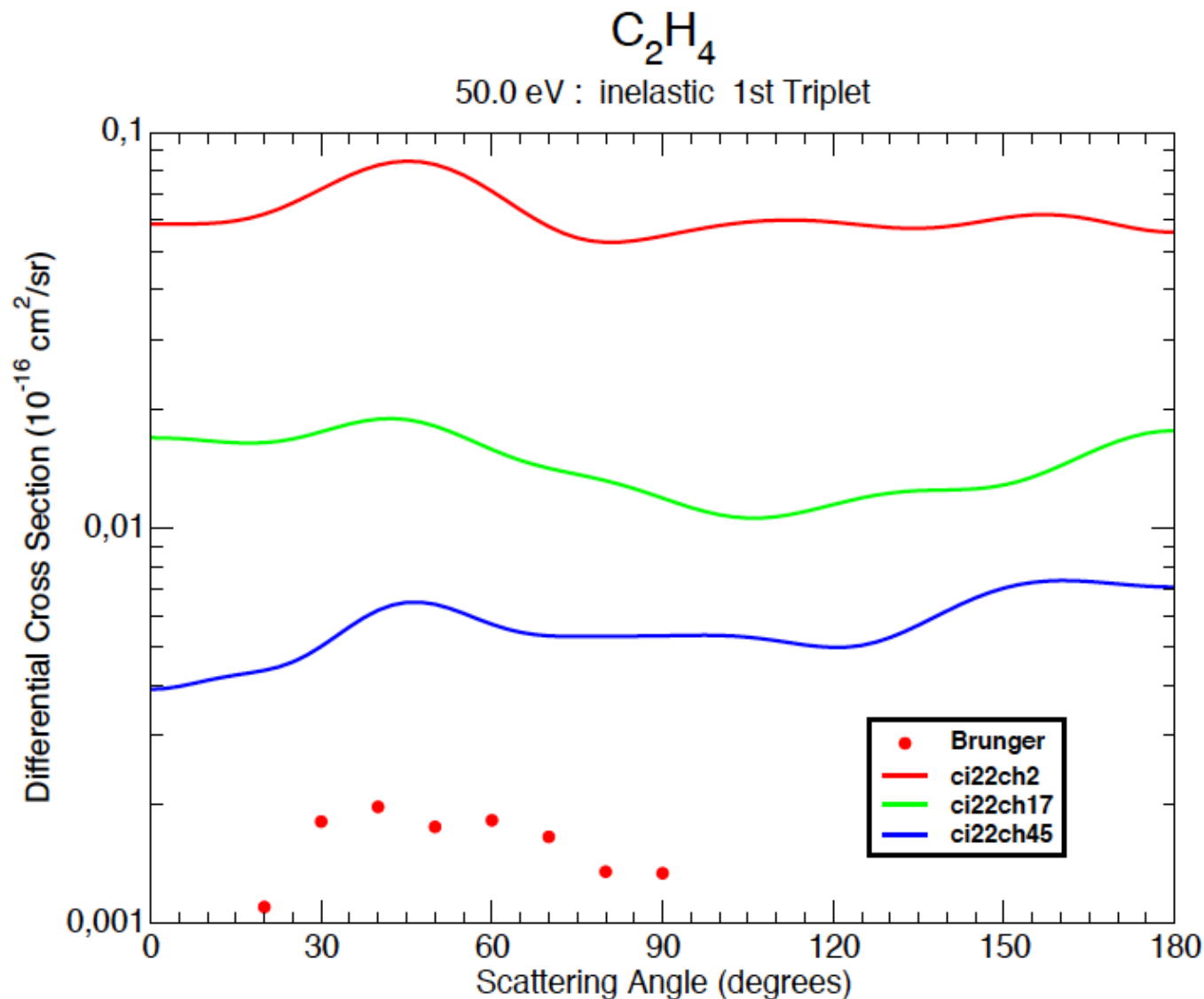
FIG. 4. (Color online) Total and integral cross sections for the energy region 0-50 eV. Thin (blue) line: 1-channel coupling plus polarization (optical theorem gives the same as the elastic transision); dashed (orange) line: elastic transitions for 2-channel coupling plus polarization; full (orange) line: total cross section for 2-channel coupling plus polarization; thick dashed (black) line: elastic transitions for 45-channel coupling plus polarization; thick full (black) line: