Transient Optical Phenomena Related to Point Defects in Pure and Doped Silica

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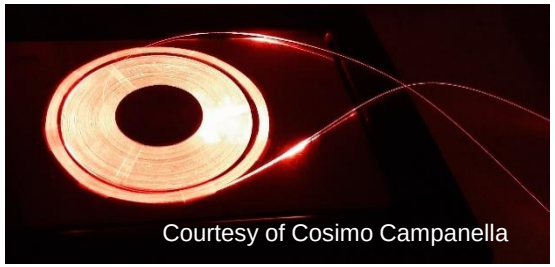
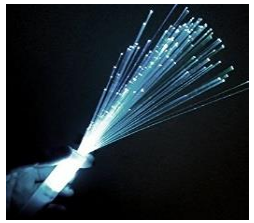
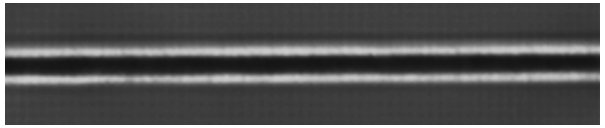
Outline

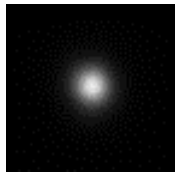
- Introduction
  - Amorphous silica
  - Point defects
- Transient absorption spectroscopy
- The NonBridging Oxygen Hole Center (NBOHC)
  - Experimental results
  - NBOHC photocycle
- The GLPC: work in progress
- Conclusions

Amorphous silica remains a key material for a wide range of technologies thanks to its unique optical and structural properties









Pure or doped silica glasses have:

- good **transmission properties** in a wide spectral range
- high **mechanical strength**, **radiation tolerance**
- possibility to **modify its optical properties** **by varying the dopants or through the laser micromachining**

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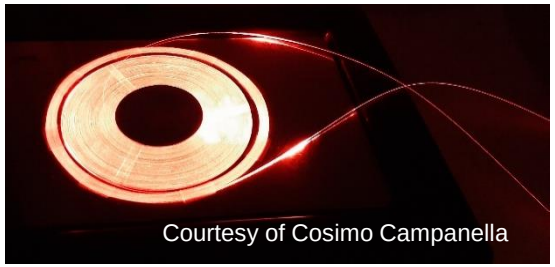
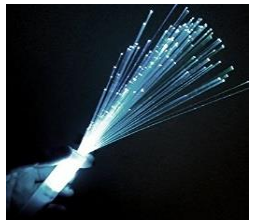
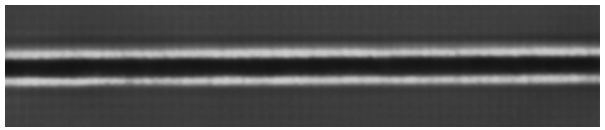
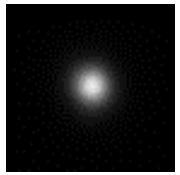
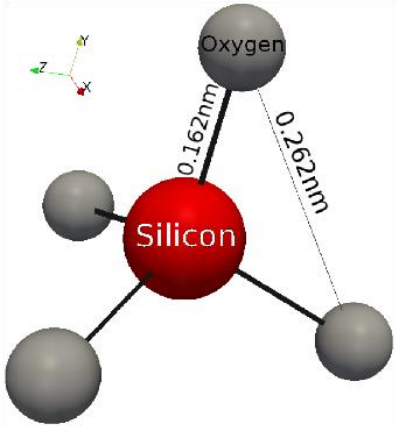








Silica structural unit shape



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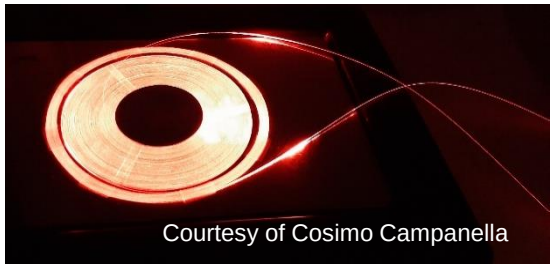

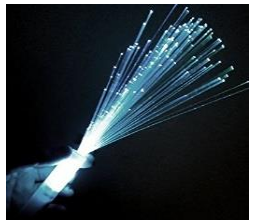

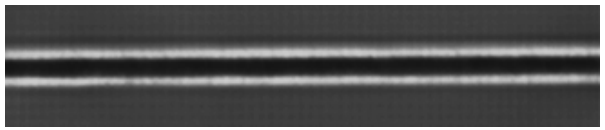

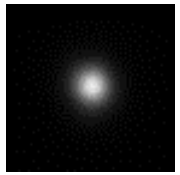

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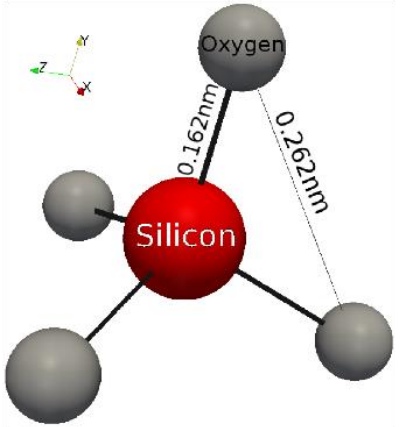

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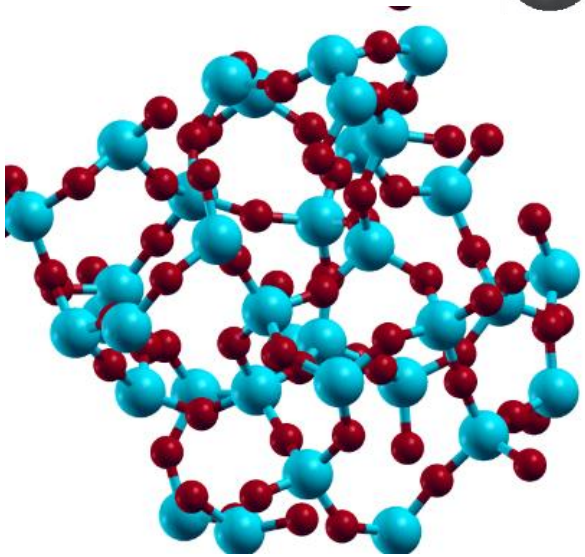
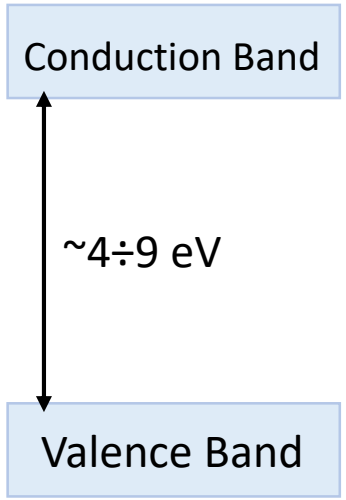


3D silica network: in blue Si atoms and in red O atoms

Transparent materials (wide bandgap materials) do not absorb visible light: good transmission properties



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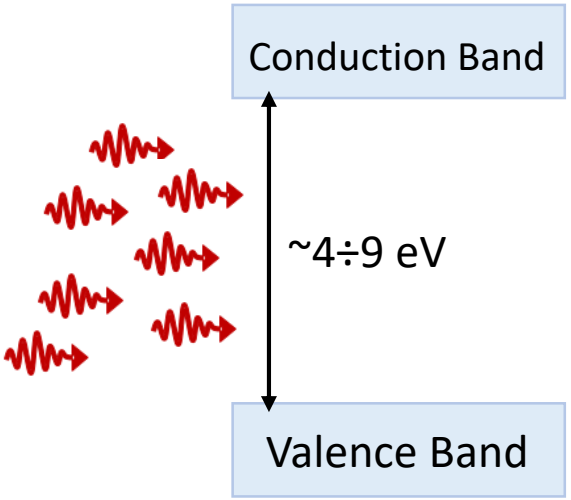

