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# Important electron scattering data for lignocellulosic ethanol production

by

Marco A. P. Lima
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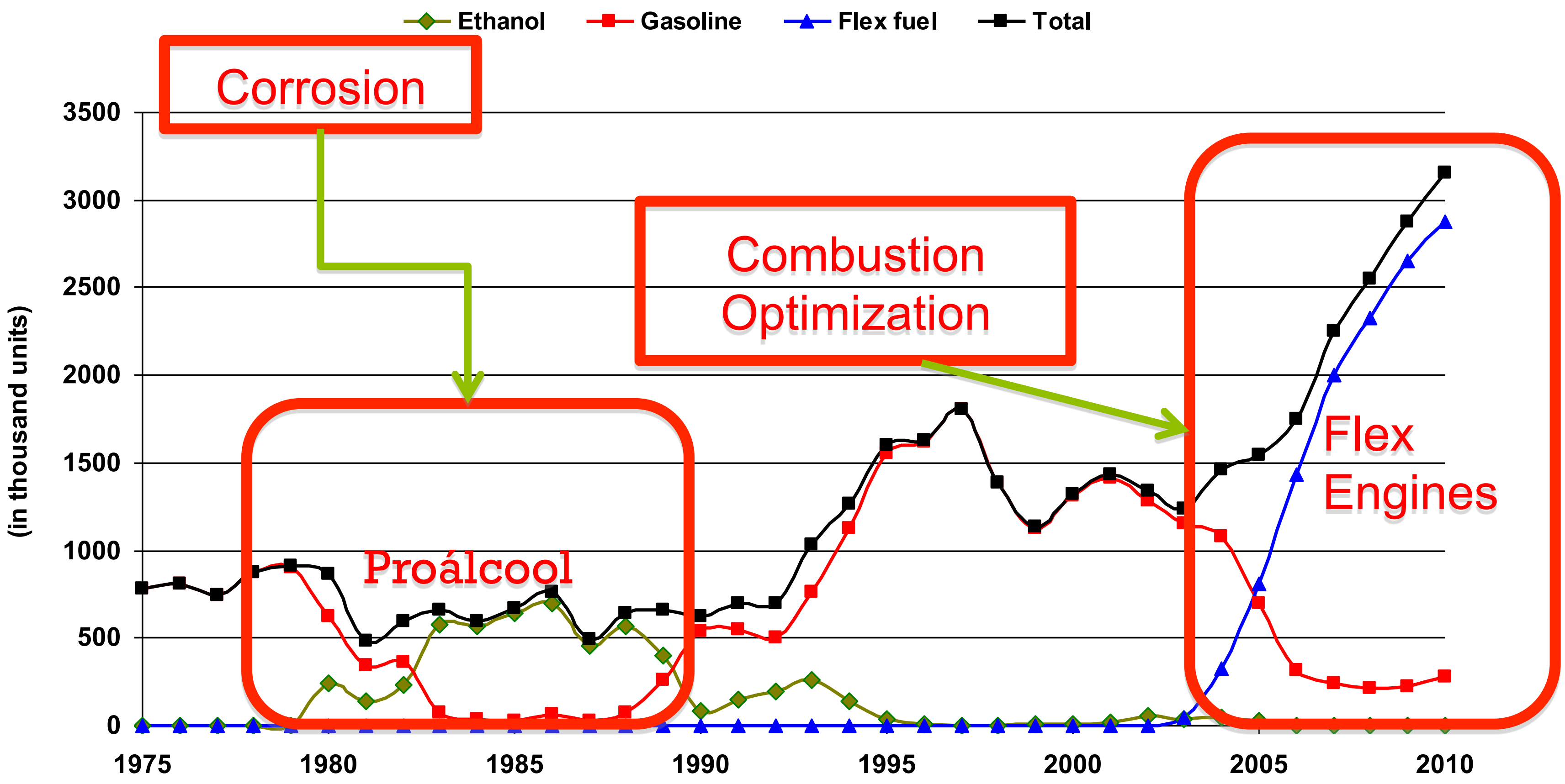
# Motivation I: large scale use of ethanol in engines




## Brazilian Sales of light fleet Vehicles (1975-2010)

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# 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.

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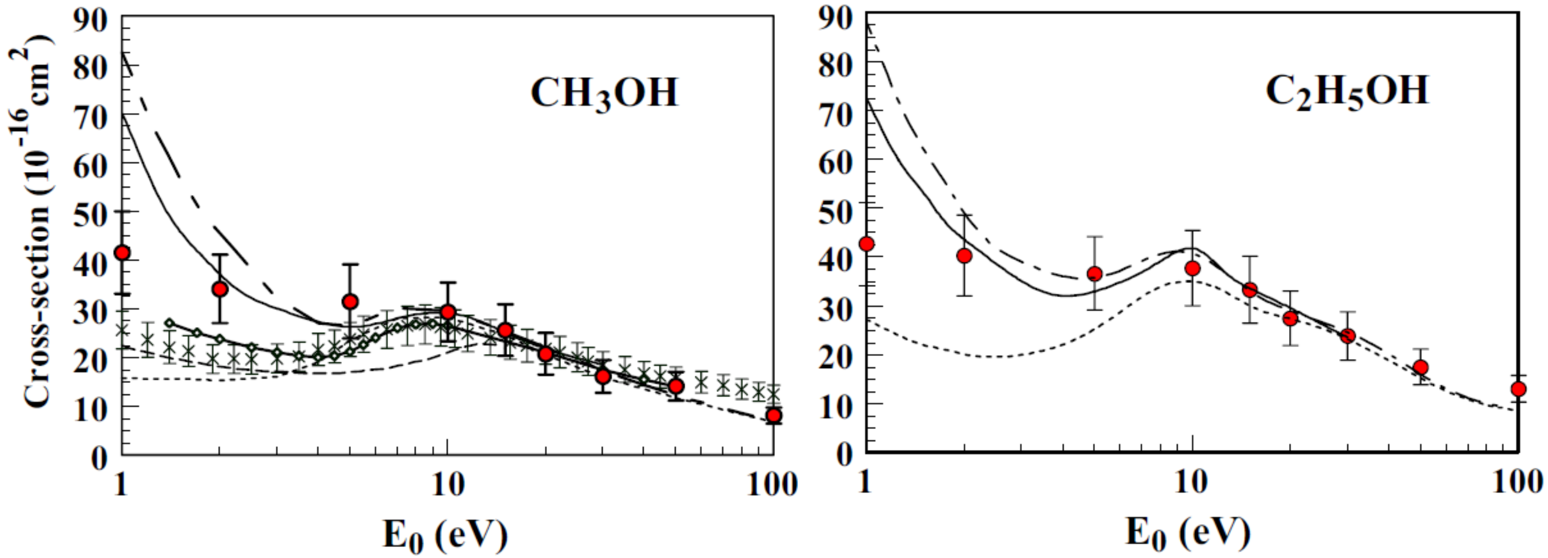
# Low-energy electron scattering from methanol and ethanol

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.

