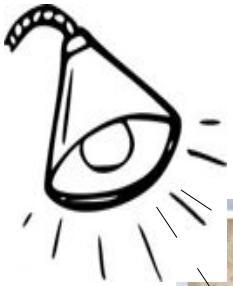
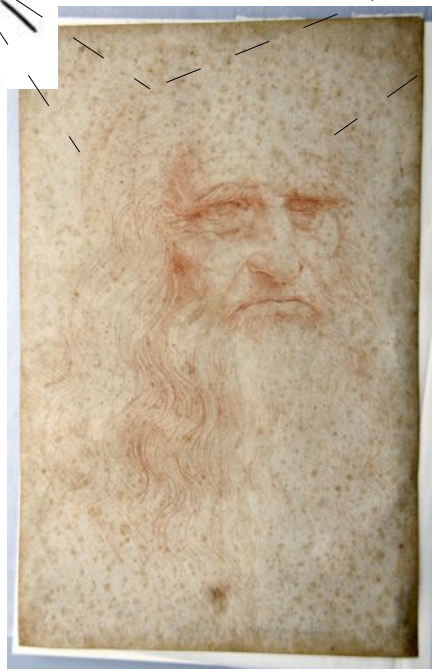
Ab-initio computational methods for the simulation of optical properties applied to cultural heritage

Adriano Mosca Conte
ETSF – MIFP – Dept. of Physics Univ. of Rome Tor Vergata





Initial work: **non-invasive** and **non-destructive** investigation approach for diagnostic of **ancient paper** documents

PRL 108, 158301 (2012) PHYSICAL REVIEW LETTERS week ending 13 APRIL 2012

Role of Cellulose Oxidation in the Yellowing of Ancient Paper

A. Mosca Conte,[1] O. Pulci,[1,2] A. Knapik,[3] J. Bagniuk,[3] R. Del Sole,[1] J. Lojewska,[3] and M. Missori[4]

[1]*ETSF, Dipartimento di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Rome, Italy*

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Applications:

in collaboration with M. C. Misiti, president of the “Istituto per la Conservazione del Patrimonio Archivistico e Librario” (Ministery of cultural heritage)

Improvements of the experimental model based on Kubelka-Munk approach (M. Missori)

Improvement of theoretical model

Temperature effects (C. Violante)

Oxidized groups dynamics (C. Violante)

Measurements

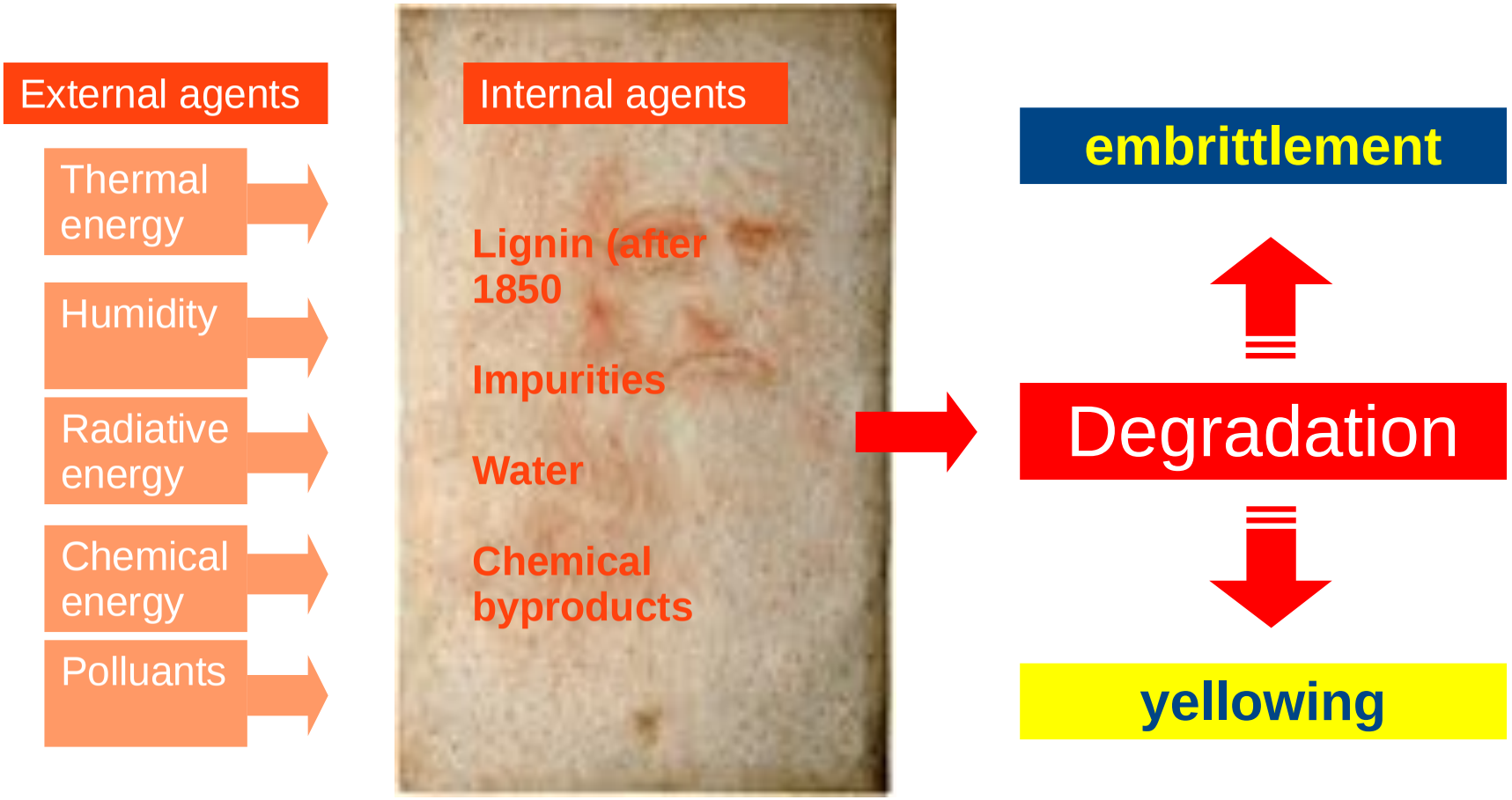
Theoretical analysis
ab-initio calculations