total cross section for 45-channel coupling plus polarization; dot-dashed (indico) line: ionization cross sections using BEB aproximation; dot-dot-dashed (indico) line: total cross sections 45-channel coupling plus polarization plus ionization using BEB aprroximation; full (black) circles, full (red) squares, full (green) diamonds, full (blue) triangles up and full (yelow) triangles down: experiments of Refs. [1–5], respectively.
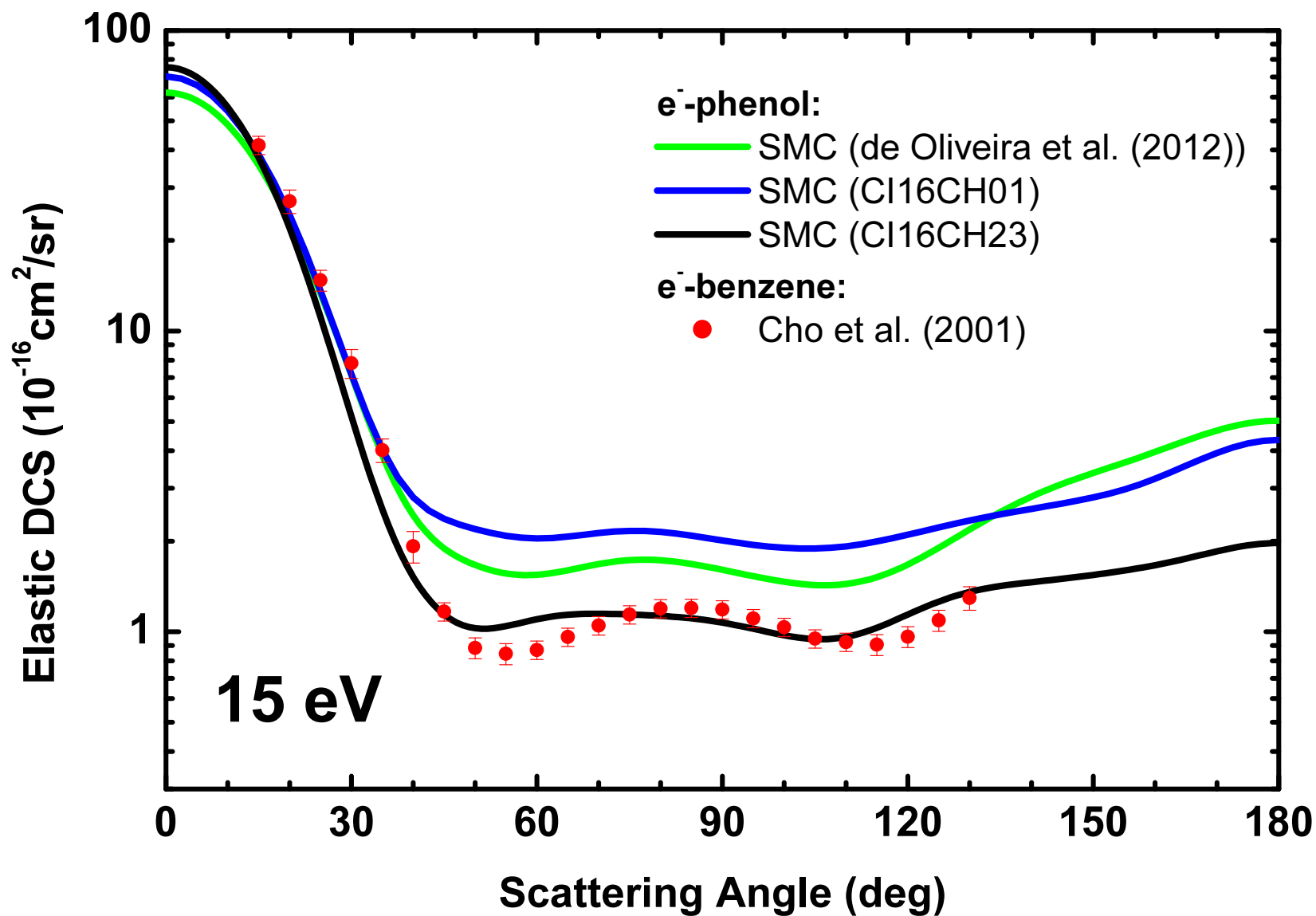
Electronic excitation of Phenol by electron impact:

TABLE I. Experimental and calculated excitation energies, assignments, dominant configurations, and optical oscillator strengths (f_0).

Band	Expt. energy (eV)	State	TD-DFT Energy (eV)	TD-DFT Dominant excitation(s)	f_0	MOB-SCI Energy (eV)	f_0	Full-SCI Energy (eV)	f_0
I	3.4–4.3	$^3A'$	3.71	$3a''{\to}5a''$; $4a''{\to}6a''$	0	3.57	0	3.29	0
		$^3A'$	4.10	$4a''{\to}5a''$	0	4.73	0	4.49	0
II	4.3–5.4	$^3A'$	4.53	$3a''{\to}5a''$; $4a''{\to}6a''$	0	4.90	0	4.78	0
		$^1A'$	4.99	$3a''{\to}6a''$; $4a''{\to}5a''$	0.0312	6.09	0.0248	5.82	0.0381
		$^3A''$	5.06	$4a''{\to}22a'$	0	6.16	0	5.94	0
		$^1A''$	5.13	$4a''{\to}22a'$	0.0001	6.21	0.0001	6.06	0.0001
		$^3A'$	5.30	$3a''{\to}6a''$	0	6.03	0	5.73	0
III	5.4–6.3	$^3A''$	5.53	$4a''{\to}23a'$	0	6.78	0	6.53	0
		$^1A''$	5.57	$4a''{\to}23a'$	0.0034	6.86	0.0274	6.68	0.0177
		$^1A'$	5.76	$3a''{\to}5a''$; $4a''{\to}6a''$	0.0328	6.80	0.0031	6.12	0.0025
		$^3A''$	5.90	$3a''{\to}22a'$; $4a''{\to}24a'$	0	6.92	0	6.73	0
		$^1A''$	5.92	$4a''{\to}24a'$	0				
		$^3A''$	5.95	$3a''{\to}22a''$; $4a''{\to}24a'$	0				
		$^1A''$	5.98	$3a''{\to}22a'$	0.0021	6.99	0	6.86	0.0020
		$^3A''$	6.27	$4a''{\to}25a'$	0				
IV	6.3–7.3	$^1A''$	6.31	$4a''{\to}25a'$	0.0115				
		$^3A''$	6.32	$3a''{\to}23a'$	0				
		$^1A''$	6.35	$3a''{\to}23a'$	0.0010				
		$^3A''$	6.52	$4a''{\to}26a'$	0				
		$^1A''$	6.54	$4a''{\to}26a'$	0				
		$^3A''$	6.63	$3a''{\to}24a'$	0				
		$^1A'$	6.66	$3a''{\to}6a''$	0.3744				
		$^1A''$	6.66	$3a''{\to}24a'$	0.0202				
		$^1A'$	6.71	$3a''{\to}5a''$; $4a''{\to}6a''$	0.5827				
		$^3A''$	6.84	$4a''{\to}27a'$; $4a''{\to}28a'$	0				
		$^3A'$	6.85	$2a''{\to}5a''$	0				
		$^3A'$	6.93	$4a''{\to}7a''$	0				
		$^1A''$	6.93	$4a''{\to}27a'$; $4a''{\to}28a'$	0.0009				
		$^1A'$	7.01	$4a''{\to}7a''$	0.0148				
		$^3A''$	7.07	$3a''{\to}25a'$	0				
		$^1A''$	7.08	$3a''{\to}25a'$	0				
		$^3A'$	7.11	$2a''{\to}6a''$	0				
		$^3A''$	7.19	$4a''{\to}27a'$; $4a''{\to}28a'$	0				
		$^1A''$	7.22	$4a''{\to}27a'$; $4a''{\to}28a'$	0.0005				
		$^3A''$	7.27	$21a'{\to}5a''$	0				
		$^3A''$	7.29	$3a''{\to}26a'$	0				
V	7.3–8.6	$^1A''$	7.32	$3a''{\to}26a'$	0.0002				
		$^1A''$	7.57	$21a'{\to}5a''$	0.0043				
		$^3A''$	7.58	$4a''{\to}29a'$	0				
		$^3A''$	7.59	$3a''{\to}27a'$; $3a''{\to}28a'$	0				

Our scattering calculations have 5 singlets and 7 triplets below 7eV in good agreement with the full single configuration interaction. We also included 20 additional pseudo states as possible open channels (a total of 33 channels)

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)

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Electronic excitation of Phenol by electron impact:
Effects on the Elastic channel

Electronic excitation of Phenol by electron impact:
Effects on the Elastic channel

Electronic excitation of Phenol by electron impact:
Effects on the Elastic channel

e⁻-phenol:
- SMC (de Oliveira et al. (2012))
- SMC (CI16CH01)
- SMC (CI16CH33)

e⁻-benzene:
- Cho et al. (2001)

40 eV

Electronic excitation of Phenol by electron impact: Effects on the Elastic channel

To be published (2014)