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

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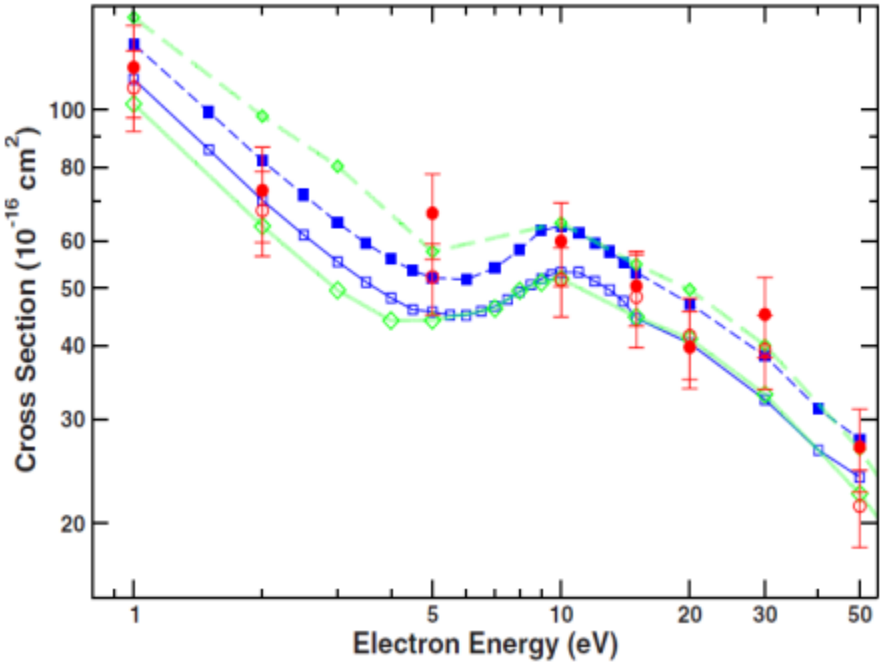
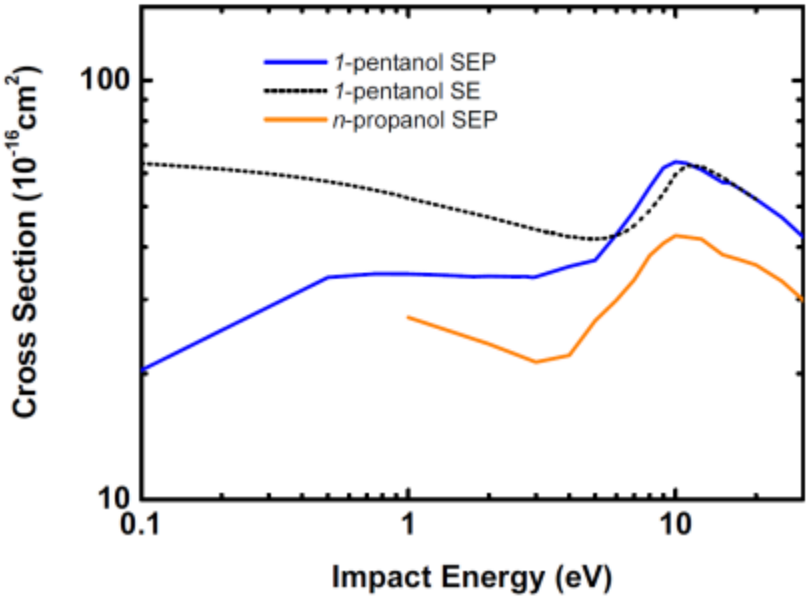
# Elastic scattering of slow electrons by *n*-propanol and *n*-butanol

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

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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

**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**

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# Motivation II: large scale production of ethanol

First generation ethanol: crushing the cane for the juice

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# 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

# Funding Motivation

- Feedstock, processing, green chemistry, engines, sustainability

- 300+ scientists (50 from abroad); 600+ graduate students

- Value awarded 2009-2012:
  US$ 45 million (FAPESP);
  US$ 28 million (State Government);
  US$ 5 million (industry);
  US$ 28 million (Universities)

- 35 industrial business plans ($2^{nd}$ generation ethanol; new products for sugarcane; gasification) approved will result in a potential investment of BRL 3.1 billion (~US$ 1.5 billion)

# Theoretical co-authors

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Marco A. P. Lima

UFPR
UNIVERSIDADE FEDERAL DO PARANÁ

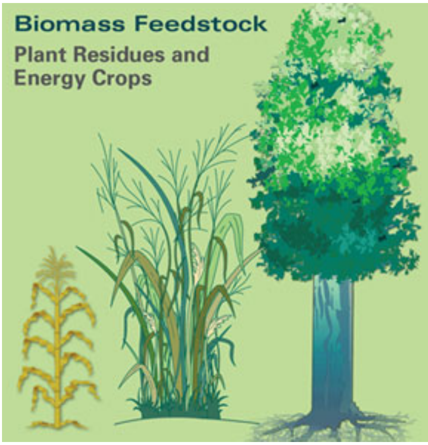
Sergio d'A. Sanchez
Márcio H. F. Bettega

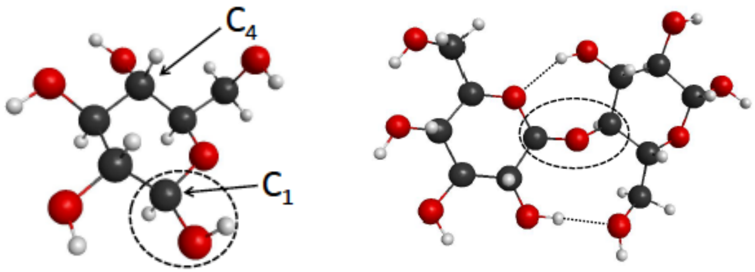
Universidade Federal do ABC

Romarly F. da Costa

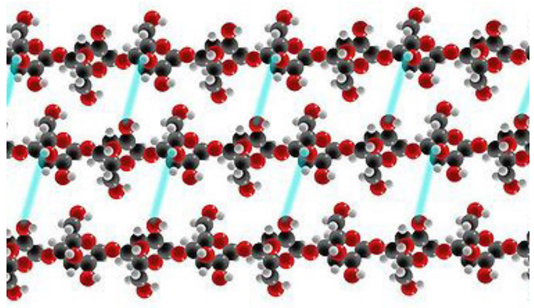
Márcio T. do N. Varella (coordinator)

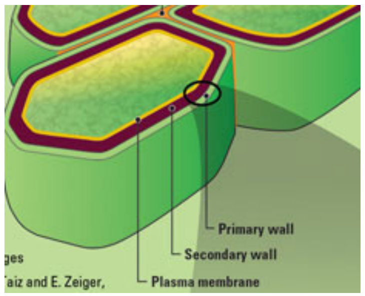
# Biomass is Made Up with Fermentable Sugars

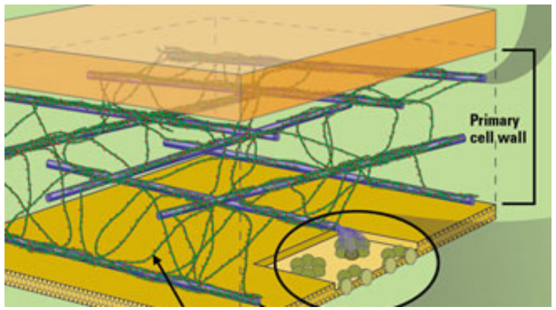


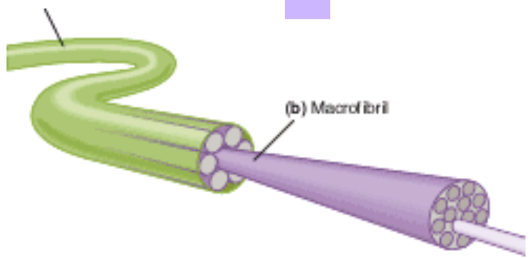




β-D-glucose cellobiose



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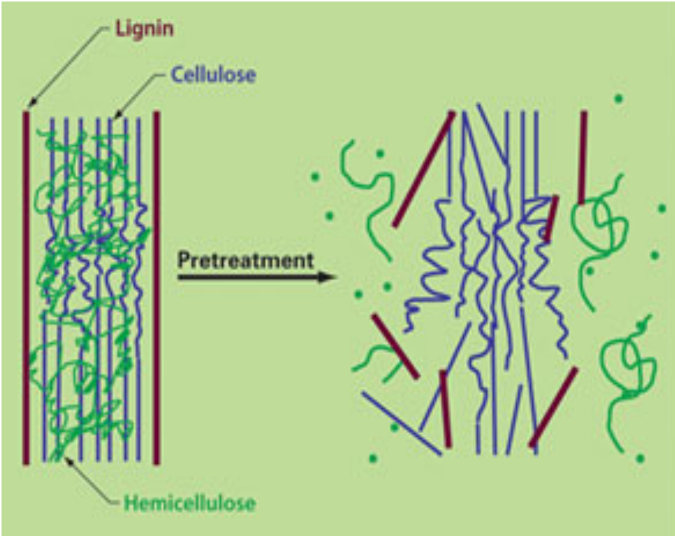
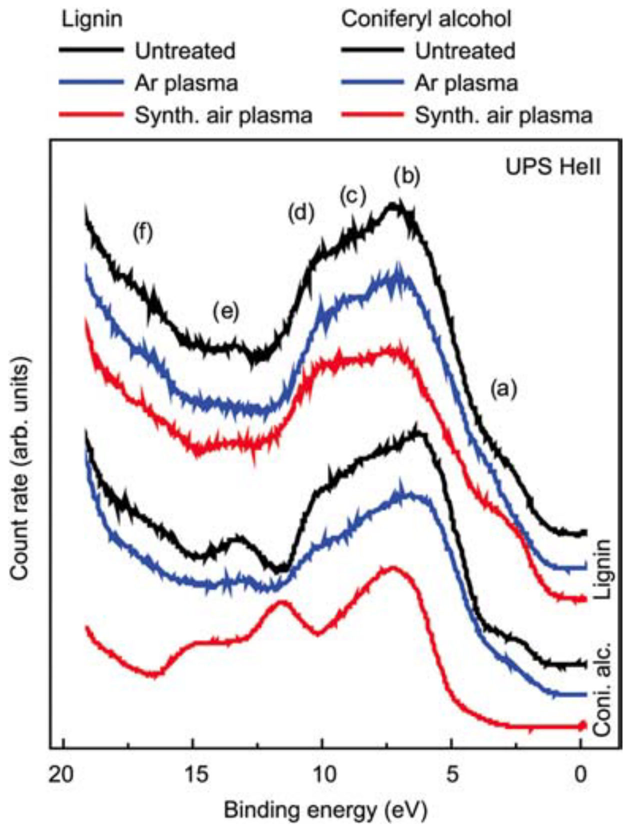
# Lignocellulose is Resistant to Hydrolysis