Sample supplier
and drawing
expert

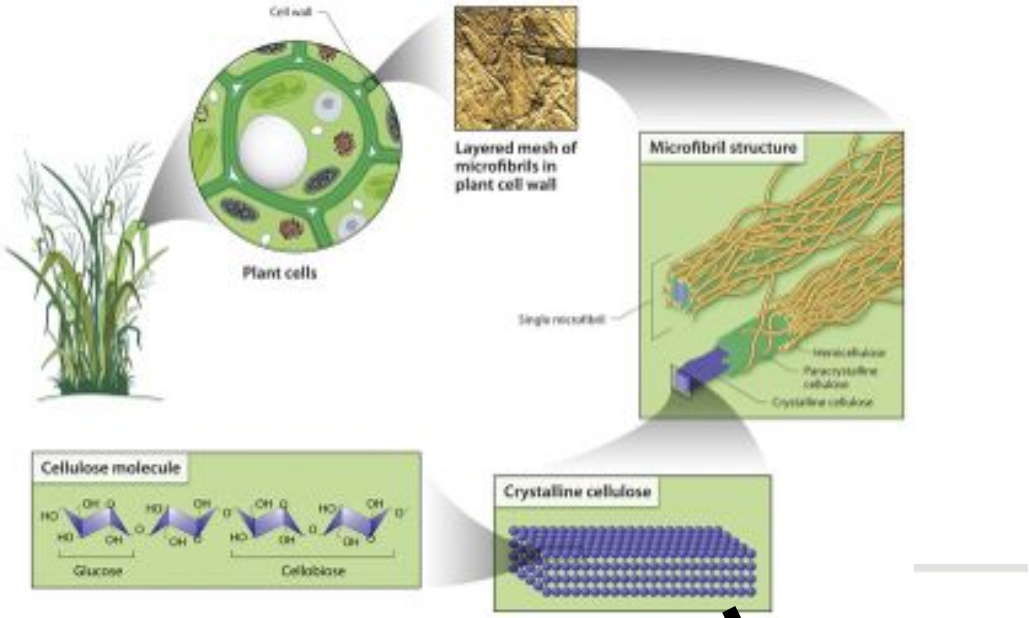
Conservation

Maria Cristina Misiti (ICPAL)

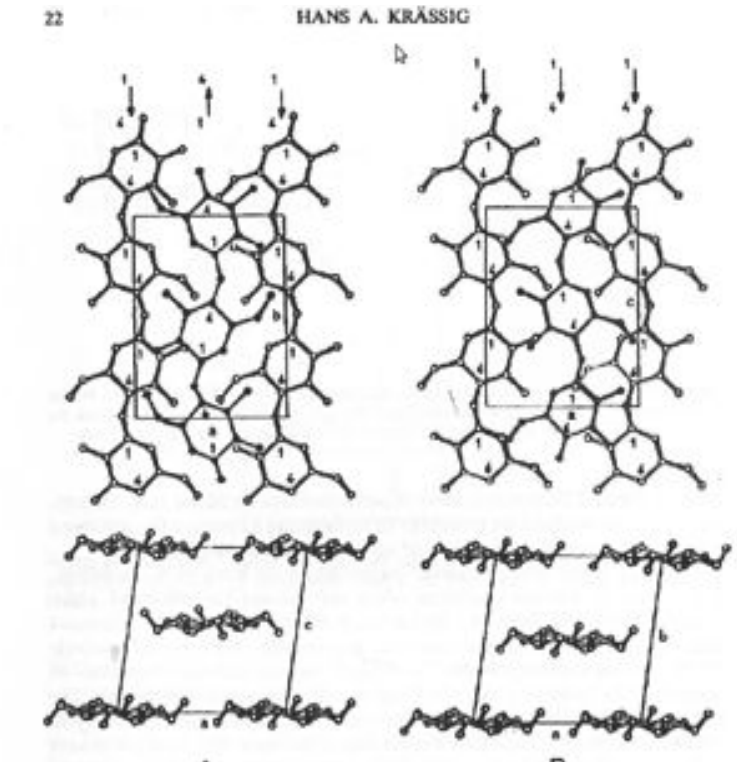
Causes of physico-chemical degradation of paper



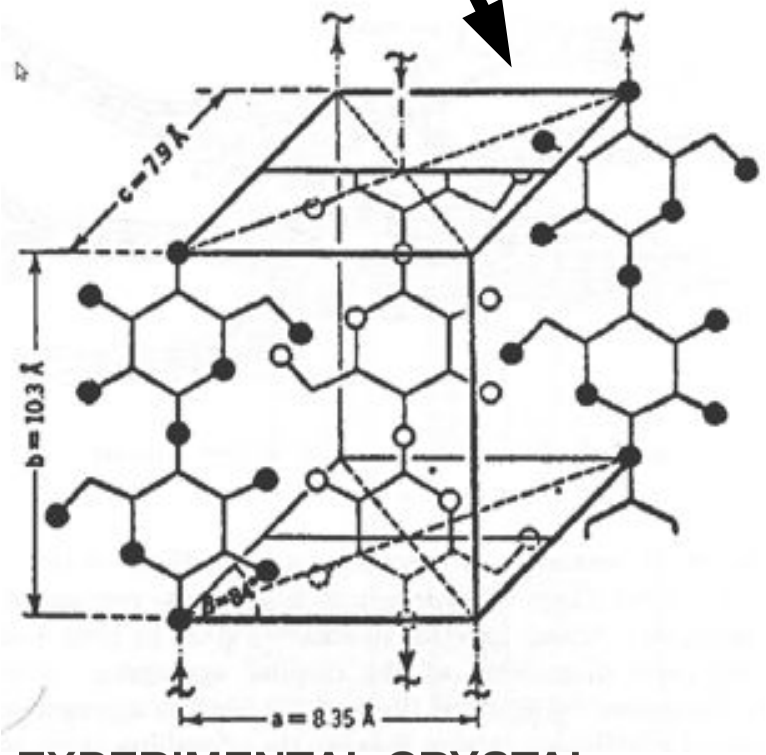
Cellulose: 40% of the annual production of biomass on Earth!