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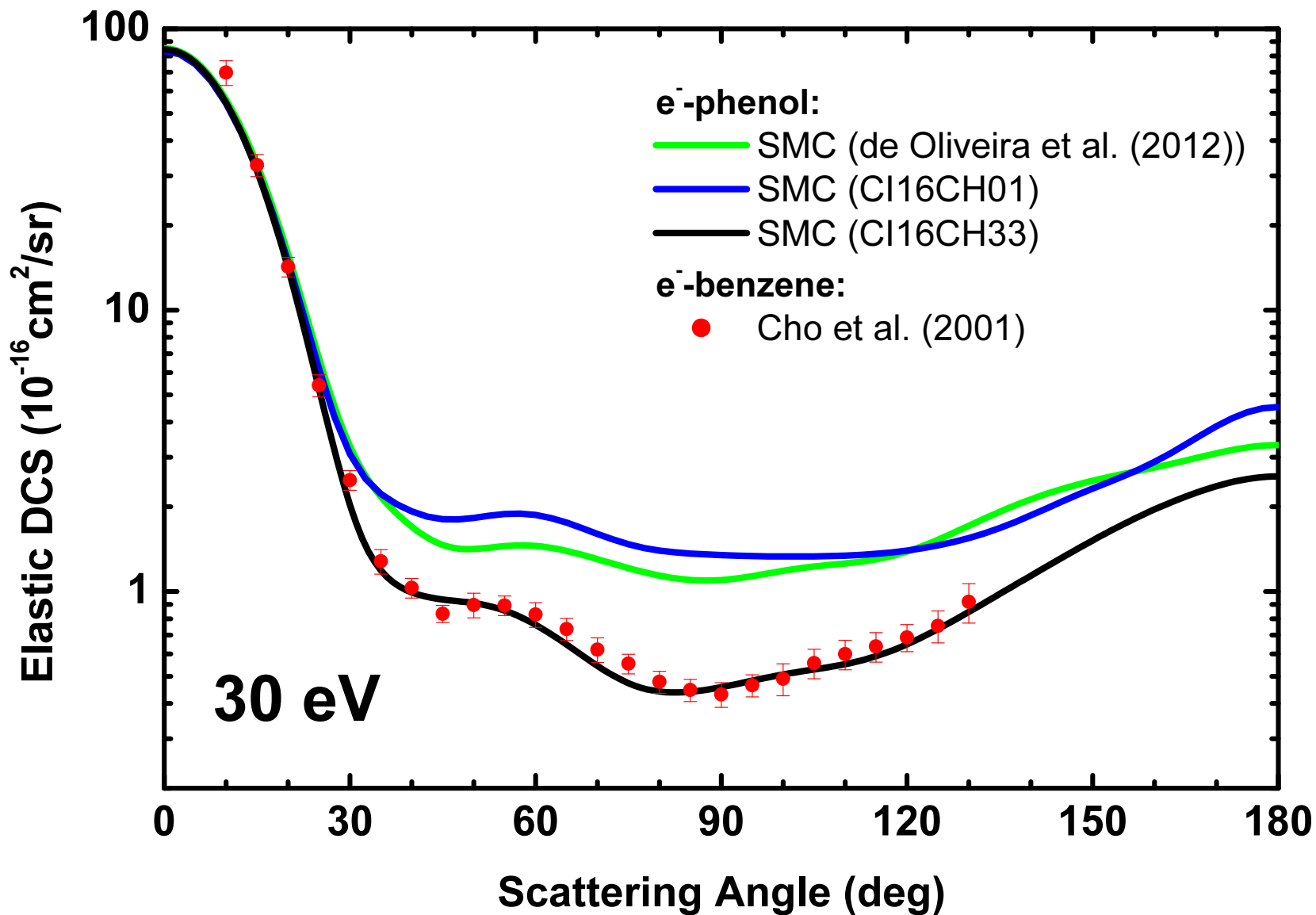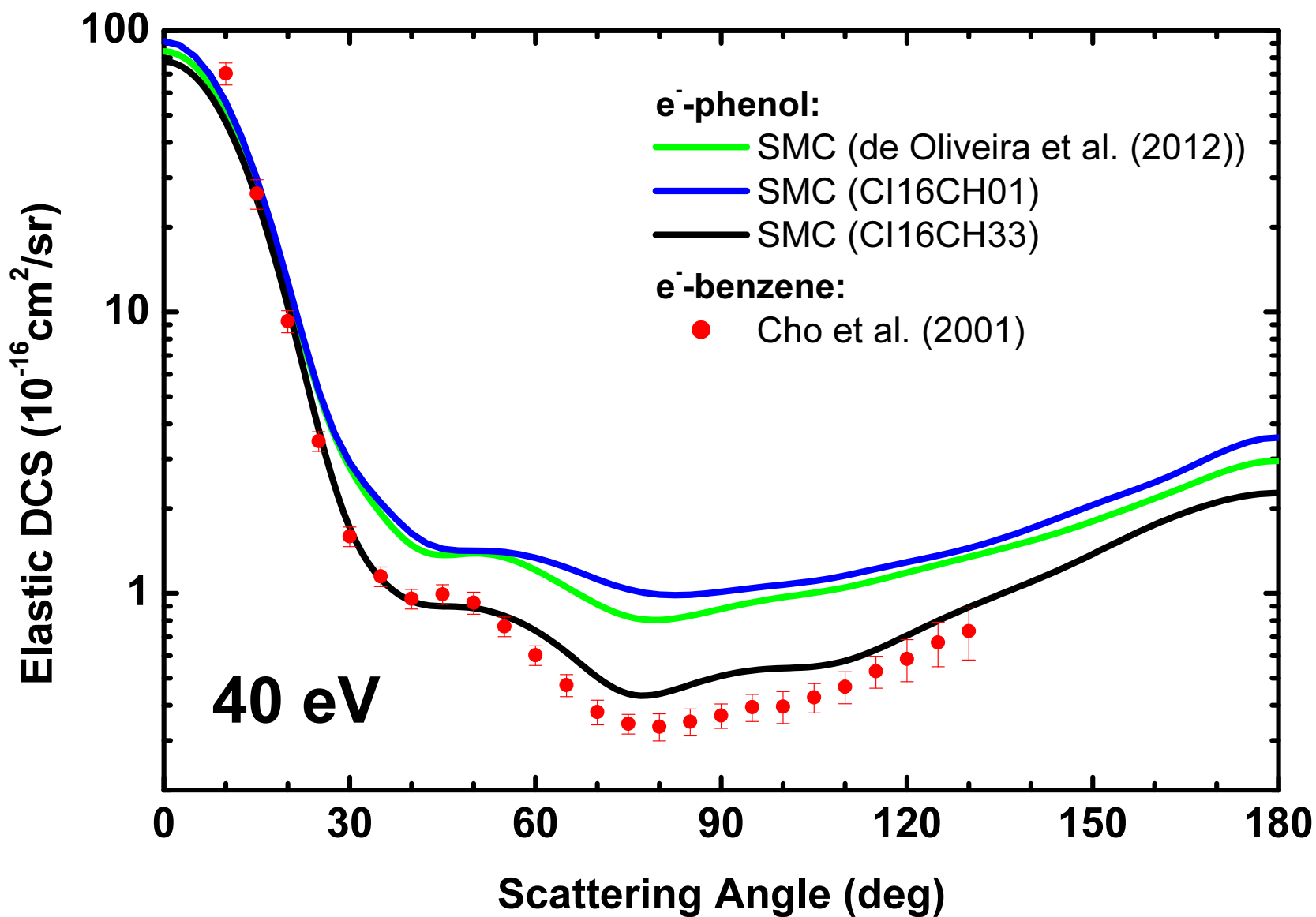