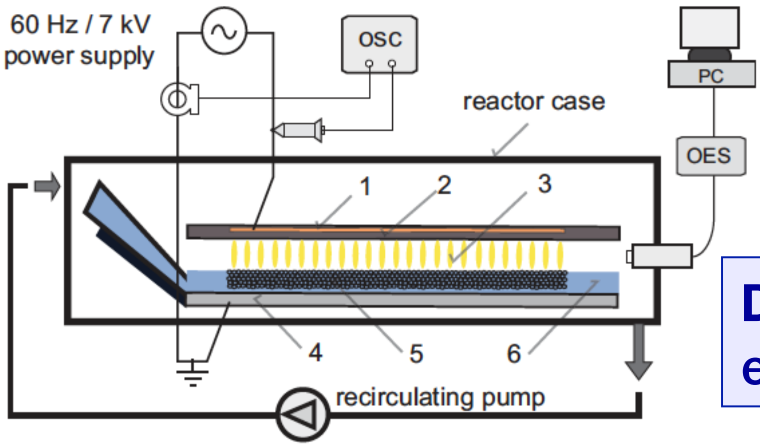



**Pretreatment**: bio- and physical-chemical processes to expose the cellulose fibers




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

Holzforschung, Vol. 64, pp. 331–336, 2010




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

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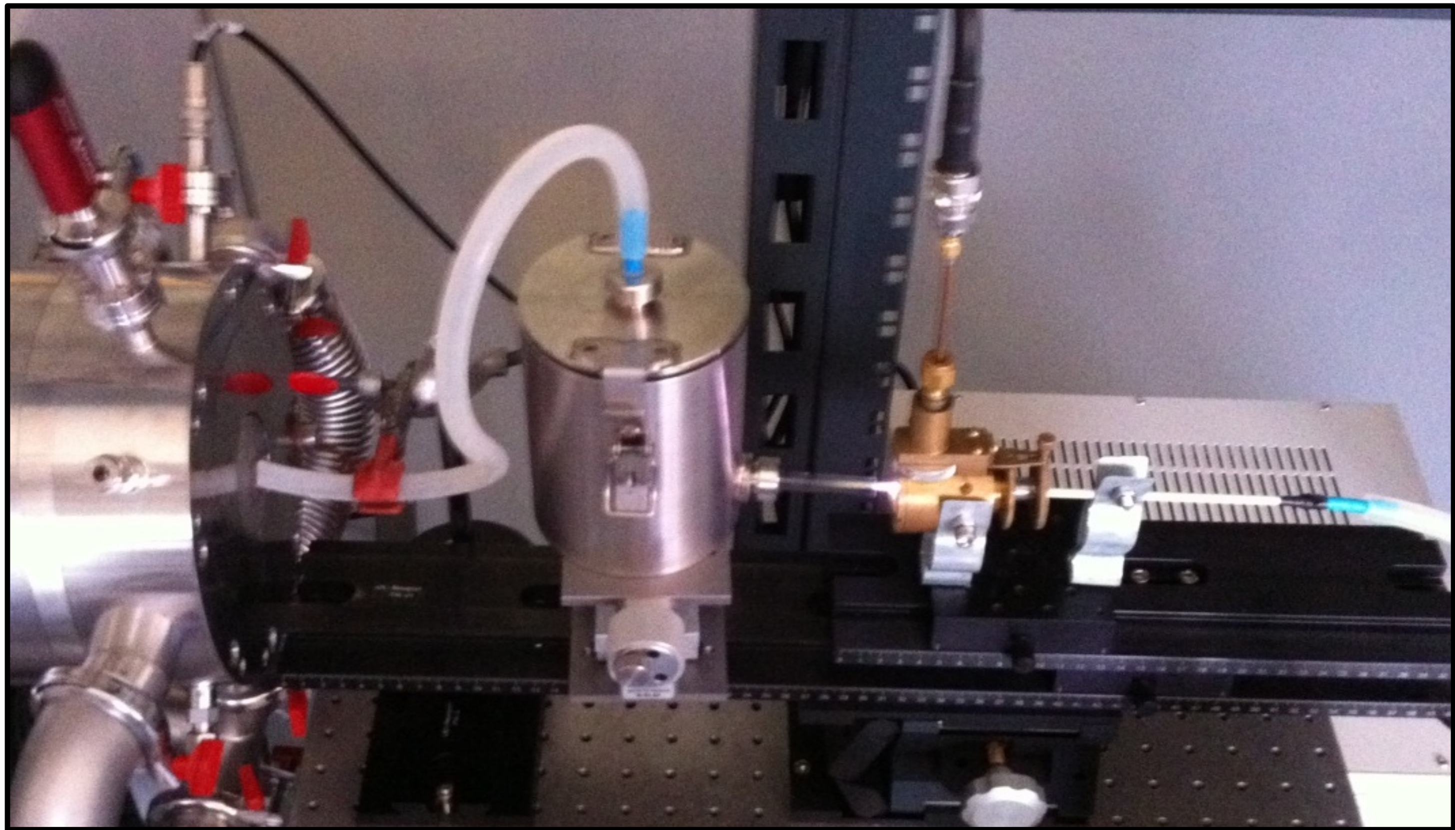
# Sugarcane Bagasse Plasma Pretreatment



**Treatment conditions**

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

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# 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!!!**

Jayr Amorim, Carlos Oliveira, Jorge A. Souza-Correa, Marco A. Ridenti
Plasma Process. Polym. 2013, DOI: 10.1002/ppap.201200158

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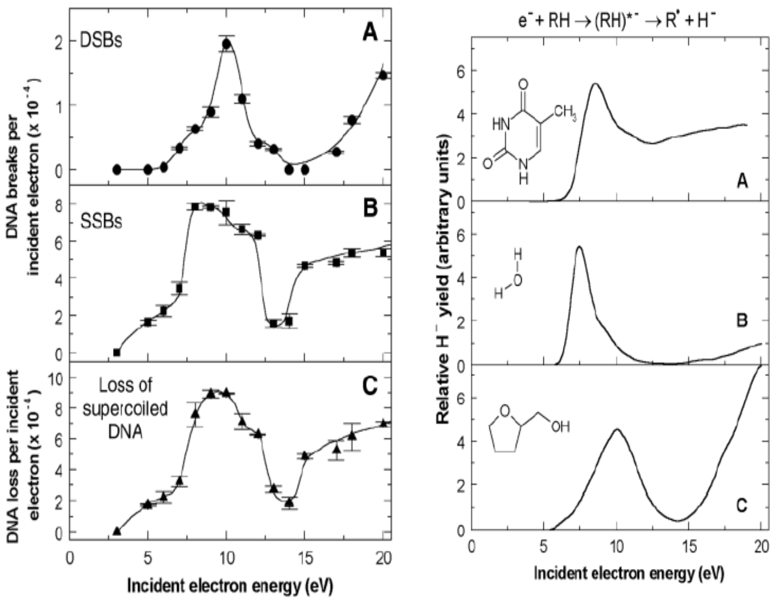
# Electron-Induced Damage to Biomolecules

## 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



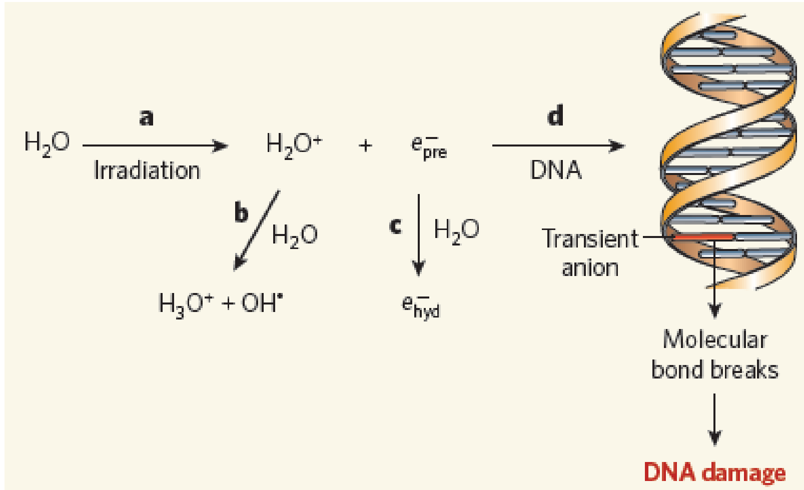

Science, **287** 1658 (2000)