CRYSTAL STRUCTURE

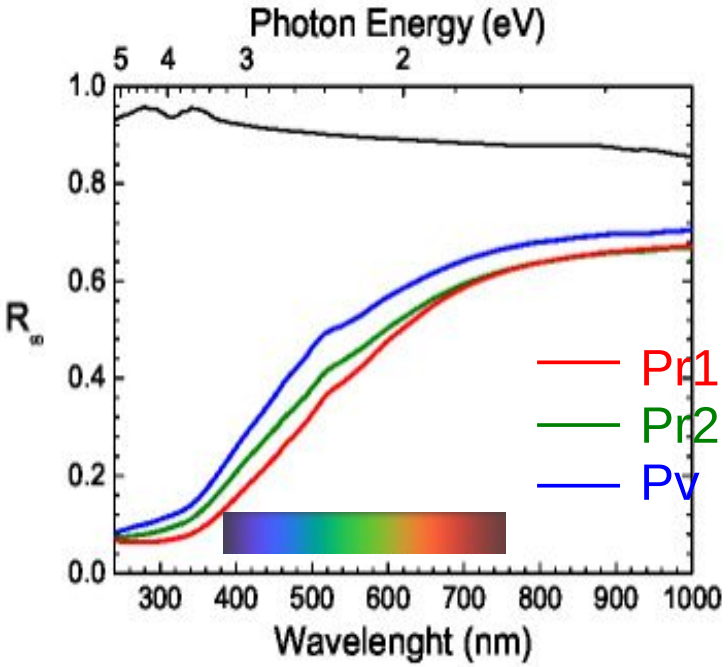


ANTI-PARALLEL PARALLEL



EXPERIMENTAL CRYSTAL PARAMETERS

EXPERIMENTAL OBSERVATIONS



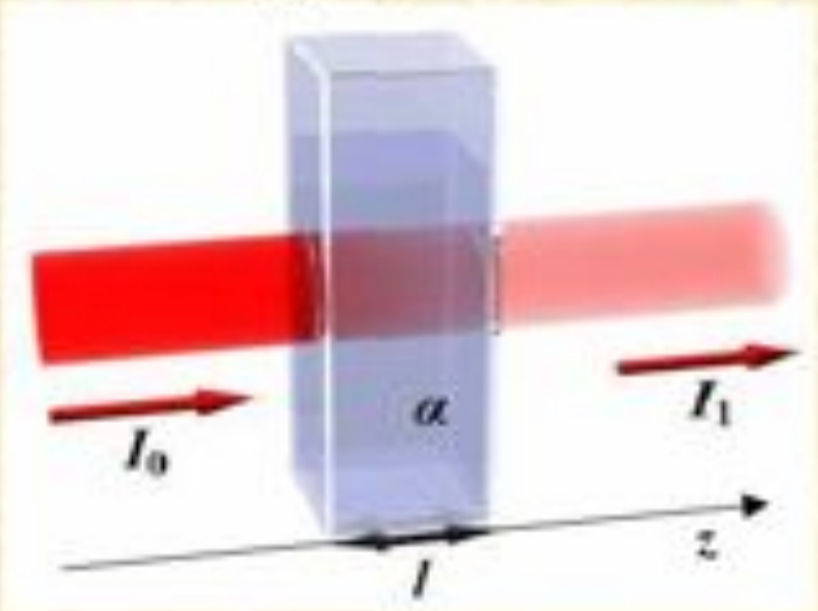
Observations:

Yellowing and **foxing**: reflectance main contributions are in the yellow-red range

Unaged paper is white while cellulose is transparent: **diffusion**

Optical spectroscopy

Homogeneous medium



$$dI(z) = -\alpha I(z)dz$$

$$T = \frac{I_1}{I_0} = e^{-\alpha l}$$

$$\alpha = \frac{1}{l}\ln\frac{I_0}{I_1}$$

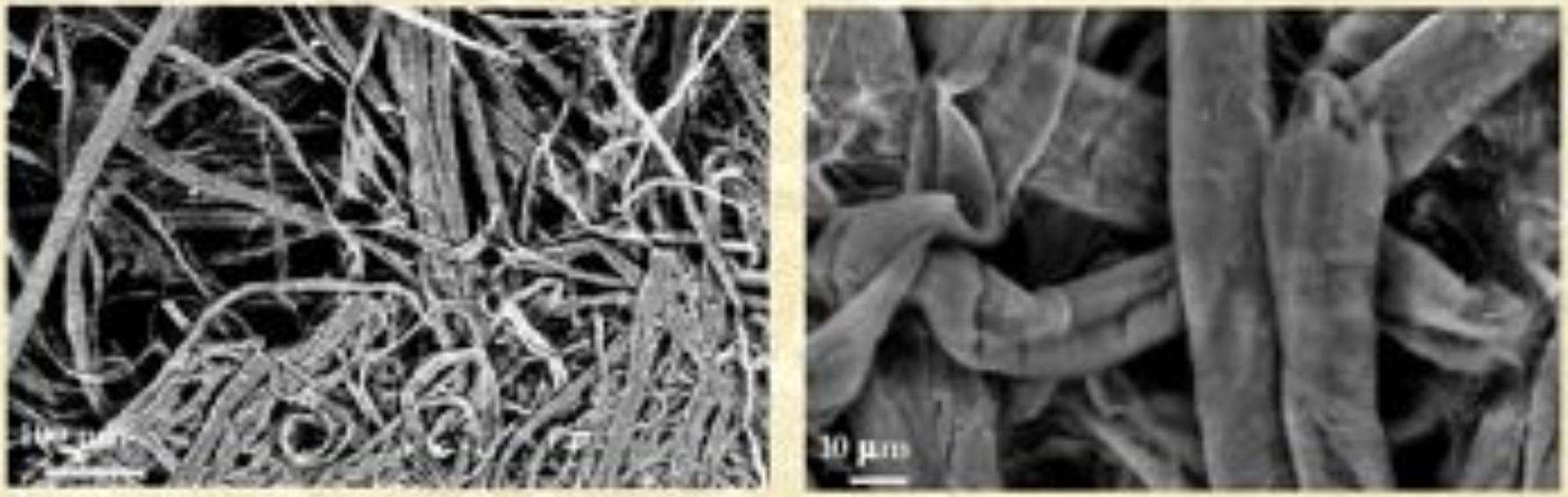
$$\alpha = \frac{4\pi k}{\lambda}$$

$$\tilde{n} = n + ik$$

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = (n+ik)^2$$

Each molecule has a specific α that depends on λ

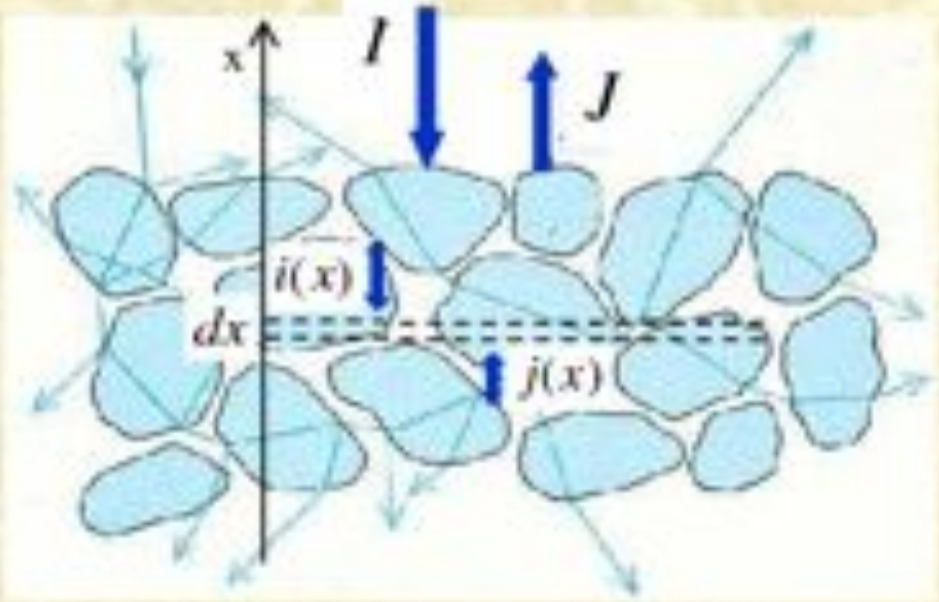
Paper is a complex system, chiefly composed of a web of cellulose fibers