Visible light
1.5 eV ≲ Energy ≲ 3 eV

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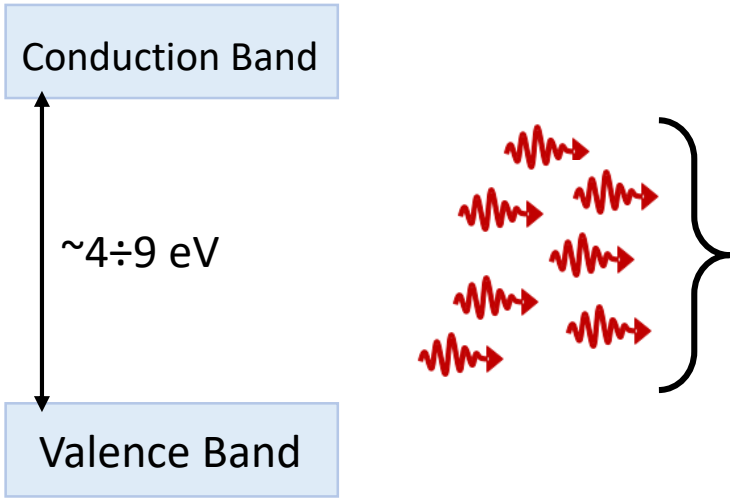

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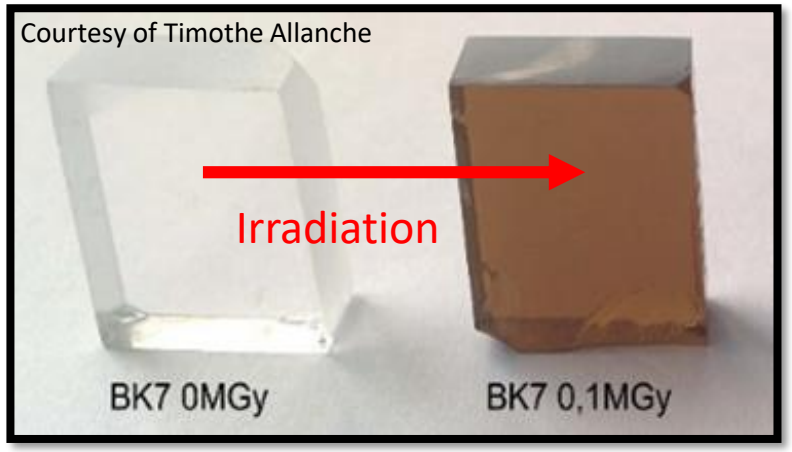
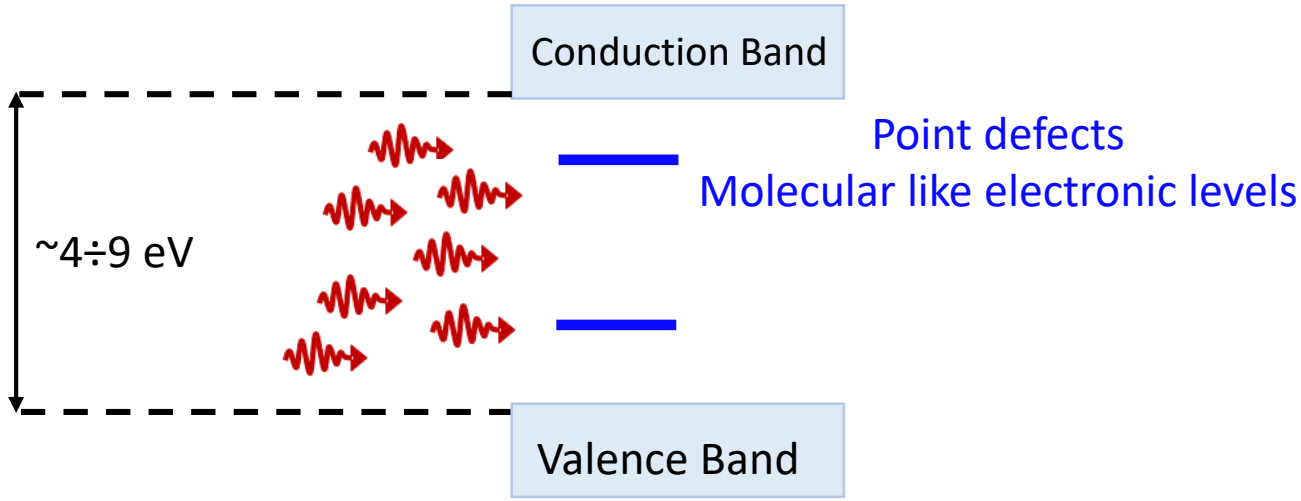
Ionizing irradiation lead to the generation of point defects: appearance of molecular like electronic levels





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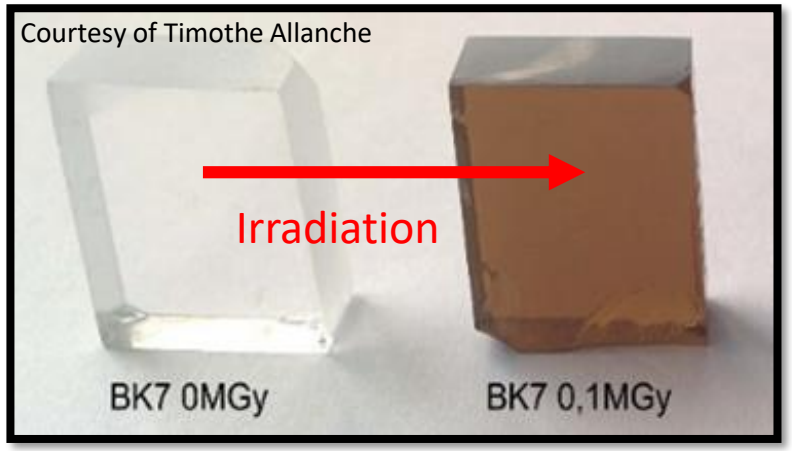

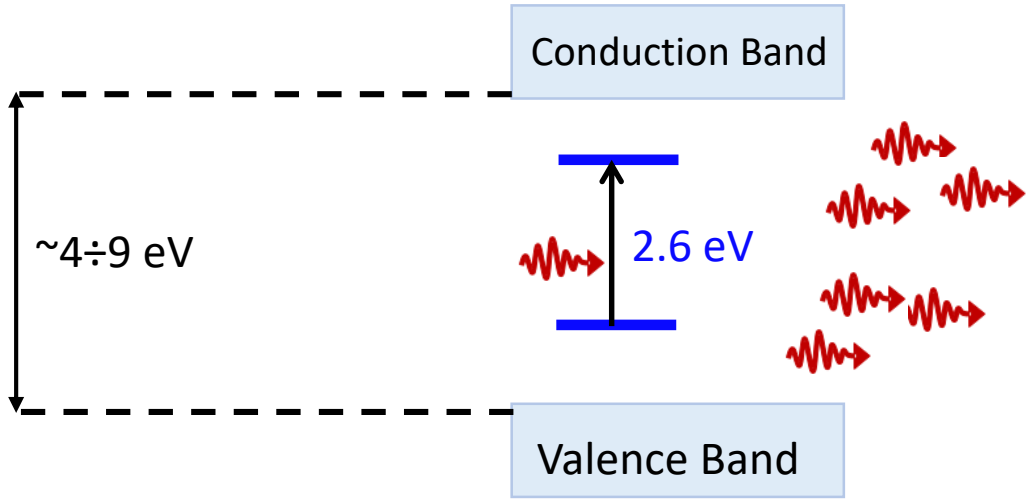

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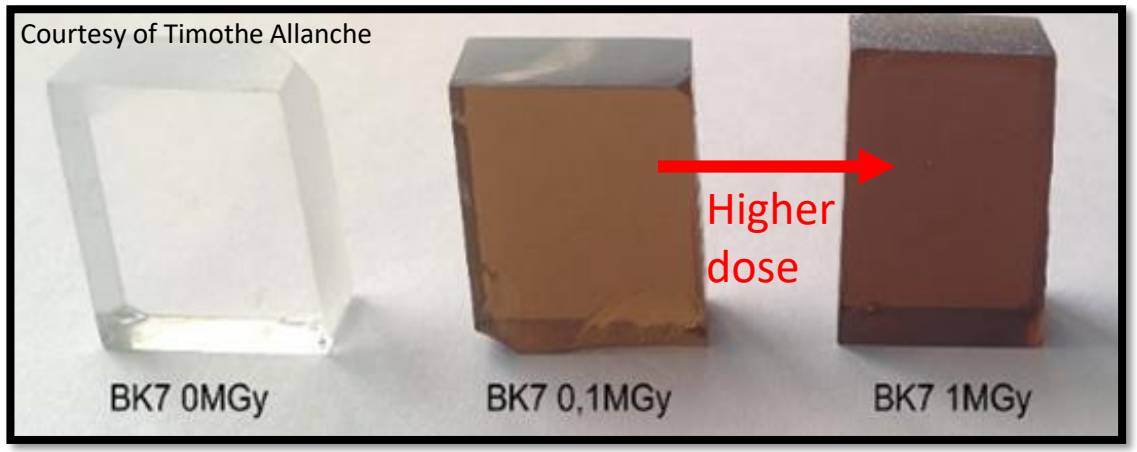