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

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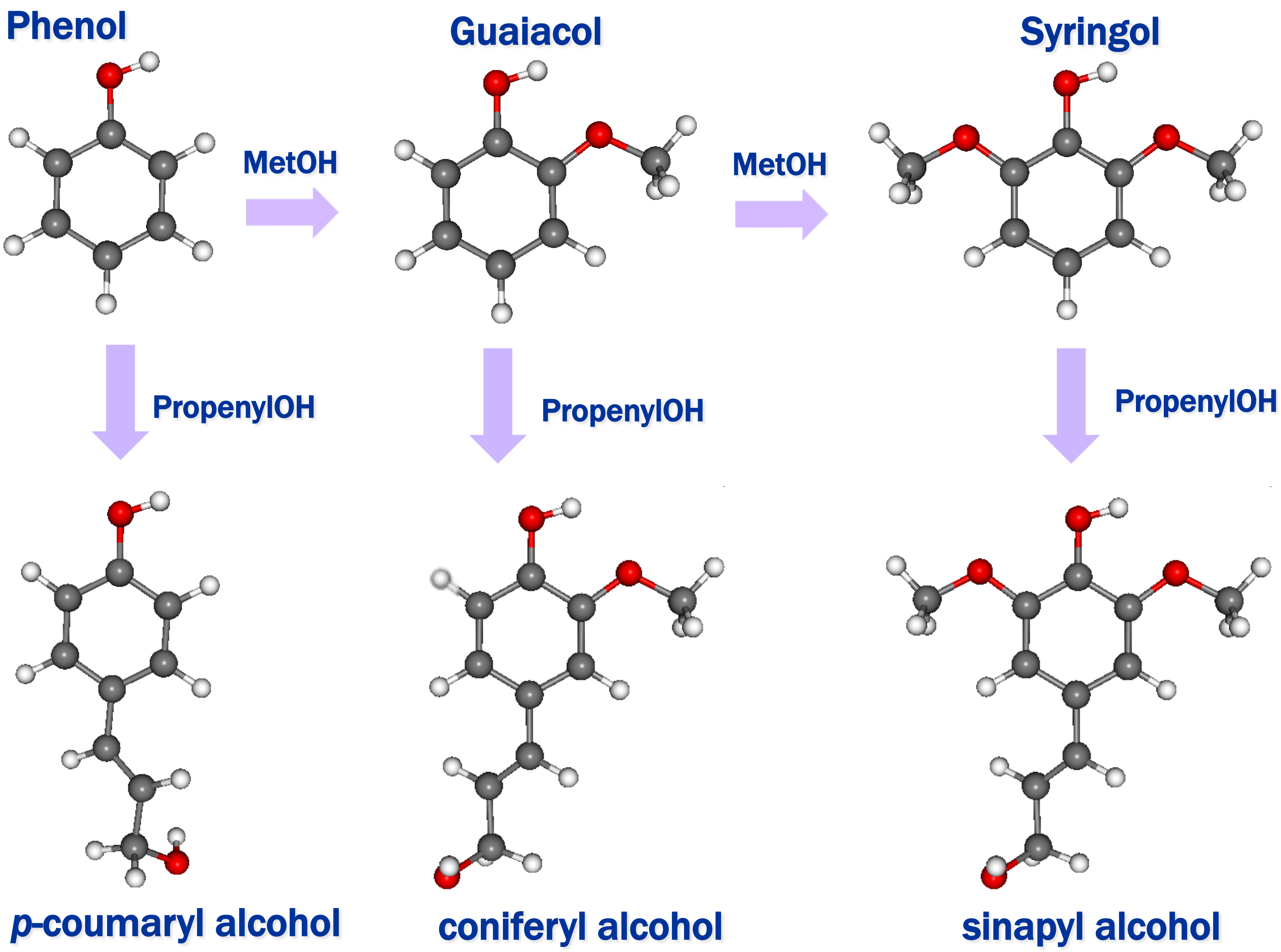
# Lignin Subunits

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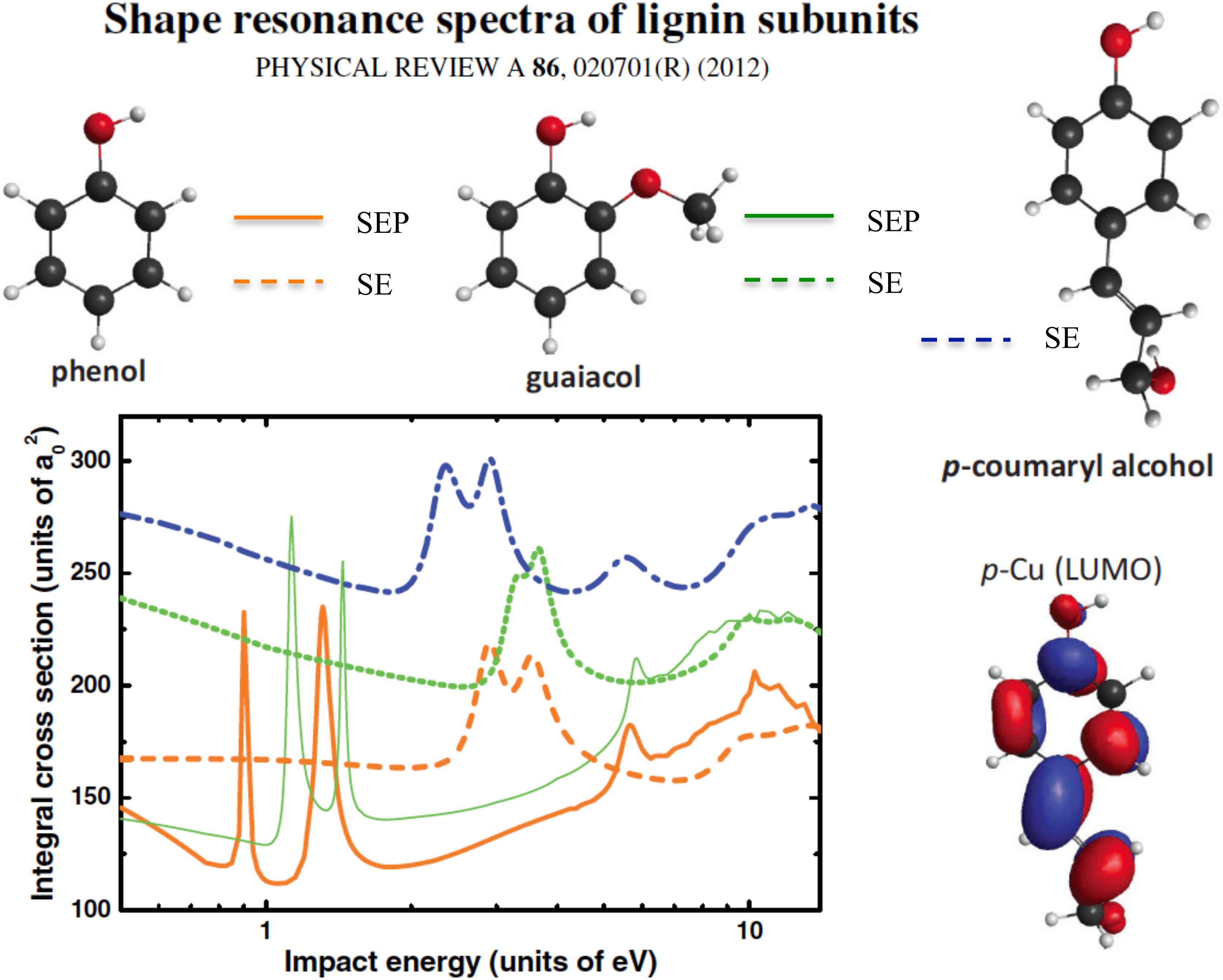
RAPID COMMUNICATIONS

# Shape resonance spectra of lignin subunits

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






IFGW Instituto de Física Gleb Wataghin UNICAMP

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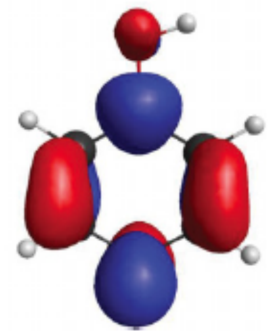
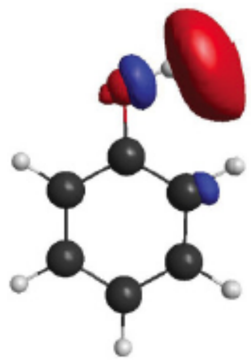
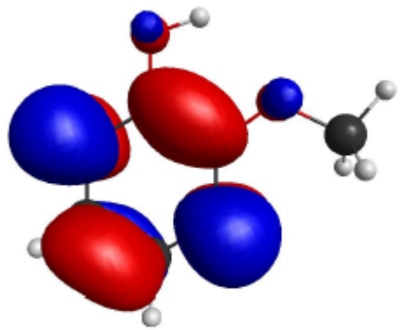