Inomogeneous: empty spaces larger than λ

Two flux model (Kubelka-Munk)

Paper is made of fibres and voids ⇨ inhomogeneous material



$$\frac{di}{dx} = -(k+s)i + sj$$

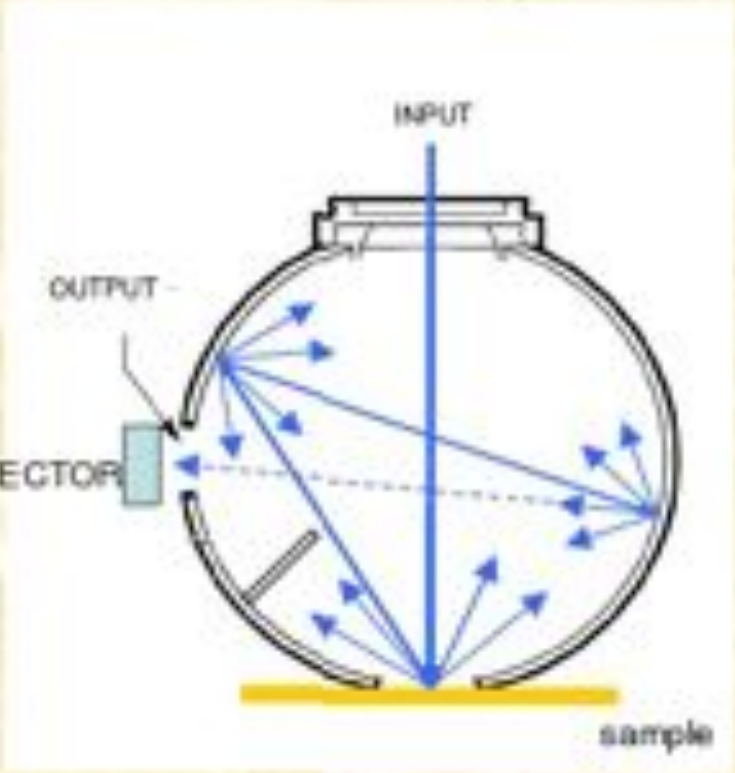
$$\frac{dj}{dx} = (k+s)j - si$$

k = absorption coefficient
s = scattering coefficient

$$R = \frac{J}{I}$$

B. Philips-Invernizzi et al., Opt. Eng. 40, 1082 (2001)

Experimental set-up



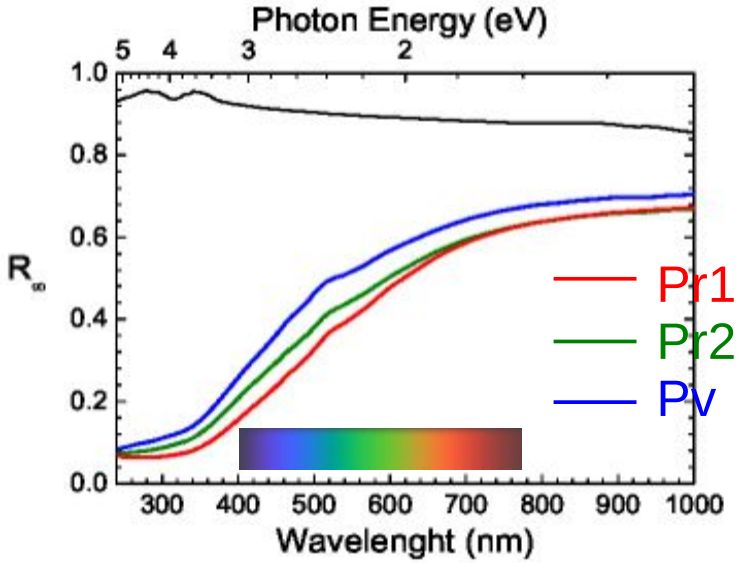
An "integrating sphere" is necessary to collect light scattered by paper over all angles (diffuse reflectance).

$$A_{KM}(\lambda) = \frac{(1 - R_\infty(\lambda))^2}{2R_\infty(\lambda)} \propto \alpha \Longleftrightarrow \alpha = 2\omega\sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}}$$

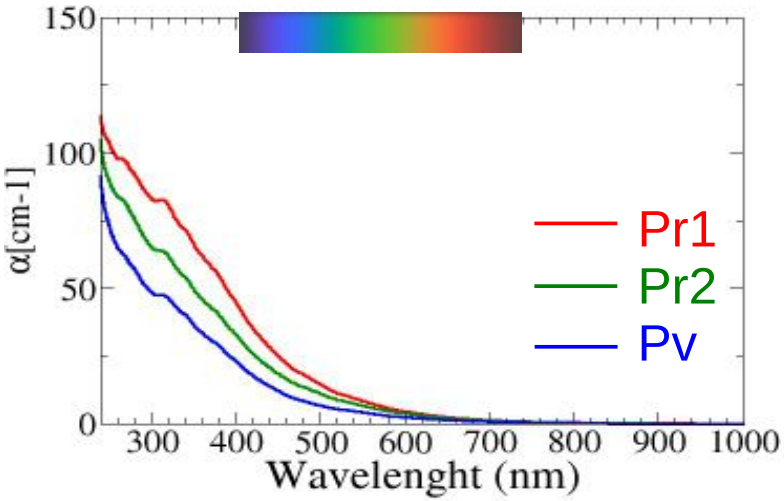
TDDFT

Absorption in the **violet-blue** region correspond to **reflectance** in the **red-yellow** region.

Oxidation induces absorption in the violet-UV region.