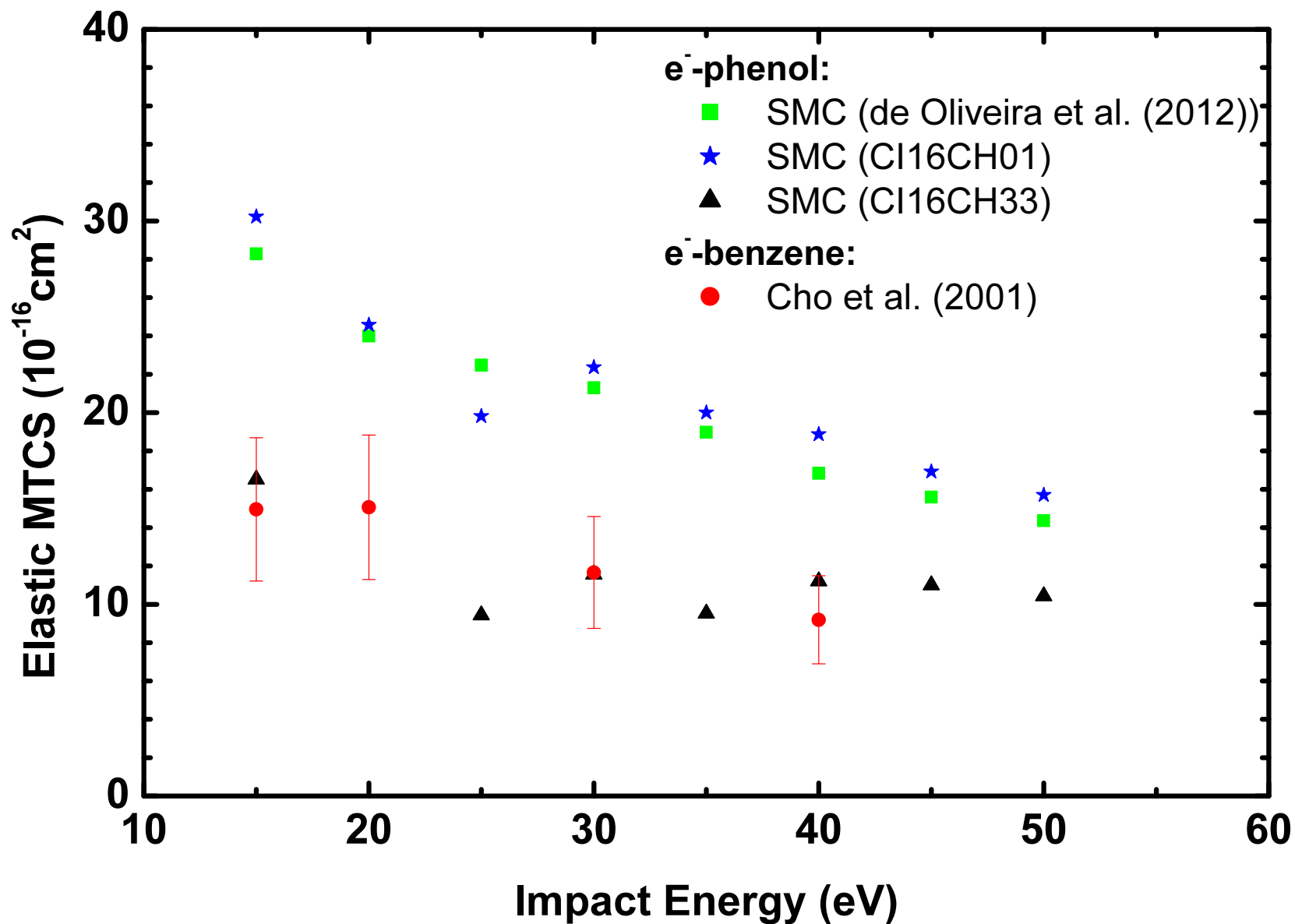
Phenol: BAND I
(very fresh data from Michael Brunger/Cristina Lopes collaboration)