π* (LUMO+1)



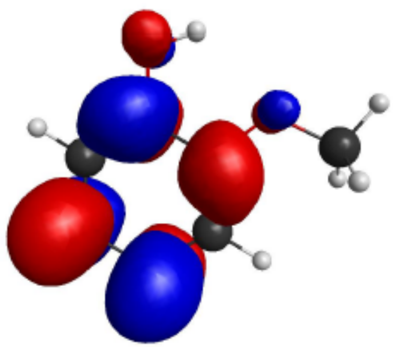
σ* (LUMO+2)

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

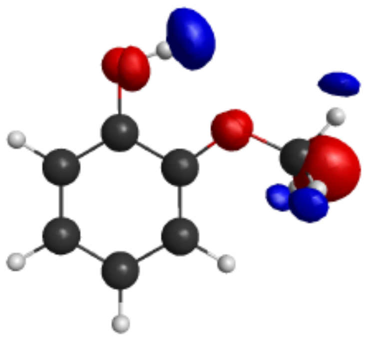


π* (LUMO)

σ* (LUMO+2)



π* (LUMO+1)

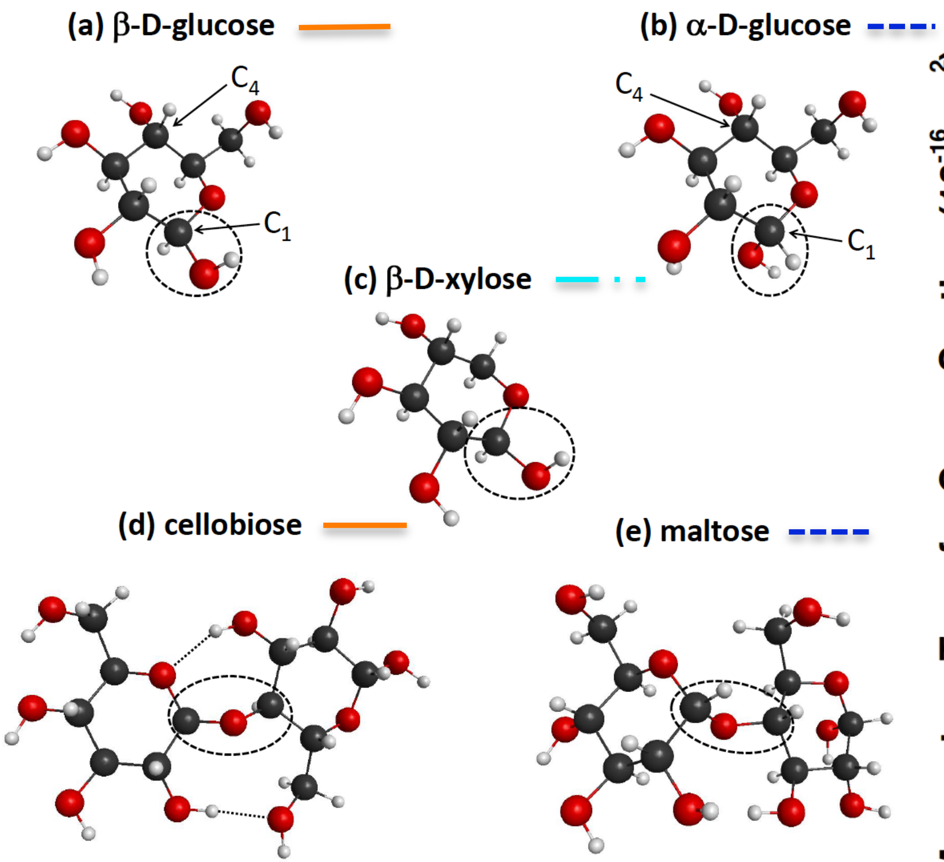


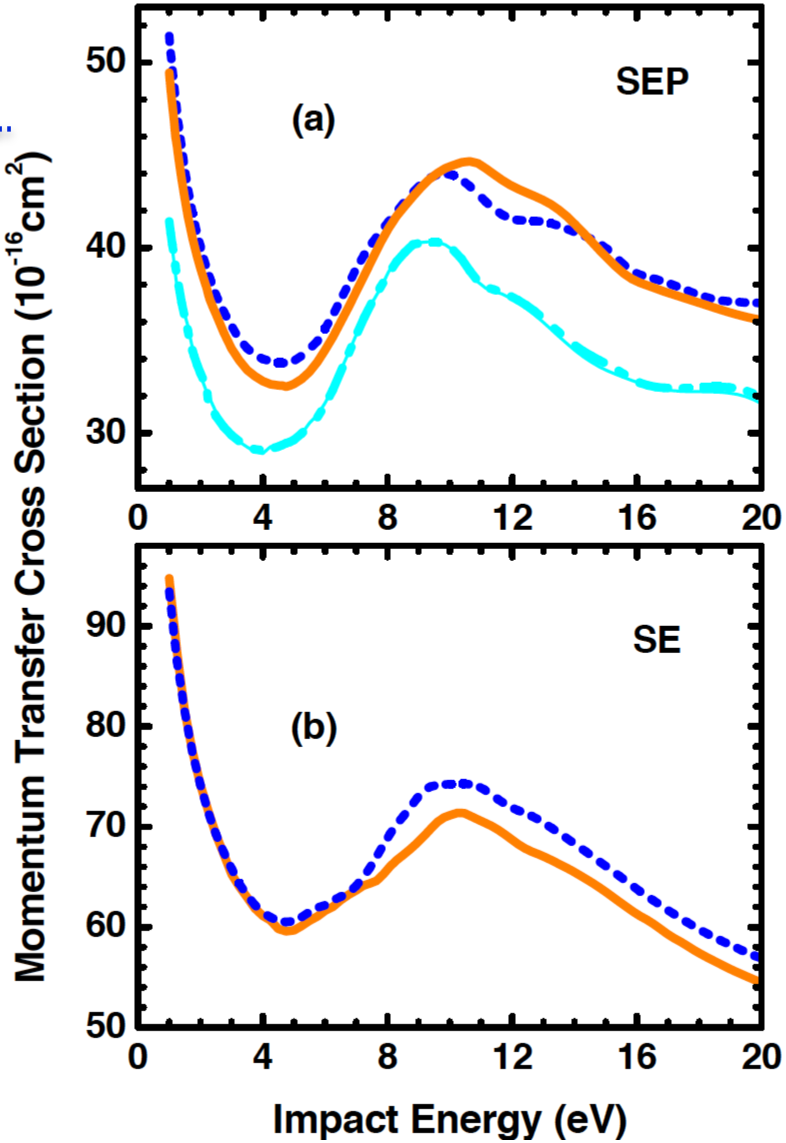
σ* (LUMO+3)

**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).



# Theoretical team on electron-scattering of microsolvated molecules

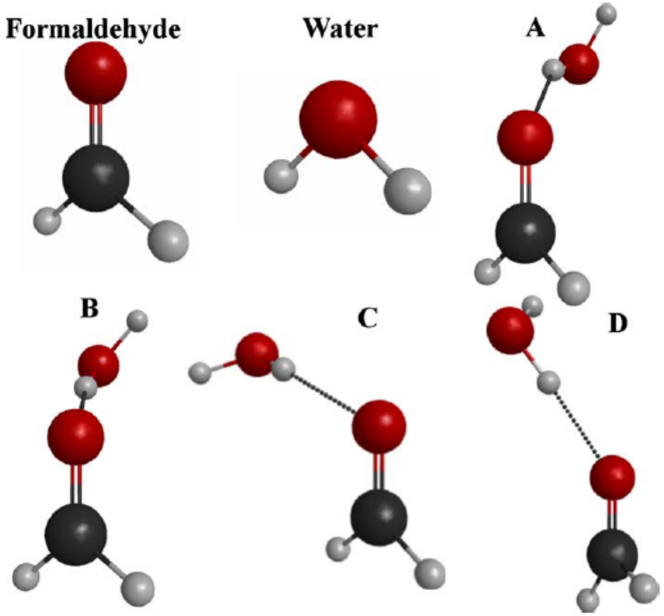
Sylvio Canuto (microsolvation)
Kaline Coutinho (microsolvation)
Márcio T. do N. Varella