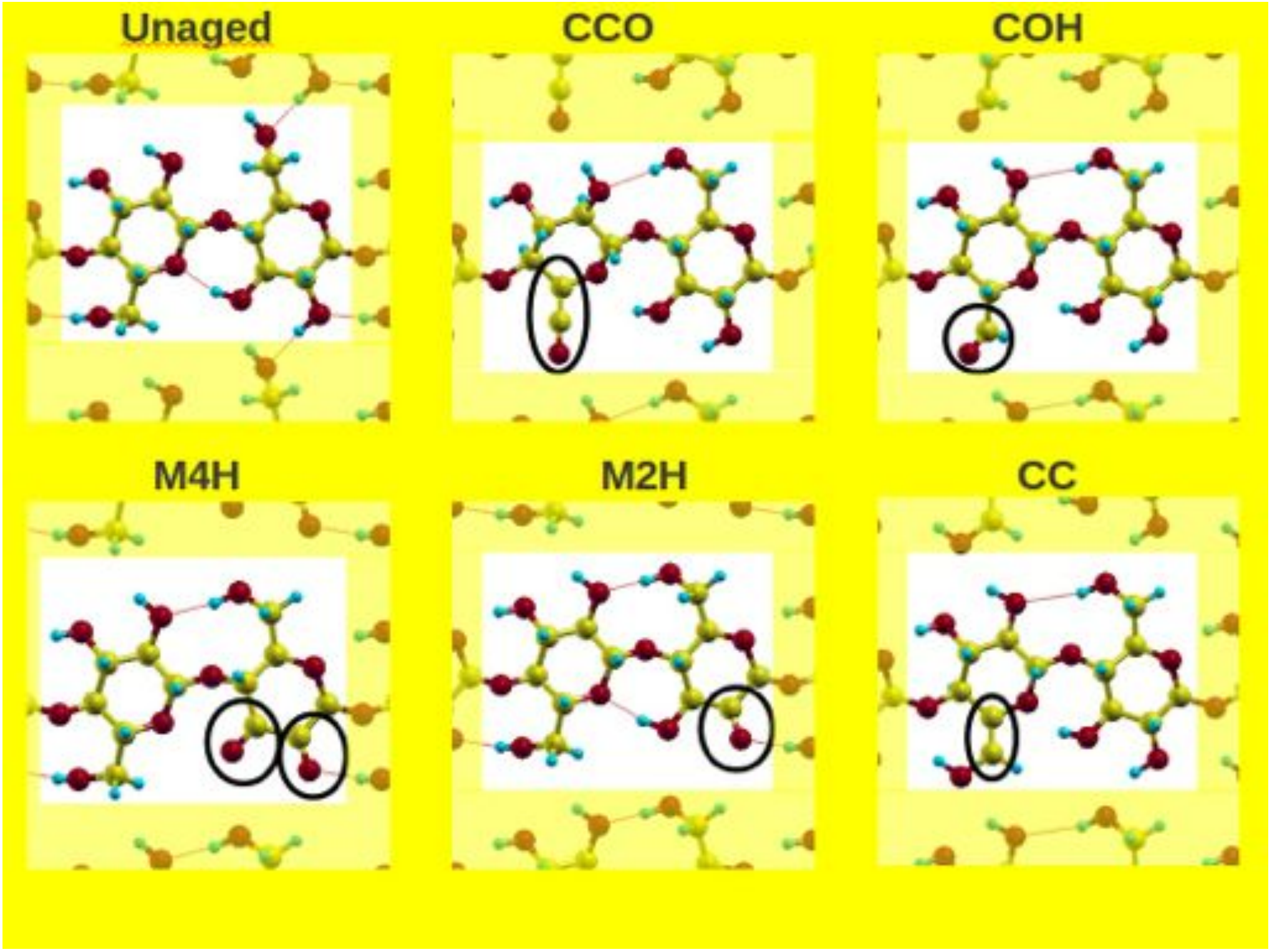


Kubelka - Munk



Vibrational spectroscopies, such as Fourier Transform Infrared (FTIR), and Raman are non-invasive but do not answer the fundamental question:

Which oxidized groups are responsible of yellowing?


Unaged
CCO
COH
M4H
M2H
CC

THEORETICAL CALCULATIONS

Ab-initio (free-parameter) theoretical method

Ab-initio (free-parameter) theoretical method

Density Functional Theory (DFT):

Walter Kohn (Nobel in chemistry in 1998)

Ground-state properties

- Forces acting on atoms
- Total energies
- Geometry optimization

Indipendent-particle approximation

- electronic and optical properties (not based on a rigourous theory)

Ab-initio (free-parameter) theoretical method

Density Functional Theory (DFT):

Ground-state properties

- Forces acting on atoms
- Total energies
- Geometry optimization

Indipendent-particle approximation

- electronic and optical properties (not based on a rigourous theory)

Time-Dependent DFT (TDDFT):

- Time evolution of physical properties
- optical properties

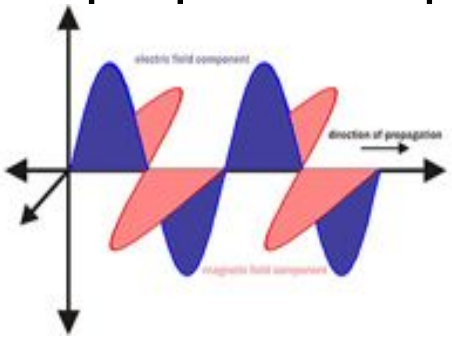
Time-Dependent DFT (TDDFT)

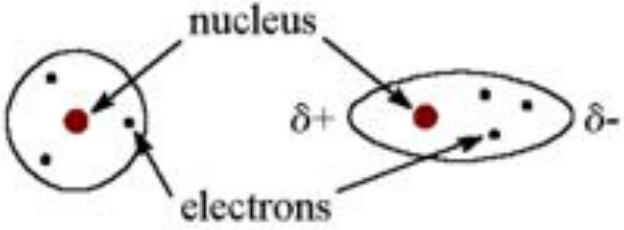
Runge-Gross (1984) → $\langle\psi[\rho](t)|\hat{o}|\psi[\rho](t)\rangle = O[\rho](t)$
Consequence: $A = \langle\psi[\rho]|(i\hbar(d/dt) - \hat{H})|\psi[\rho]\rangle = A[\rho]$

TD Kohn-Sham scheme (single particle eq.) →
$(T+V^{Nl}_{eff}[\rho^{I}_{GS}](t))\psi(t) = i\hbar(d/dt)\psi(t)$
where $V_{eff} = V_{ext} + V_H + V_{xc}$

RESPONSE FUNCTION
(gives dielectric funct., absorbance ...)