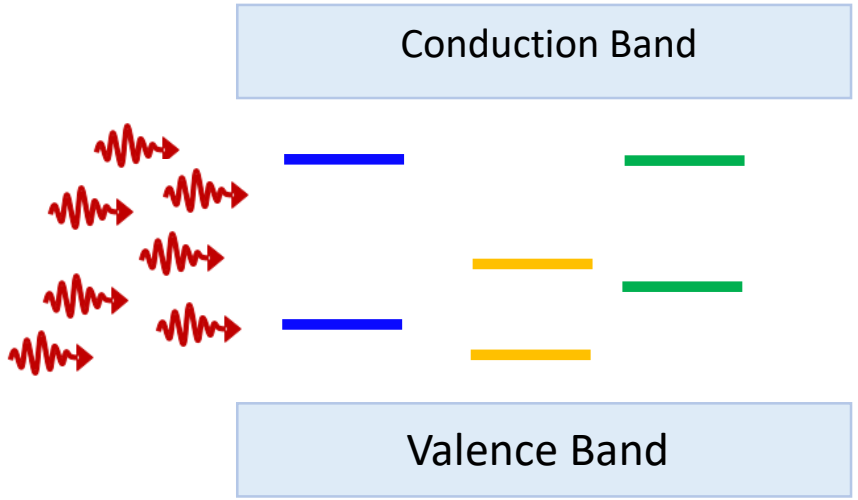

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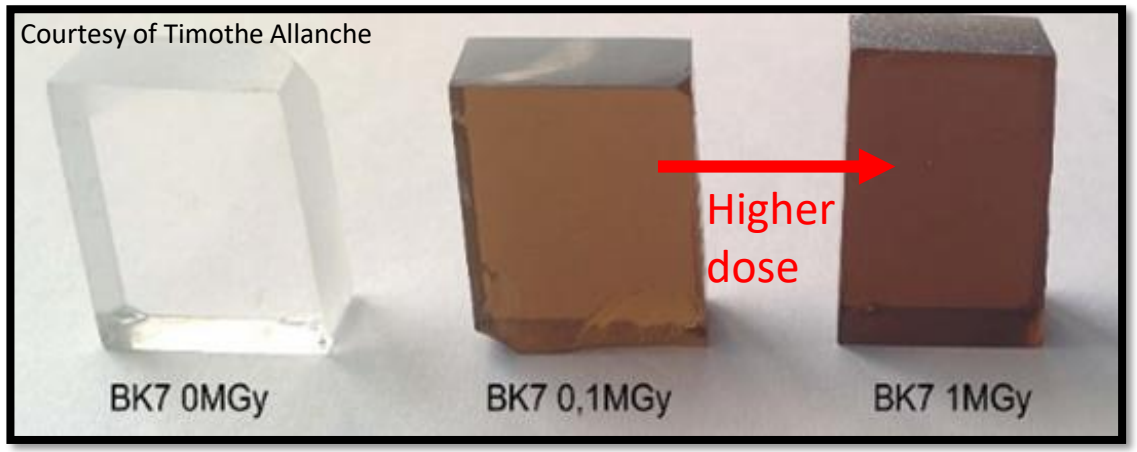

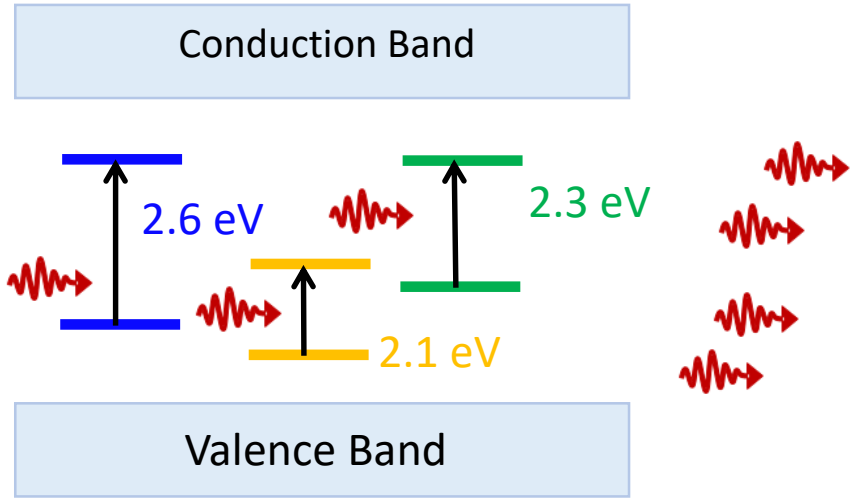

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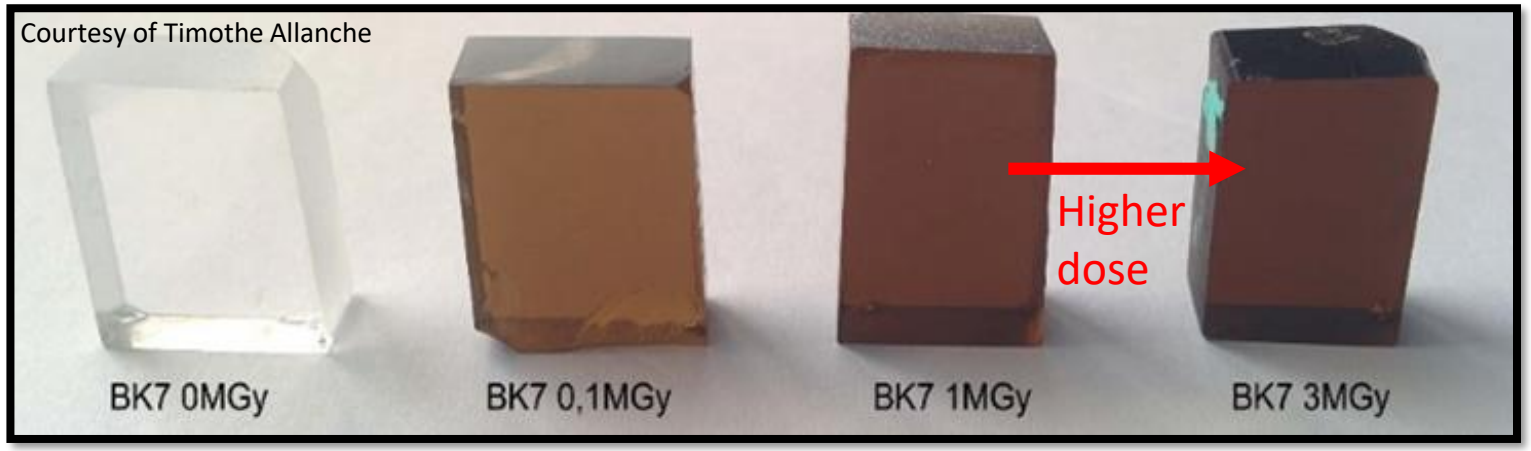