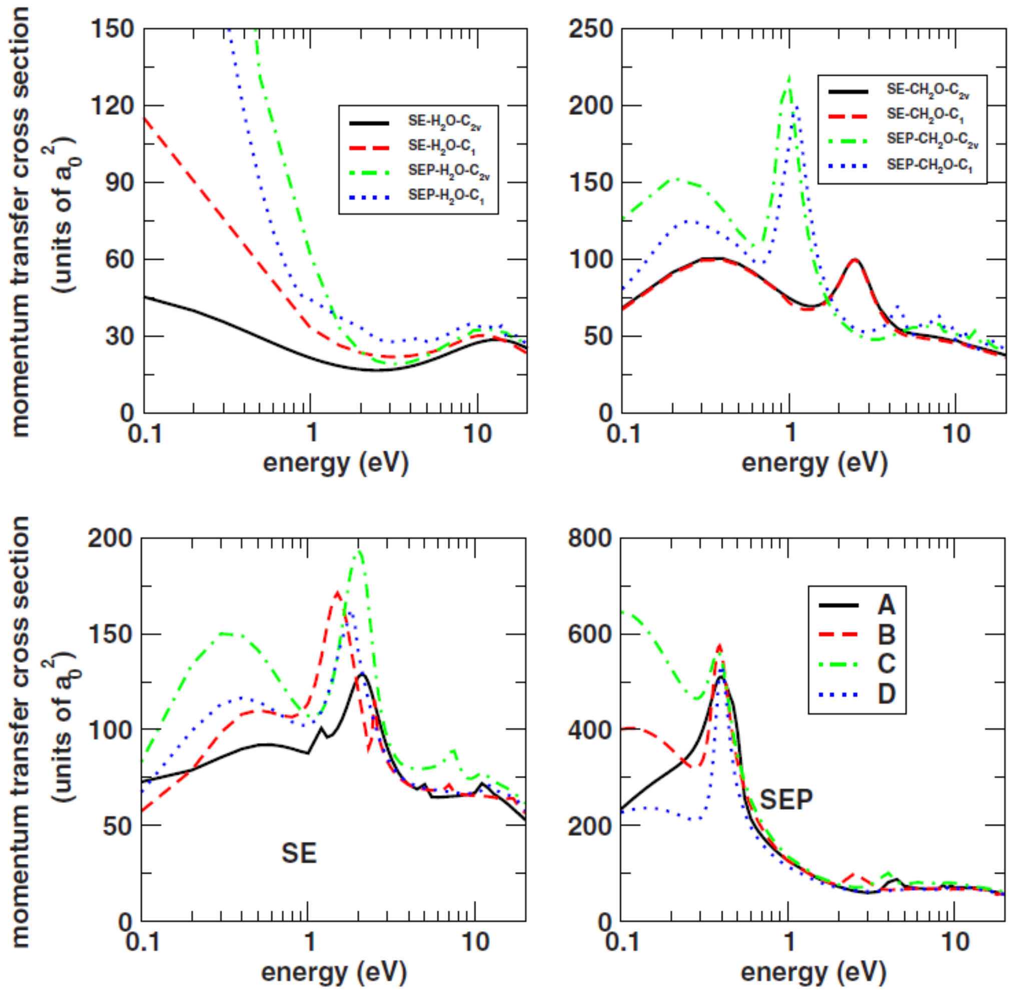
Eliane M. de Oliveira (scattering of solvated phenol)
Marco A. P. Lima

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

# Electron Collisions with the $CH_2O$-$H_2O$ complex

PHYSICAL REVIEW A 80, 062710 (2009)



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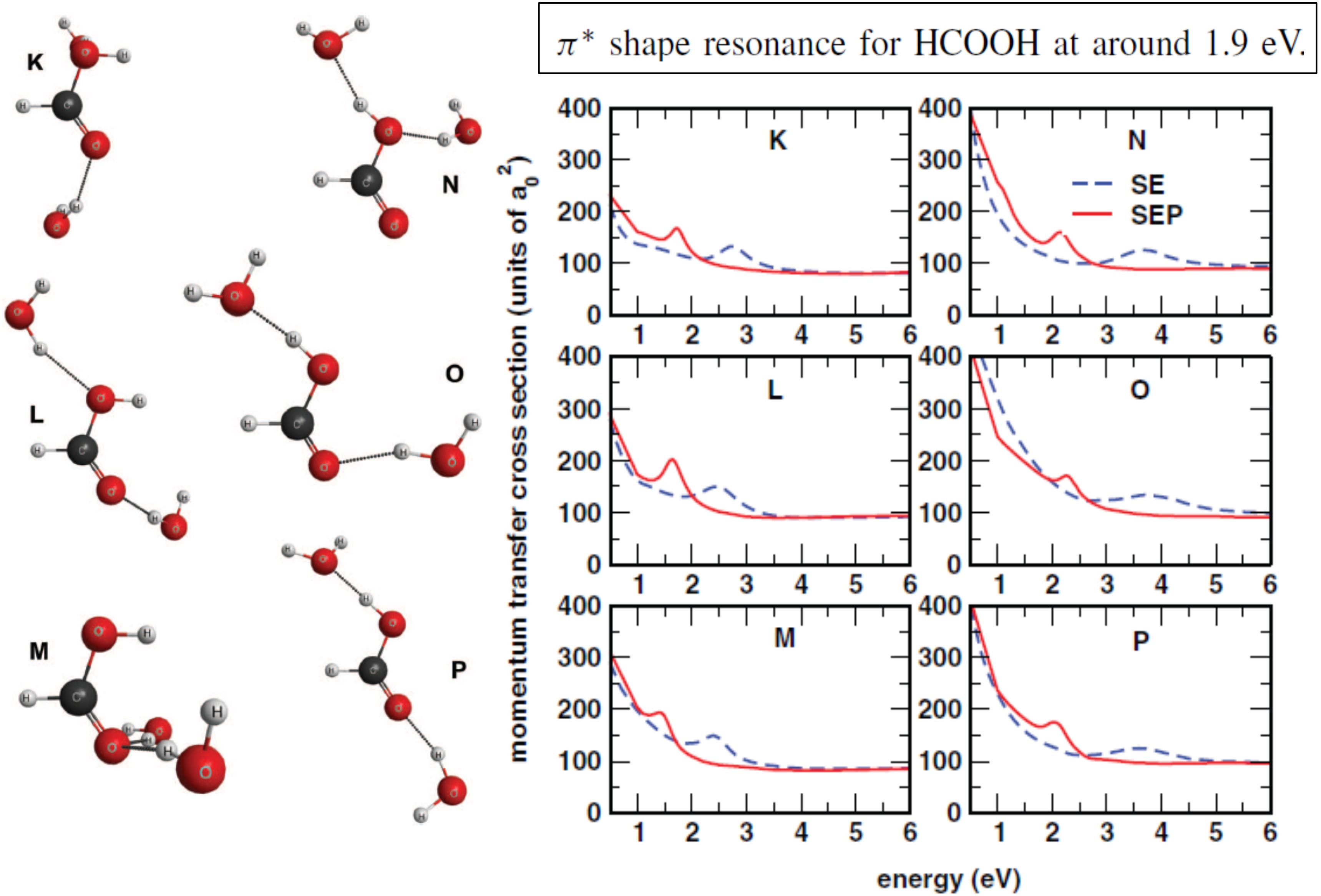
# Electron collisions with the HCOOH...$(H_2O)n$ complexes (n=1, 2) in liquid phase: The influence of microsolvation on the $\pi^*$ resonance of formic acid

THE JOURNAL OF CHEMICAL PHYSICS **138**, 174307 (2013)

$\pi^*$ shape resonance for HCOOH at around 1.9 eV.