To be published (2014)

20 eV

Legend:
- Experiment (band 1)
- ch23-SEP (L_{max}=10 for out scattering)
- ch23-SEP (L_{max}=4 for in and out scattering)
- ch23-SEP (L_{max}=2 for out scattering)
- ch23-SEP (L_{max}=2 for in and out scattering)

Y-axis: Differential Cross Section (10^{-16} cm^2/sr)
X-axis: Scattering Angle (degrees)

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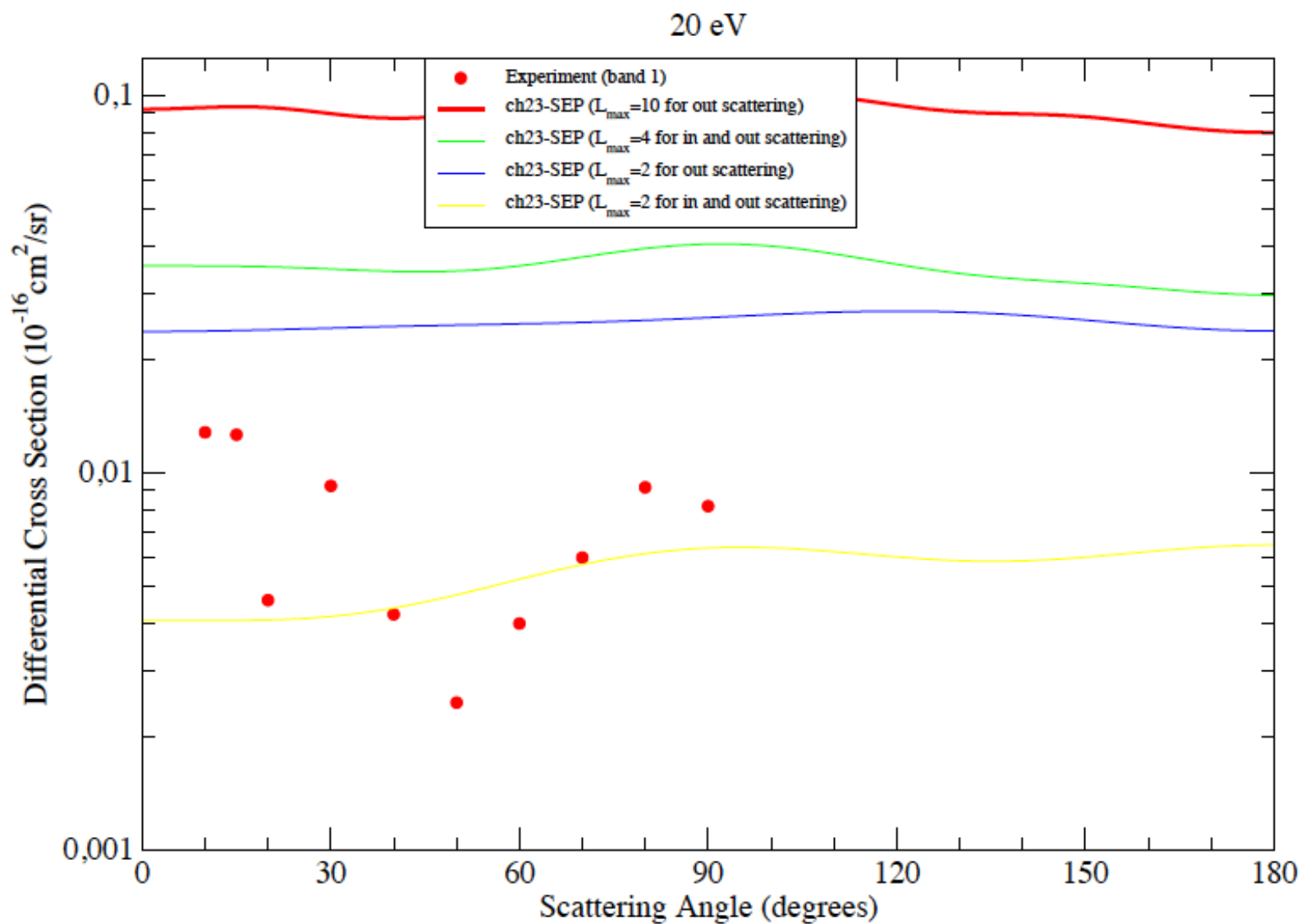
Phenol: BAND II
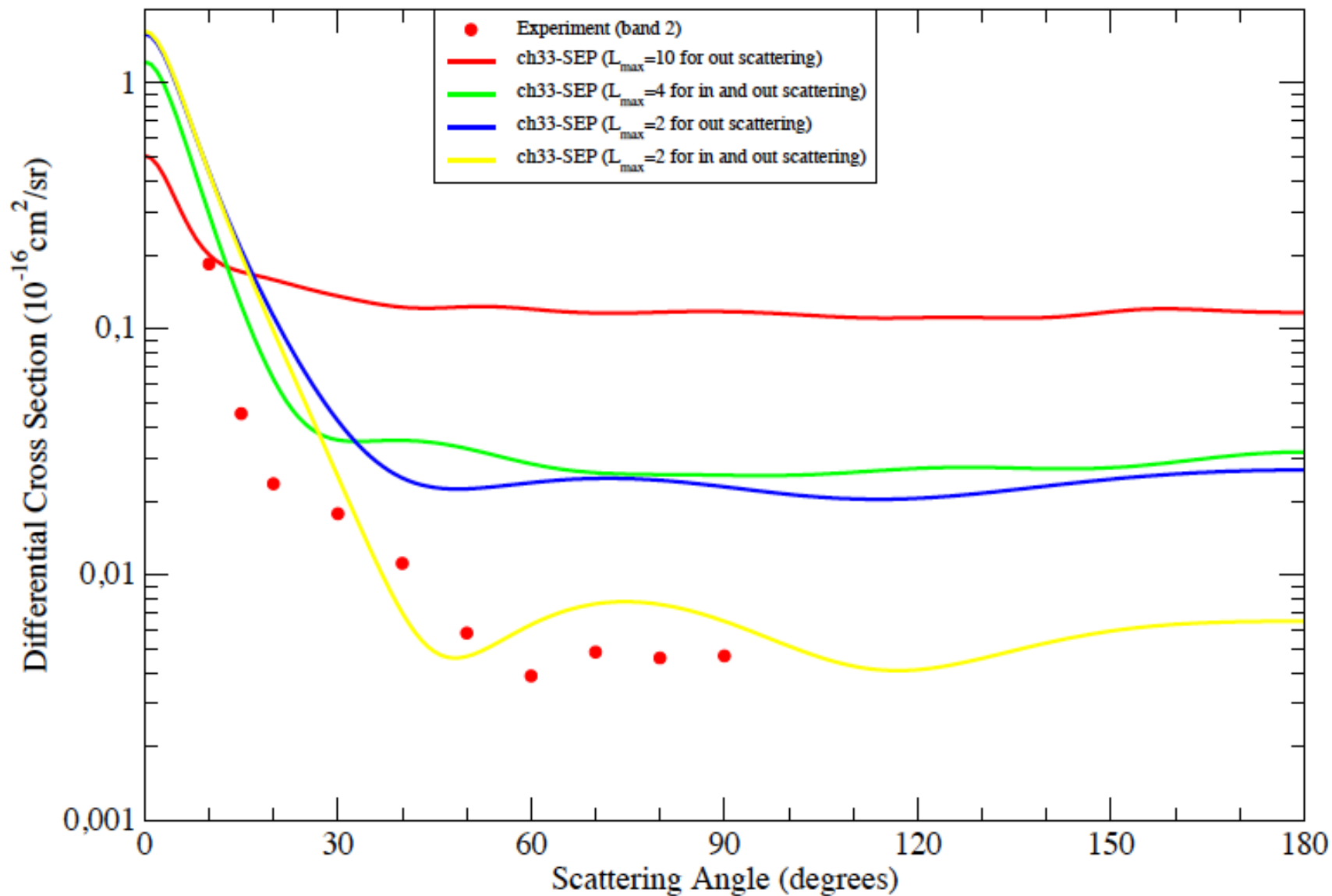# (very fresh data from Michael Brunger/Cristina Lopes collaboration)