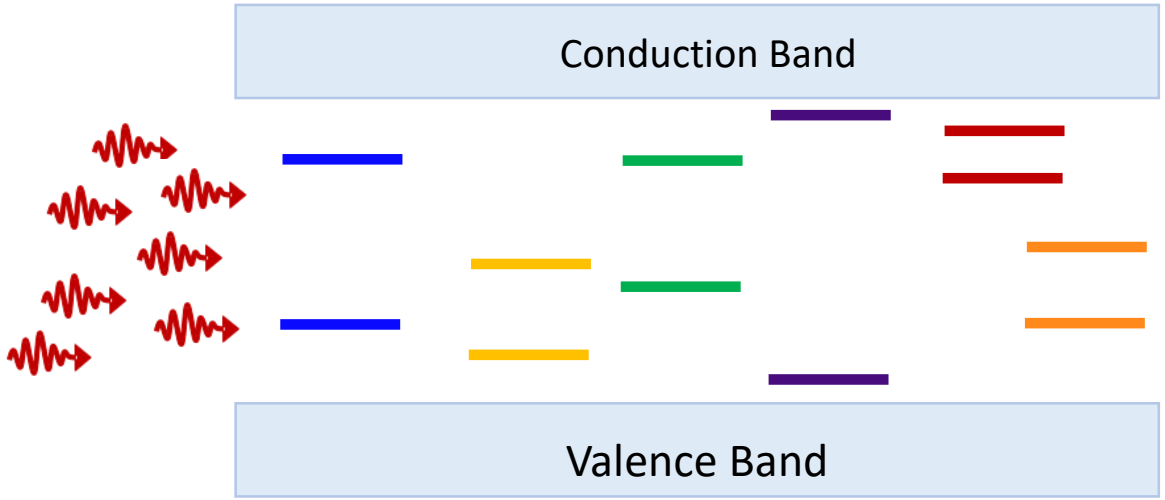

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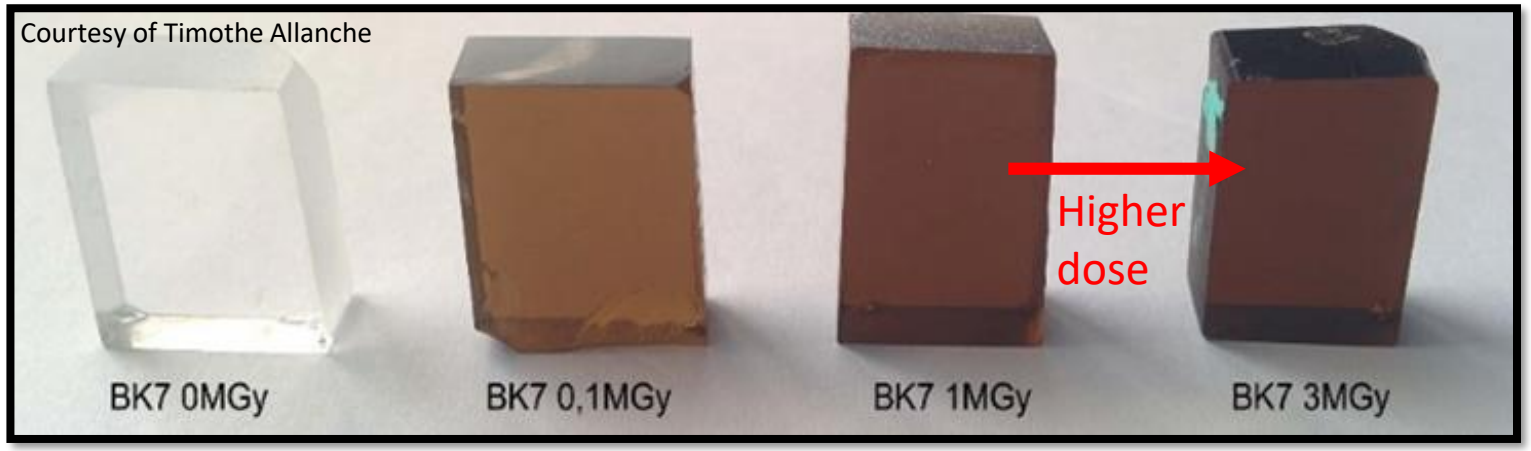
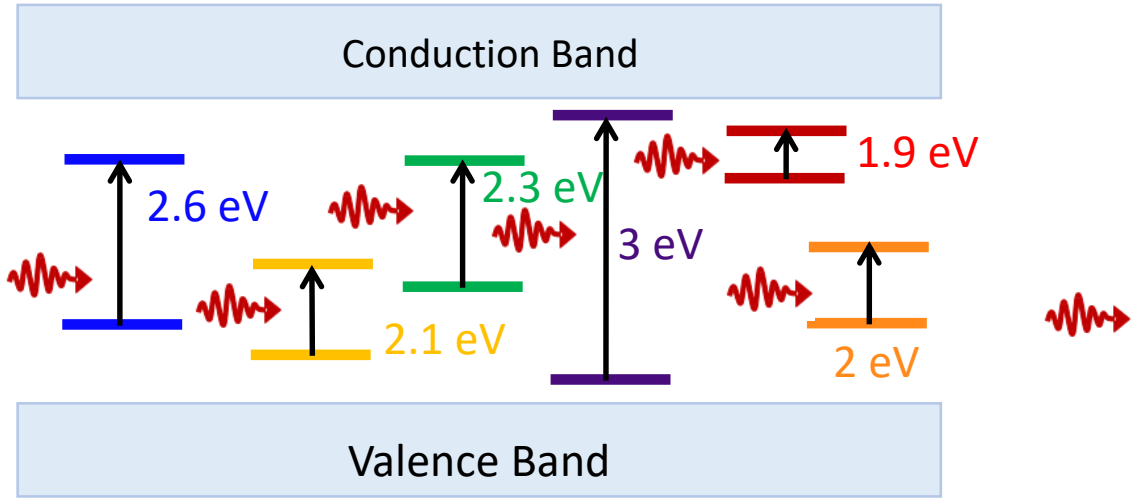
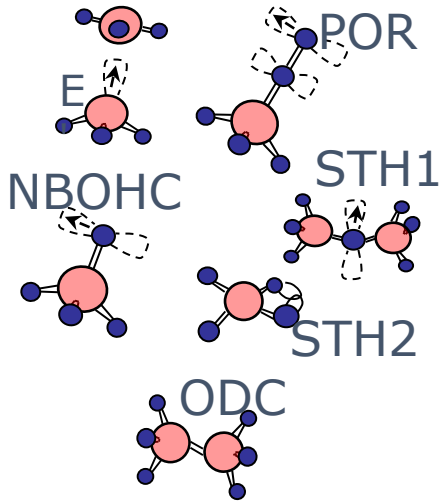




The macroscopic optical properties of silica are explained and can be controlled, by point defects either created during manufacturing or under radiation



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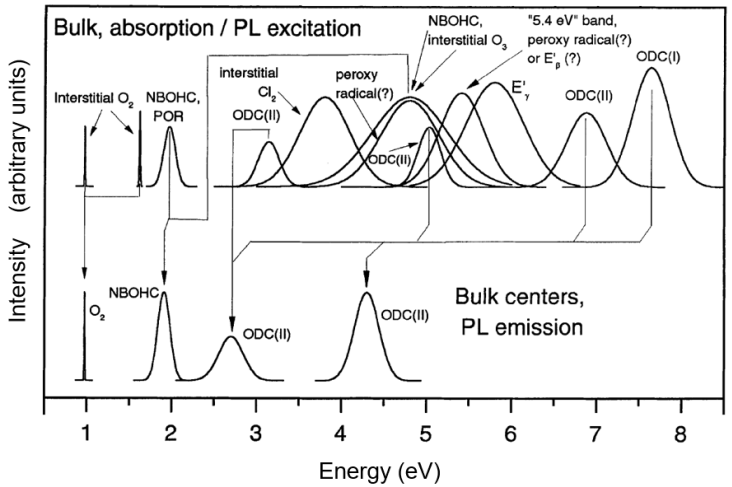
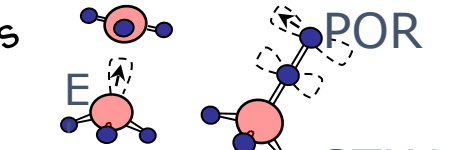
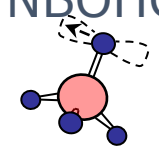
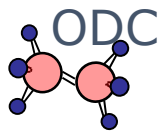


Optical properties







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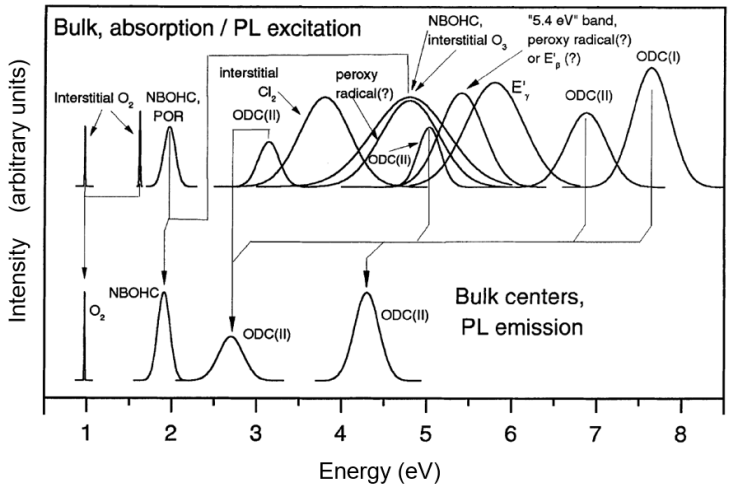