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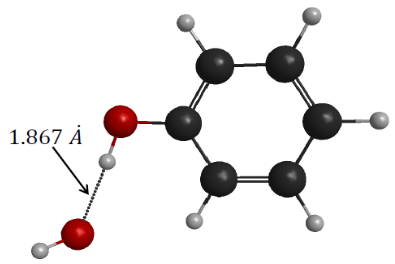
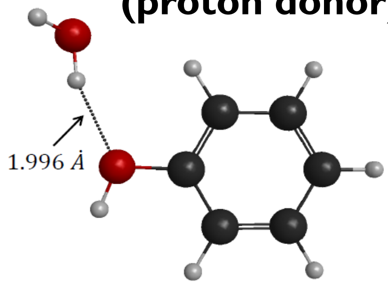
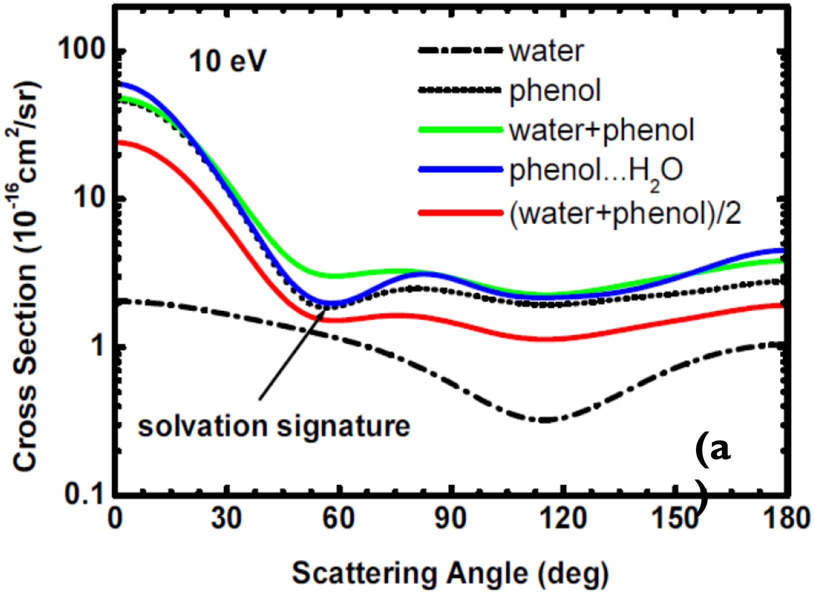
# Electron Collisions with Phenol...$H_2O$: search for microsolvation signatures in the DCS

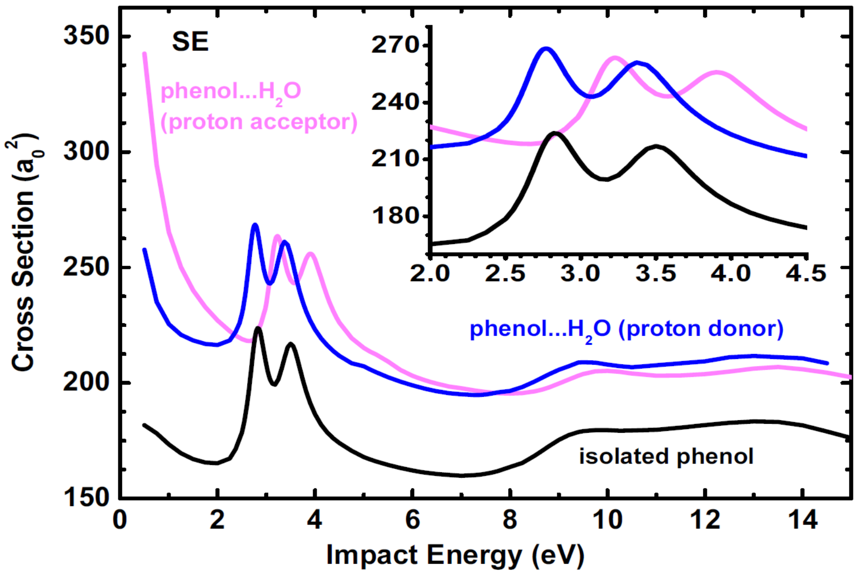
(proton acceptor)

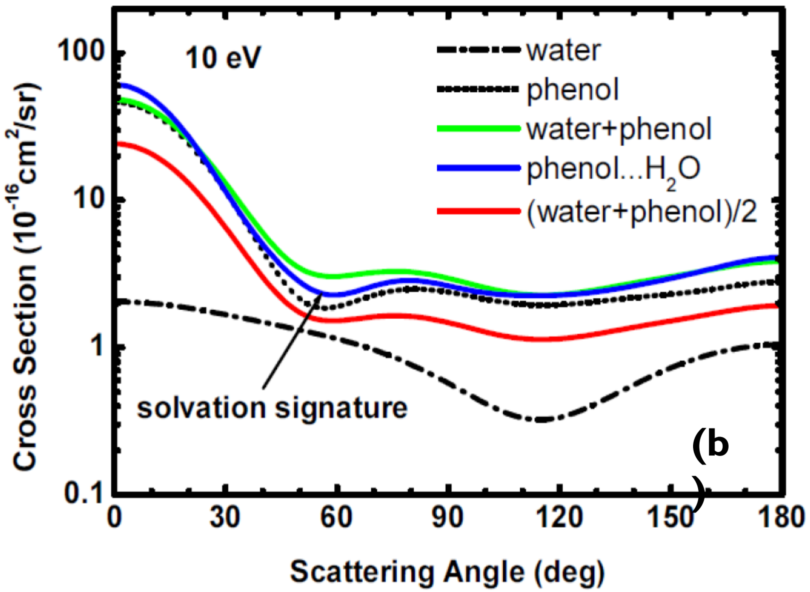



(proton donor)