30 eV

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Phenol: BAND III
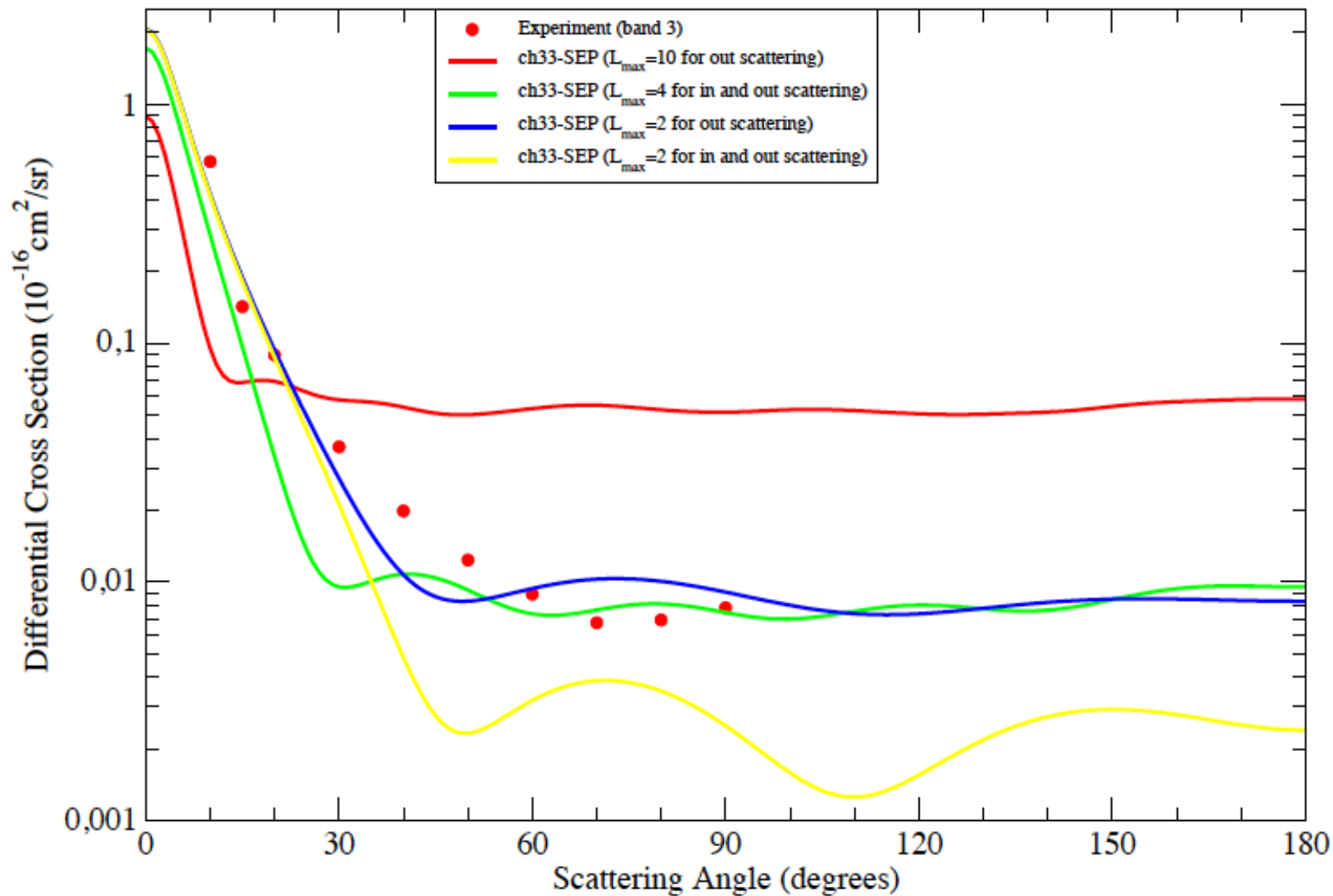## (very fresh data from Michael Brunger/Cristina Lopes collaboration)

40 eV

Legend:
- Experiment (band 3)
- ch33-SEP (L_{max}=10 for out scattering)
- ch33-SEP (L_{max}=4 for in and out scattering)
- ch33-SEP (L_{max}=2 for out scattering)
- ch33-SEP (L_{max}=2 for in and out scattering)

Differential Cross Section ($10^{-16} cm^2/sr$) vs Scattering Angle (degrees)

Thank you very much for your attention

A copy of this presentation is at
http://www.ifi.unicamp.br/~maplima/maplima-MP2-UFAM.pdf

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