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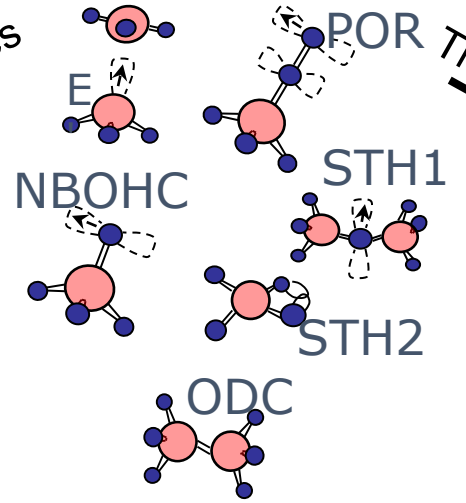
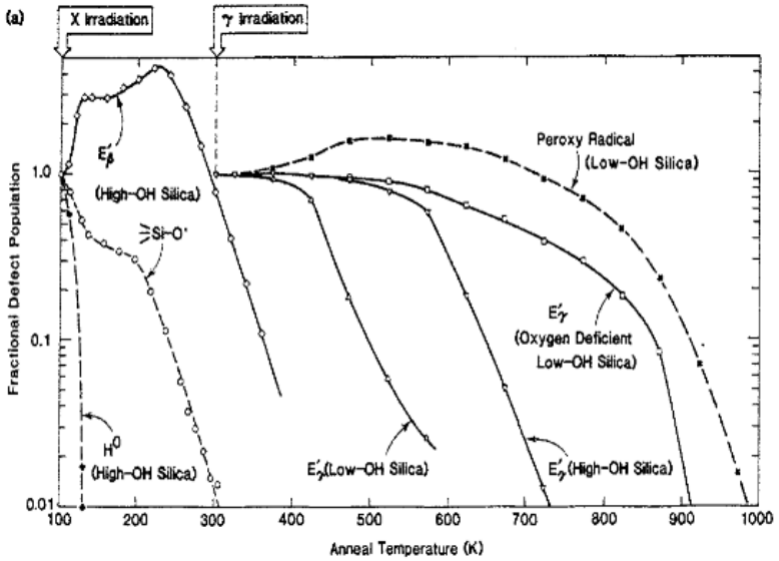


Thermal stability

D.L. Griscom SPIE vol. 541, 1985



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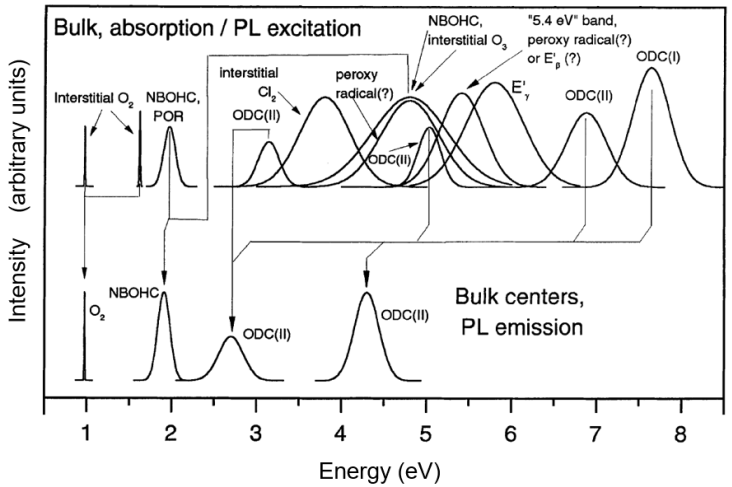

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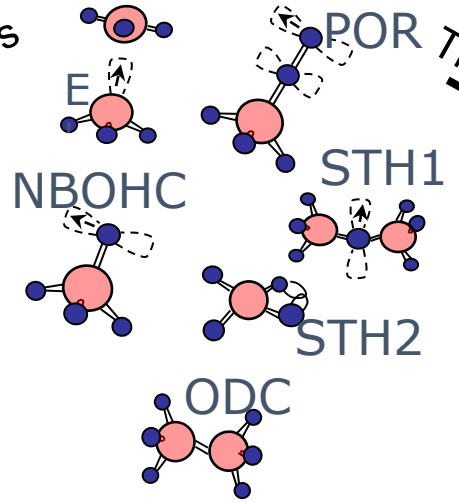

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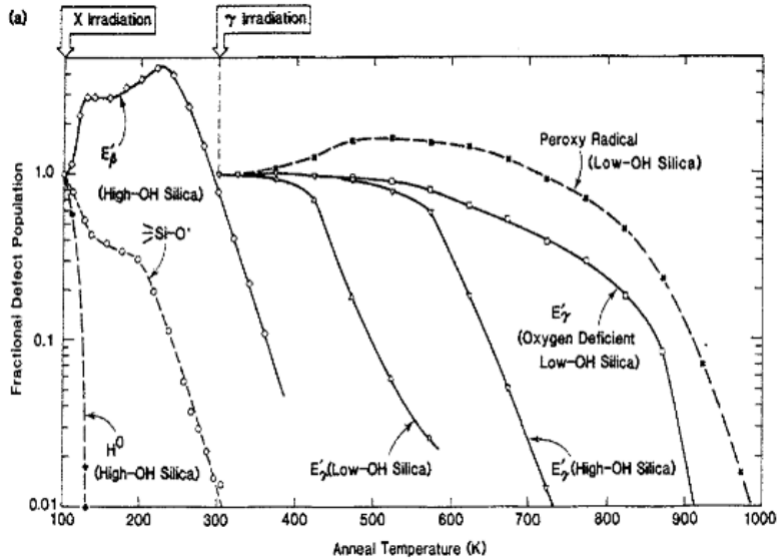

Transient optical phenomena related to point defects:

- **Unstable defects** at RT, those defects can only be studied online, not with post mortem techniques
- **Collective reorganization**
- **Defect dynamics** studied with ultrafast spectroscopic techniques

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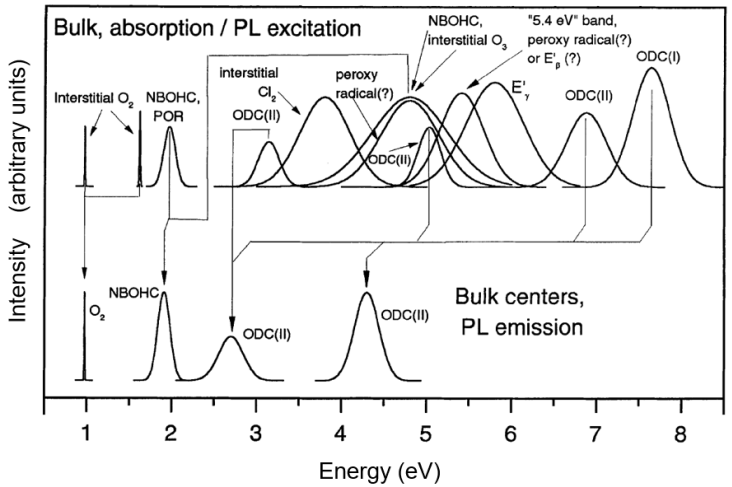

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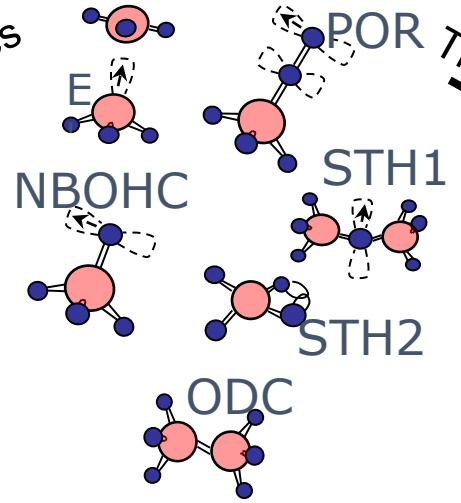

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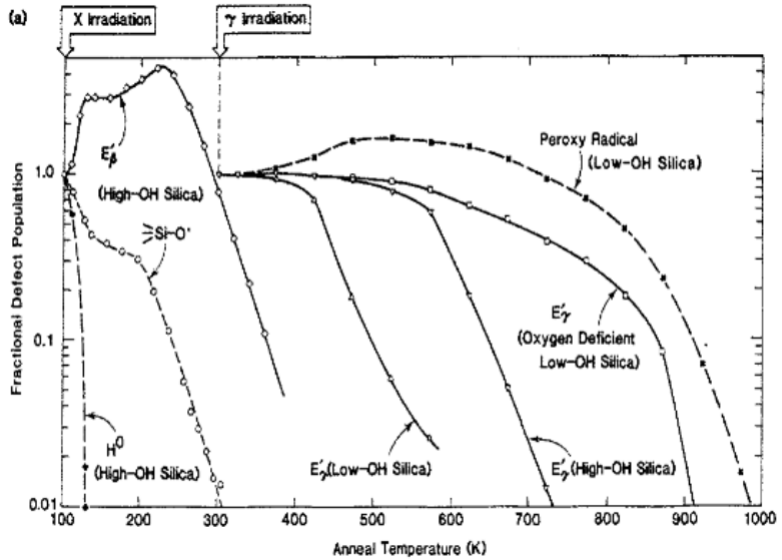