Optical properties: $\delta\rho(\mathbf{r},t) = \int \mathbf{dr'}dt'\, \chi(\mathbf{r},\mathbf{r'};t-t')V_{ext}(\mathbf{r'},t')$





$\rho(\mathbf{r},t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r},t)$

$\chi = \chi^{KS} + \chi^{KS}(v_{Coul} + f_{xc})\chi$, where $f_{xc}(\mathbf{r},\mathbf{r'},\omega) = dv_{xc}(\mathbf{r},\omega)/d\rho(\mathbf{r'},\omega)$

Local Density Adiabatic Approximation: $V_{xc}[\rho^{I}_{GS}](\mathbf{r},t) = V_{xc}(\rho^{I}_{GS}(\mathbf{r},t))$

applications

•Biological systems

GFP

•3-D

Diamond

•Liquids

water

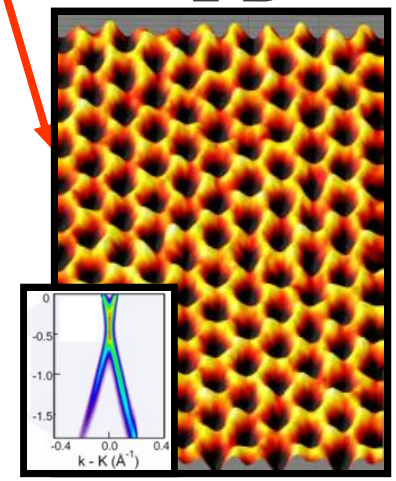
•0-D

•Nanoclusters

•1-D

Paper

•2-D



Graphene

and

Surfaces

Theoretical Method

DFT → ground state properties:
Geometry optimization

TDDFT → excited state properties:
Optical absorption spectrum

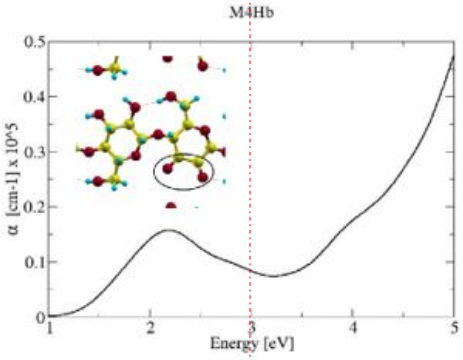
Details:

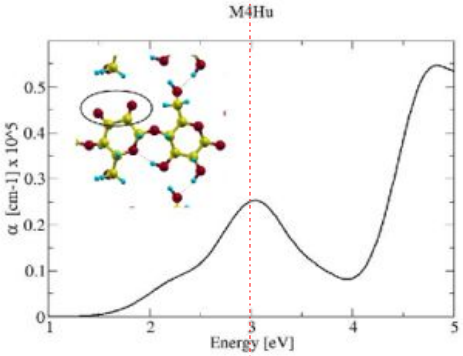
- Crystall paramenters from experiments (X-ray diffraction).
- Exchange-correlation functional used: BLYP.
- TDDFT: Casida algorithm