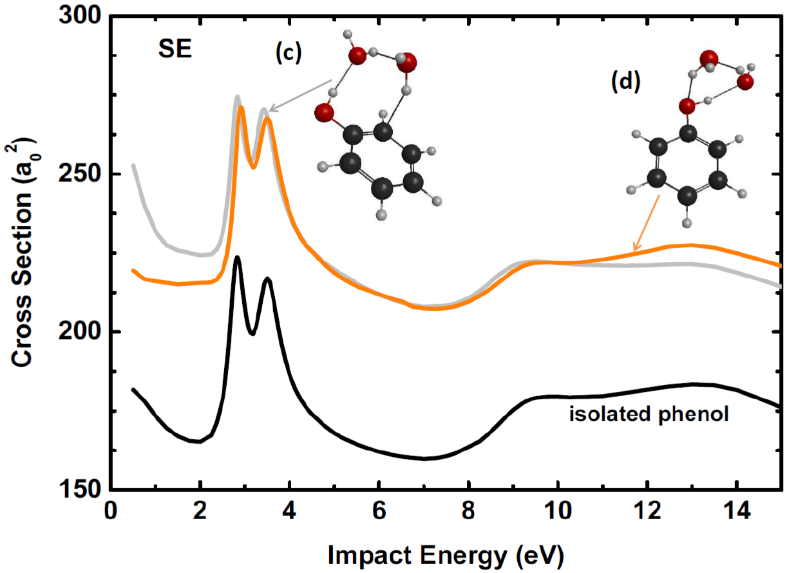



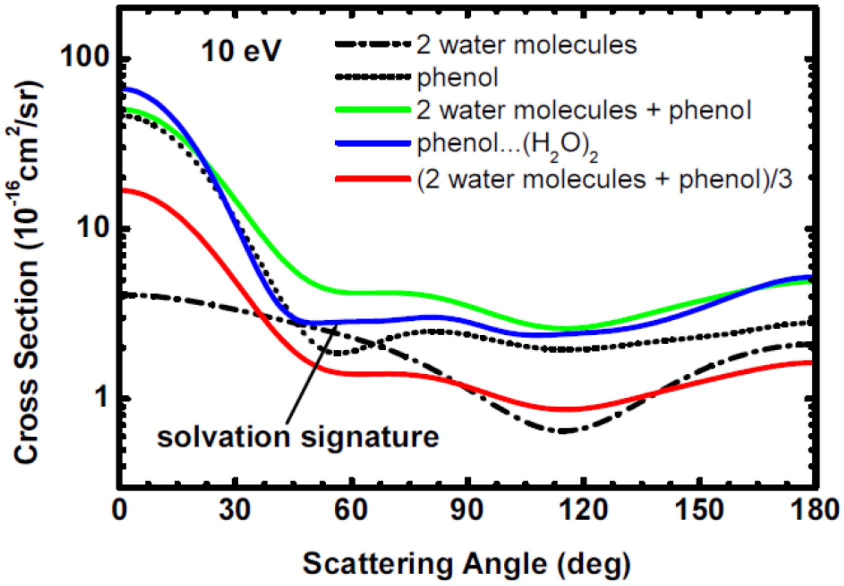



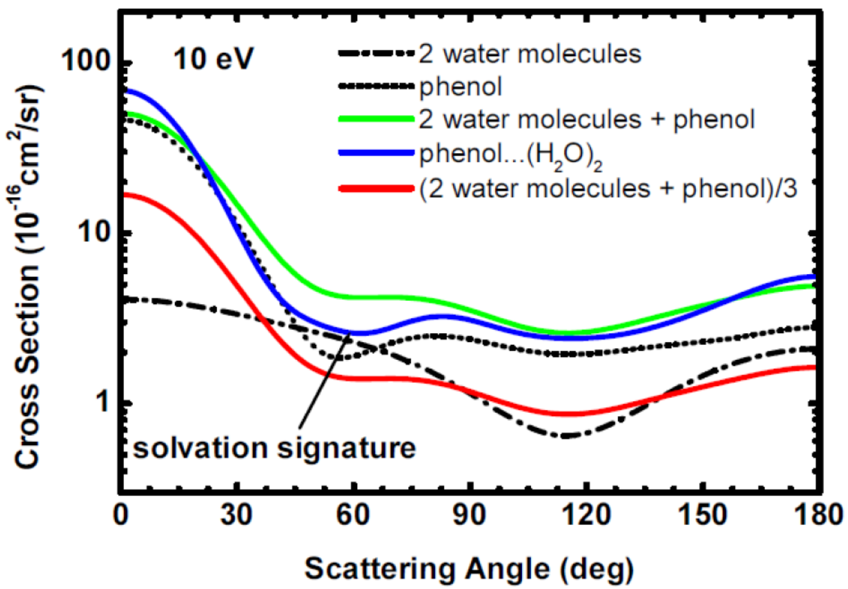



# Electron Collisions with Phenol...$(H_2O)_2$: search for microsolvation signatures in the DCS

**Static-Exchange Calculations:**

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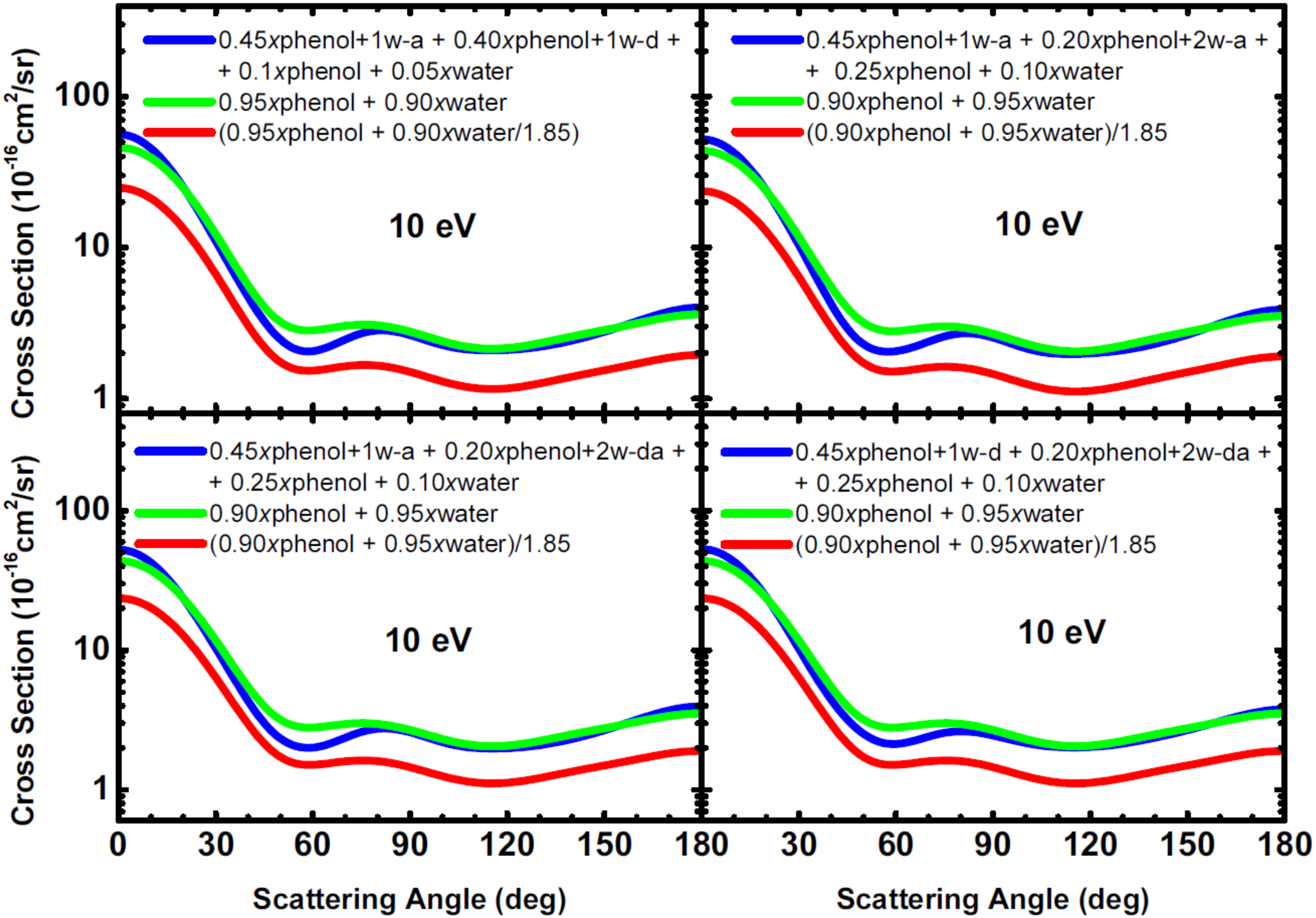
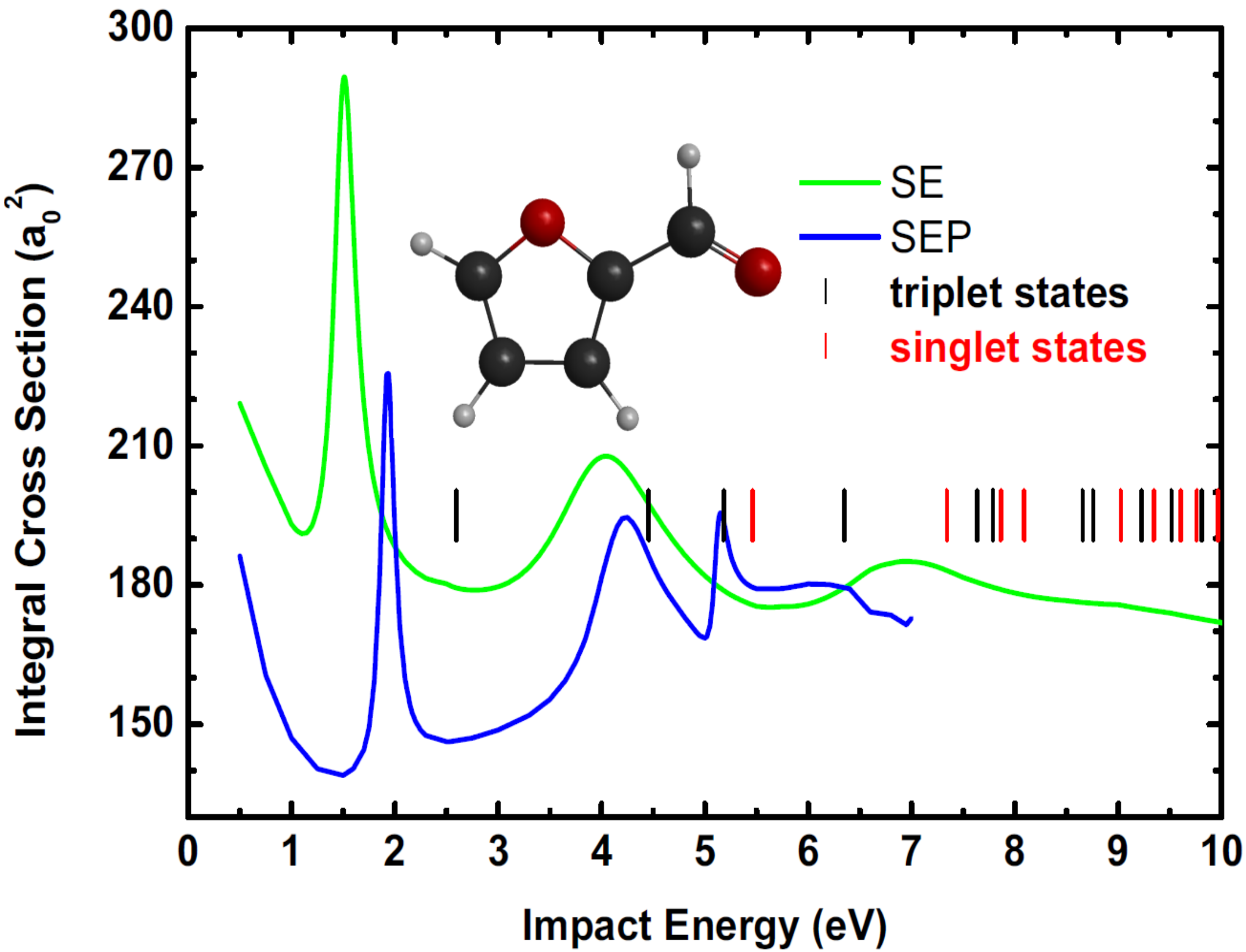
# Electron Collisions with Phenol...$(H_2O)_n$: search for microsolvation signatures in the DCS

## Static-Exchange Calculations:



# Electron Scattering of slow electrons by furfural molecules




This molecule has over 20 electronic states between 0 and 10 eV

# Thank you very much for your attention

**A copy of this presentation is at**
**http://www.ifi.unicamp.br/~maplima/maplima-posmol2013.pdf**