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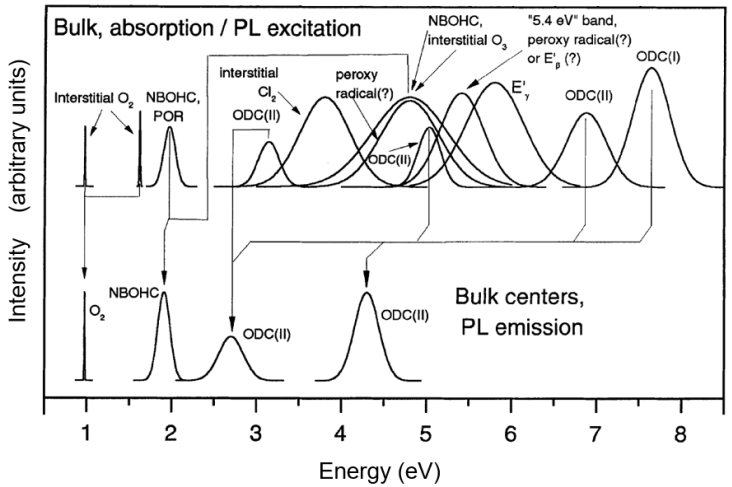

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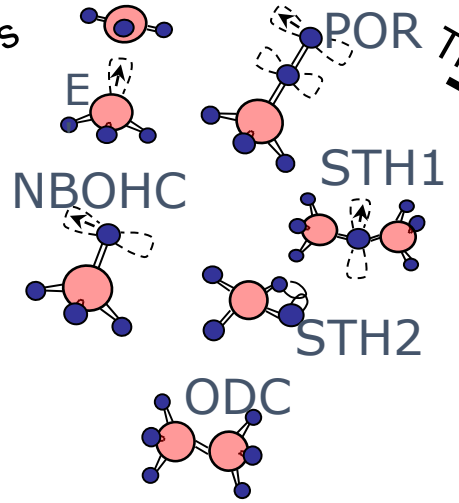

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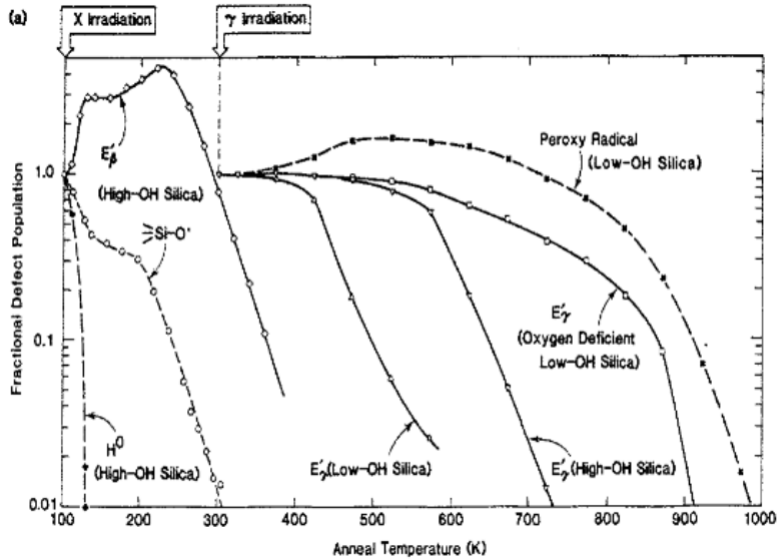

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- **Unstable defects** at RT, those defects can only be studied online, not with post mortem techniques
- **Collective reorganization**
- **Defect dynamics** studied with ultrafast spectroscopic techniques → **Transient absorption Spectroscopy**

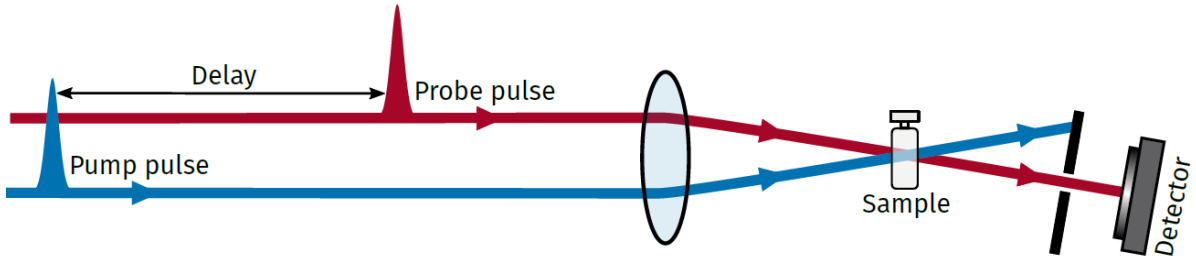
Why is it important to study the point defects properties?

- Point defects **degrade the transmission** properties of photonics devices: absorption/emission of light;
- Point defects can be used as the **base for new technologies**: control on the optical properties;
- Point defects can be **probe for fundamental phenomena**: sensible to the surrounding matrix.

The big problem to study the point defects photocycle

Transparent systems are crowded: characterized by the **simultaneous presence** of different color centers with overlapping absorption and luminescence bands

The transient absorption spectrum originates from the difference between the transmitted light of the excited sample and the one of the sample at the ground state



Transient absorption signal:

$$TA \sim -\frac{1}{2.303}\frac{I_p - I_{up}}{I_{up}}$$

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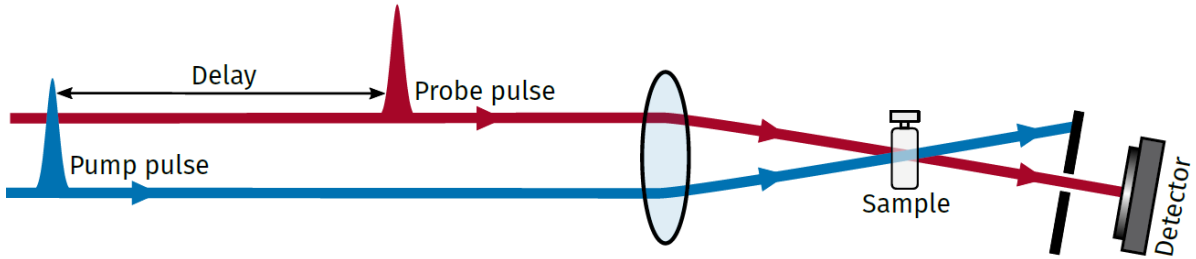

Ground state bleaching (GSB) → Negative signal

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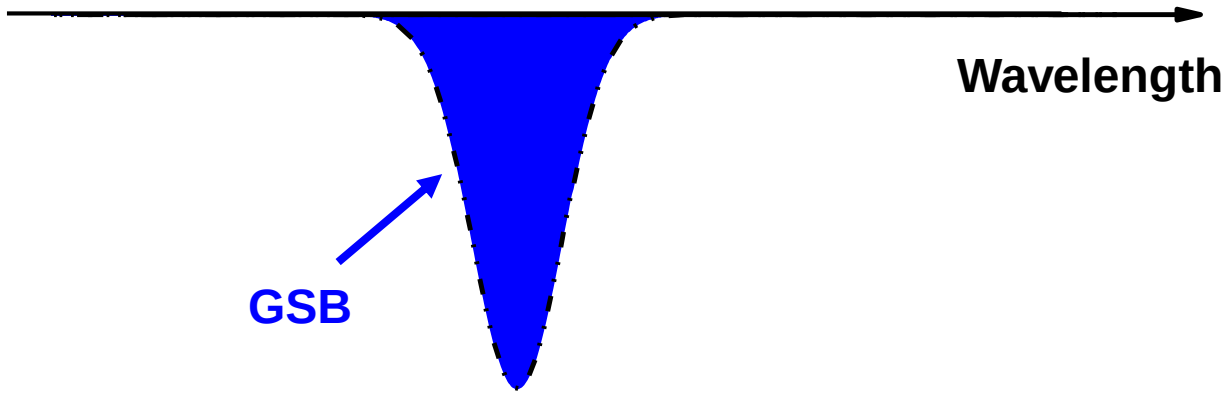