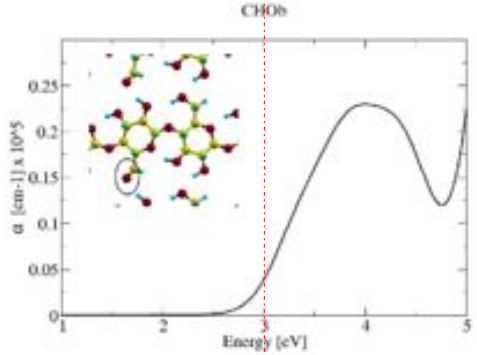
VisAG

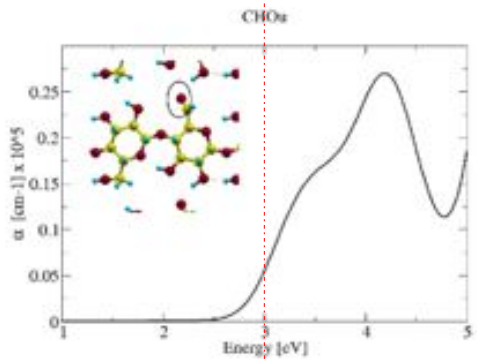
LUVAG

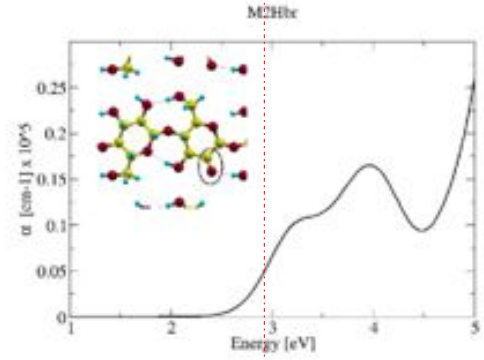
UVAG

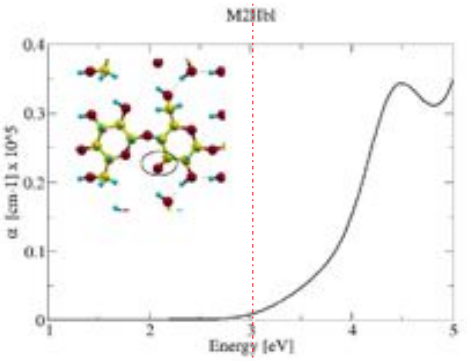


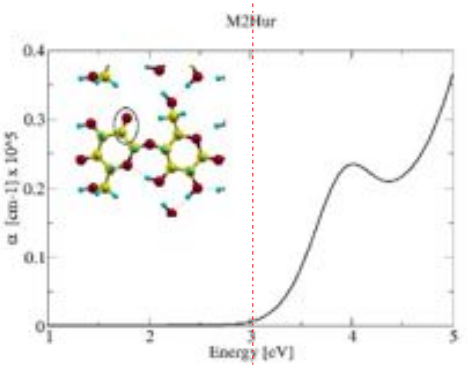


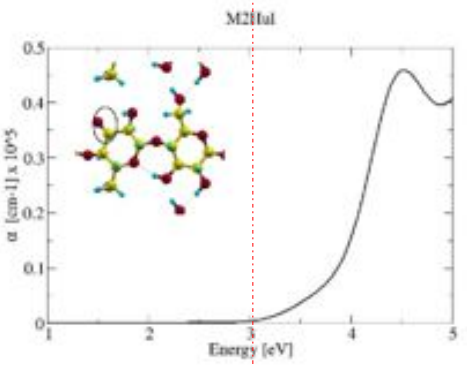


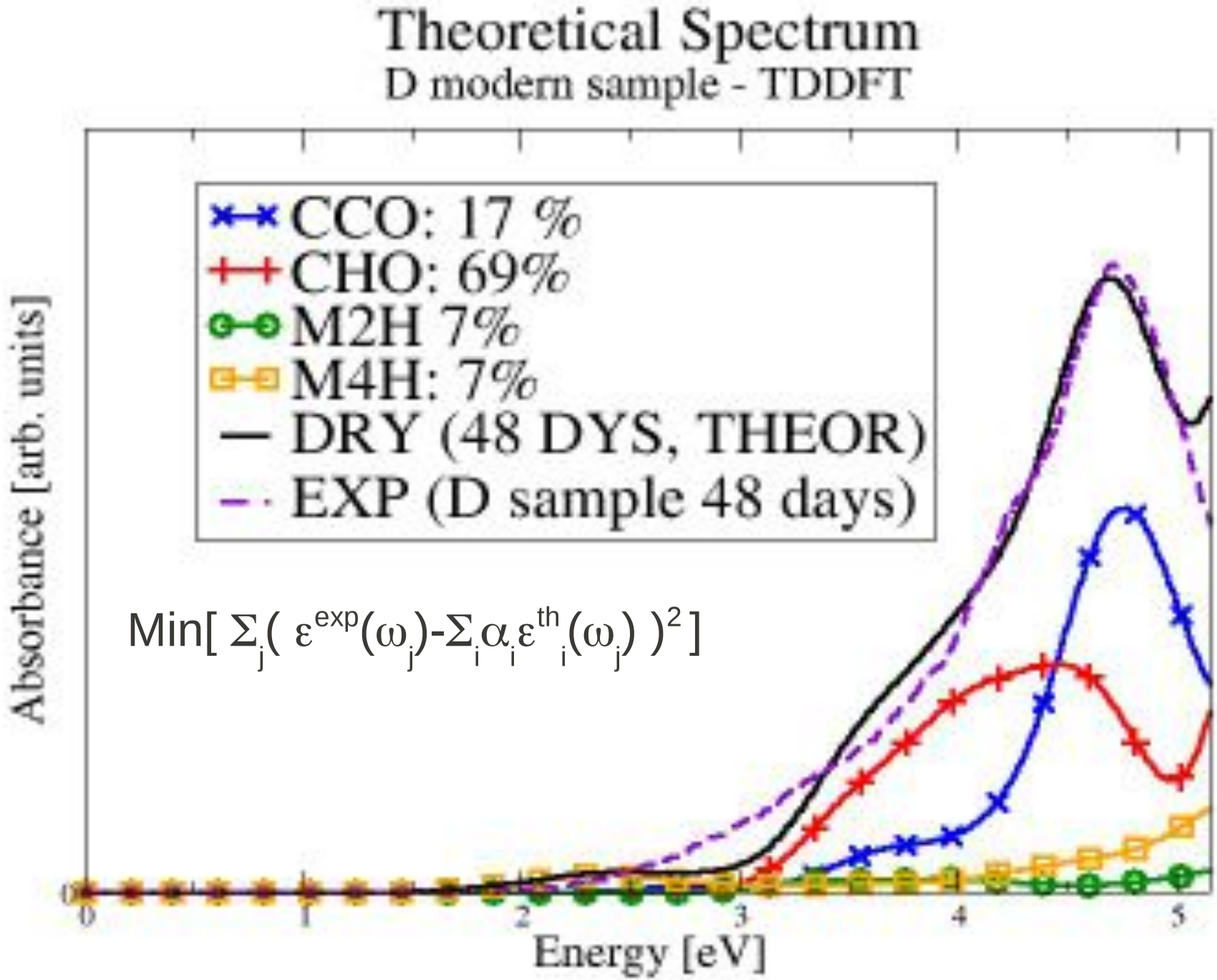


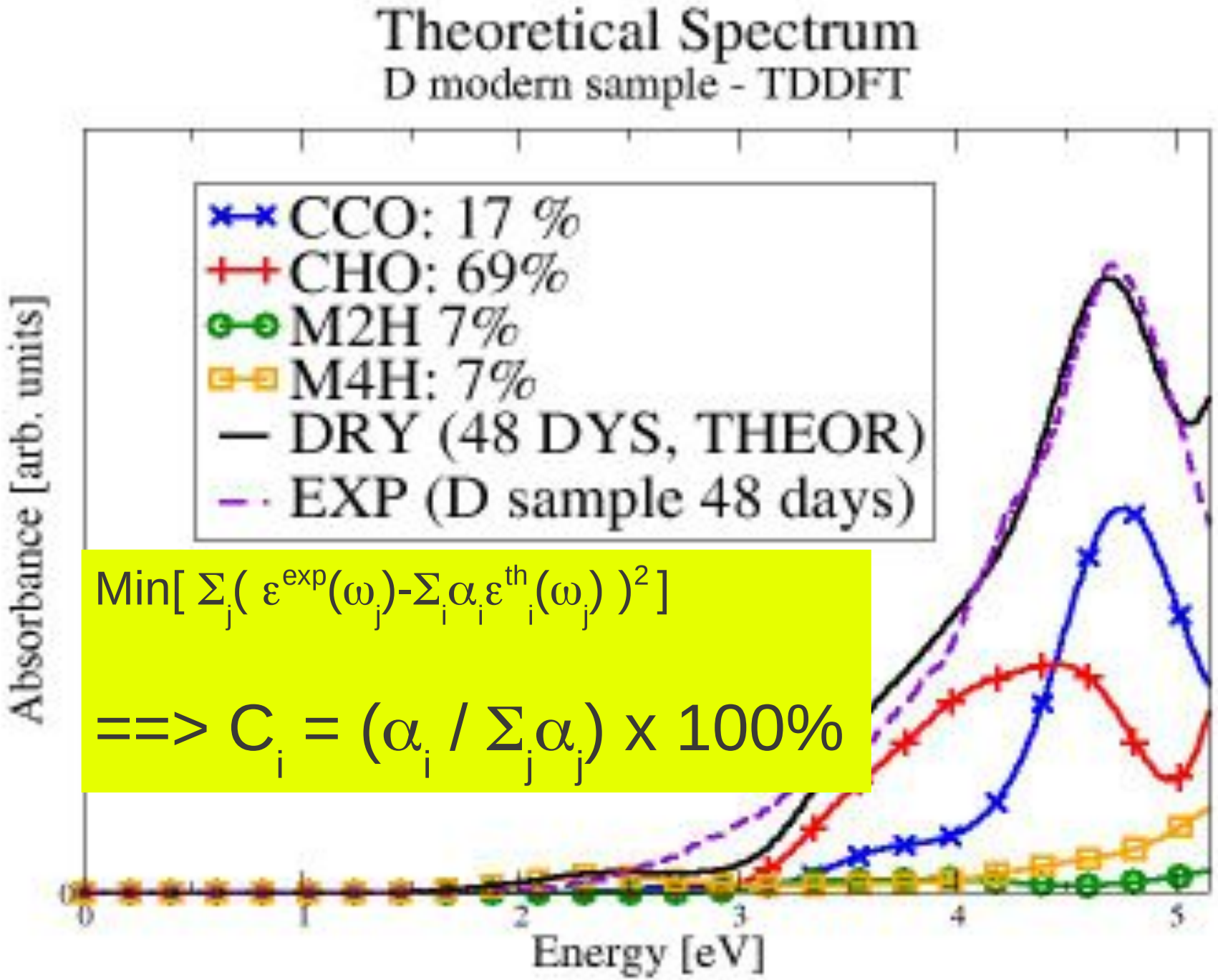









Theoretical Spectrum
D modern sample - TDDFT
CCO: 17 %
CHO: 69%
M2H 7%
M4H: 7%
DRY (48 DYS, THEOR)
EXP (D sample 48 days)
Min[Σj(ε^exp(ωj)-ΣiαiεthI(ωj))2]
Absorbance [arb. units]
Energy [eV]
0
1
2
3
4
5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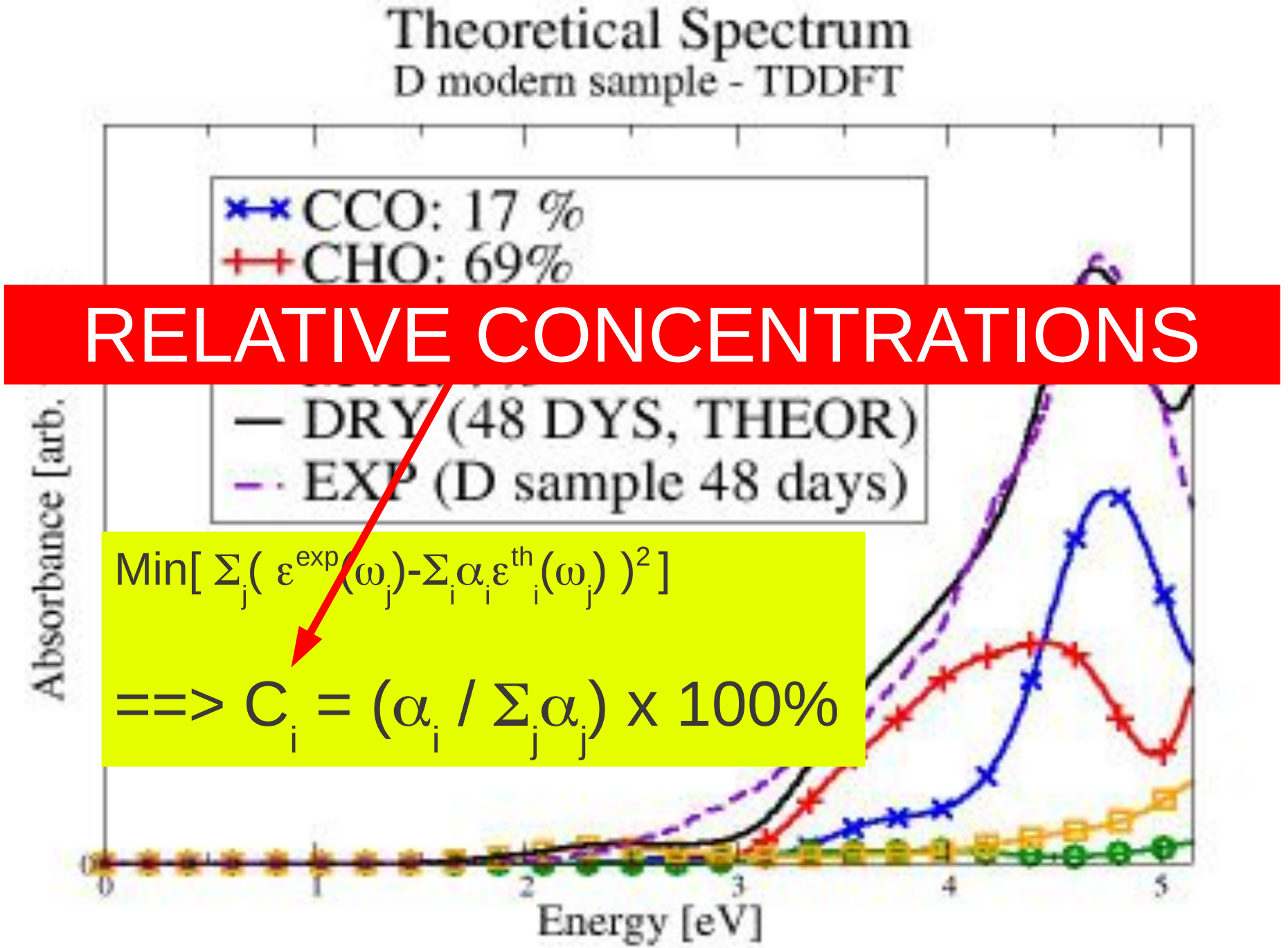
Absorbance [arb. units]
Energy [eV]
0
1
2
3
4
5
Min[Σj(ε^exp(ωj)-ΣiαiεthiωjΣ)^2]
==> Ci = (αi / Σjαj) x 100%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Absorbance [arb.
Energy [eV]
0
1
2
3
4
5
RELATIVE CONCENTRATIONS
Min[Σj(ε^exp(ωj)-ΣiαiεthI(ωj))^2]
==> Ci = (αi / Σjαj) x 100%

The theoretical spectrum is calculated with one oxidized group per cell.

Therefore the ratio between experimental and experimental absorbances is proportional to the ratio between moles of oxidized groups and moles of cellulose.

ABSOLUTE CONCENTRATIONS

$$\frac{n_{ox.gr.}}{g\ of\ cellulose} = \frac{A_{\exp}}{A_{theor} * 324\,g}$$

α [cm⁻¹]
0
100
200
300
1
2
3
4
5
ΔV [arb]
1.2
1.1
1


TOTAL MOLALITY
VisAG
UUVAG
UVAG
Pv
Pr1
Pr2
A1
A2
A3
D
C
V

CONCLUSIONS

- The state of oxidation has been quantified by our non-invasive and non-destructive method and could be applied again in the future to estimate the portrait oxidation rate.
- The portrait poor conditions could have been partially induced by conservation in closed and humid environment conditions.
- The analysis of modern samples showed that exposition to bad conditions could have effects also in the future.

PERSPECTIVES

- Improvement of the model to include the temperature effect and oxidized groups dynamics (Claudia Violante is working on it)

ACKNOWLEDGEMENTS

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http://www.etsf.eu

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