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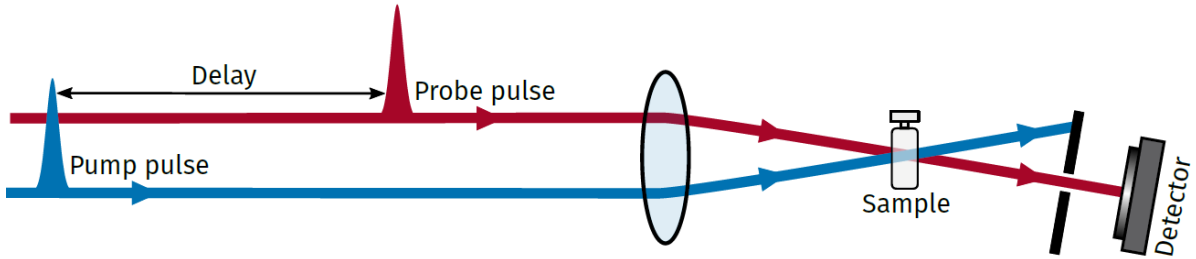

Ground state bleaching (GSB) → Negative signal

Stimulated emission (SE) → Negative signal

Transient absorption signal:

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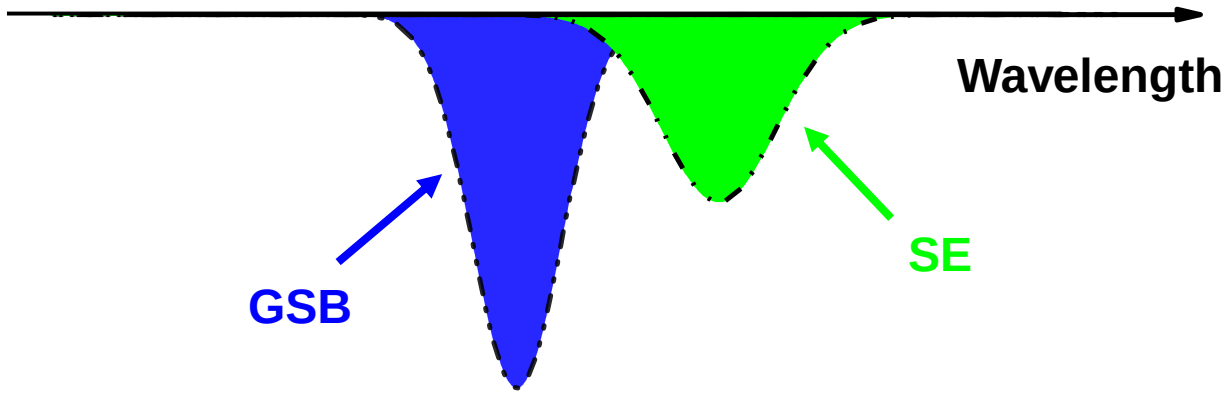
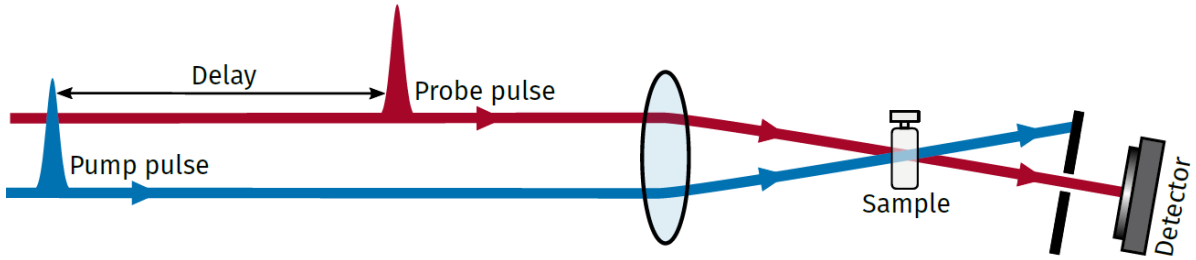


The transient absorption spectrum originates from the difference between the transmitted light of the excited sample and the one of the sample at the ground state



Ground state bleaching (GSB) → Negative signal

Stimulated emission (SE) → Negative signal

Excited state absorption (ESA) → Positive signal

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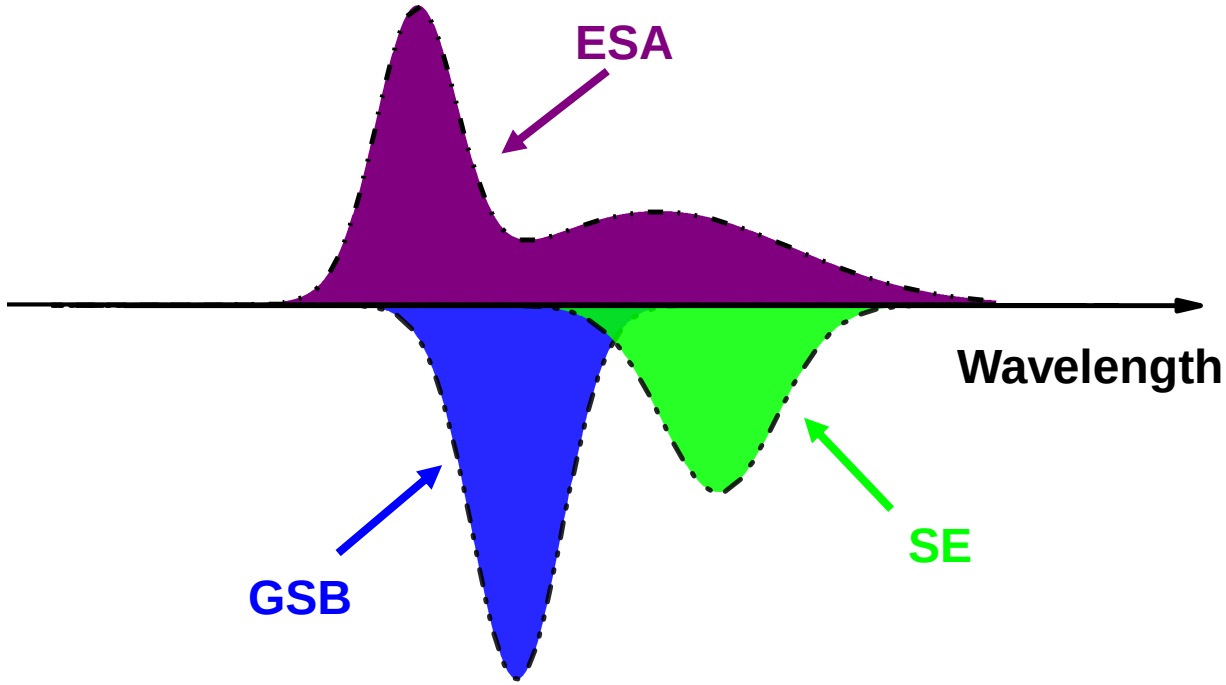

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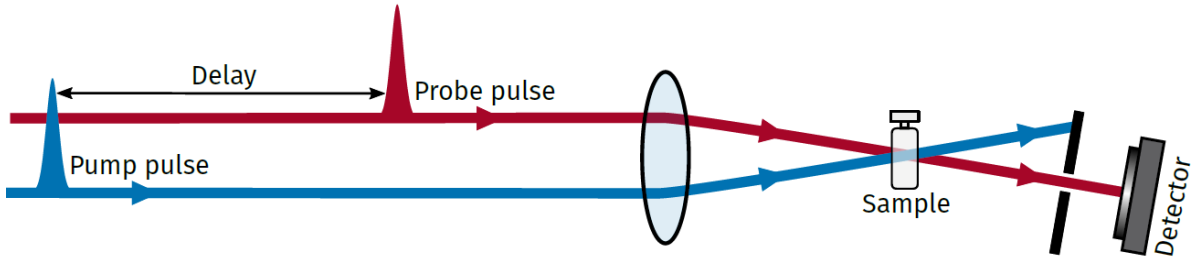

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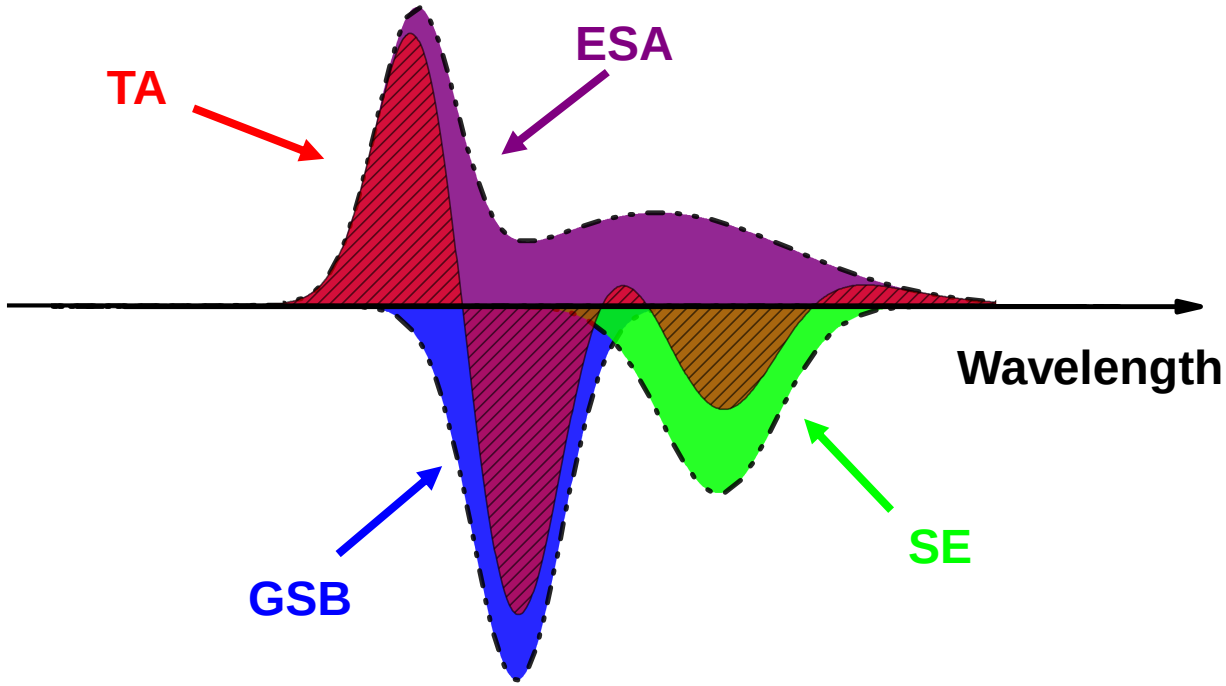
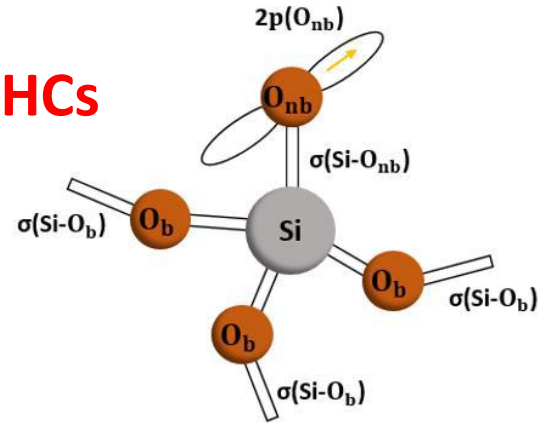


With this technique, we propose an experimental approach to study the excitation/relaxation dynamics of point defects upon UV excitation

NBOHCs



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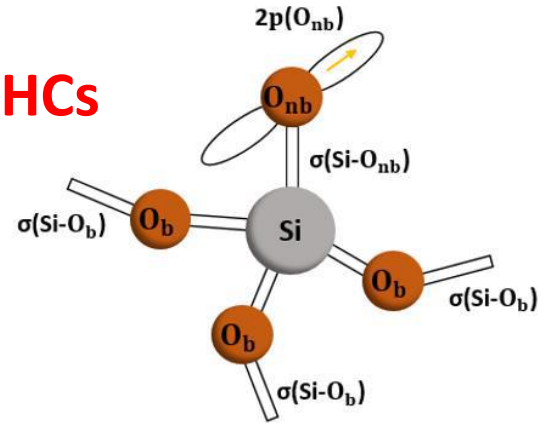

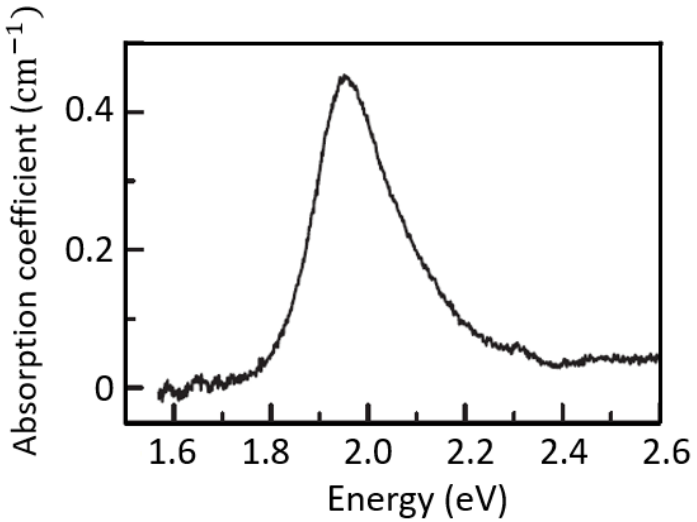

- An **asymmetric absorption band** peaked at 2.0 eV

L. Skuja et al., Phys. Rev. B (2011).

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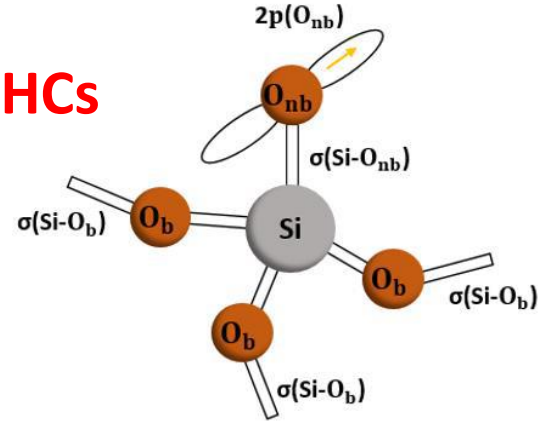

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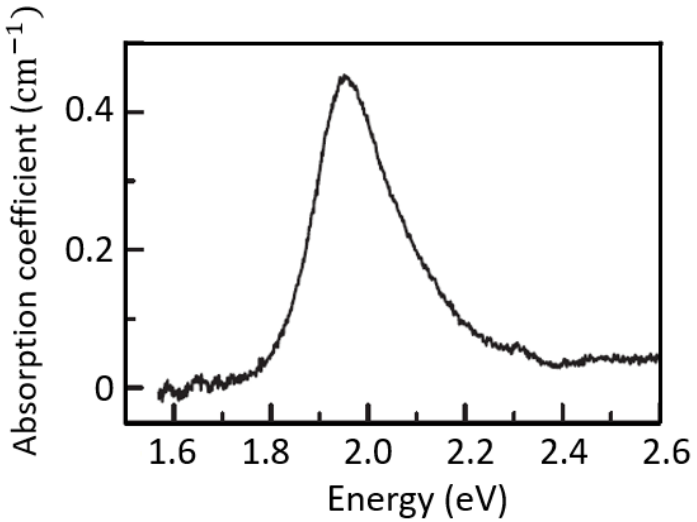
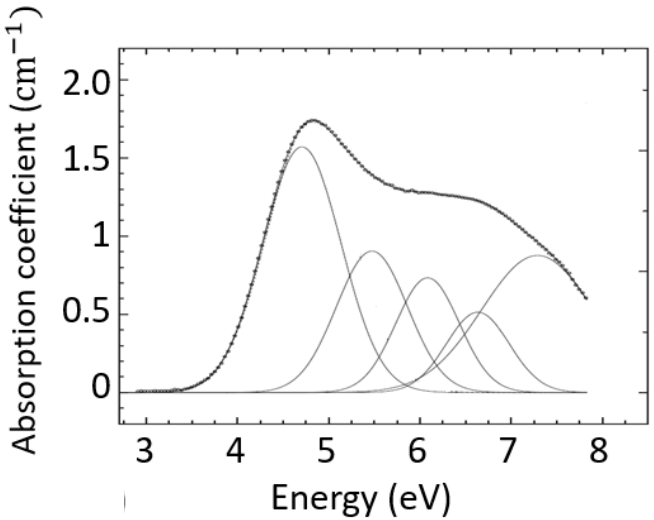
- **Wide and intense absorption bands** in the UV, from 4.8 eV to 7.5 eV





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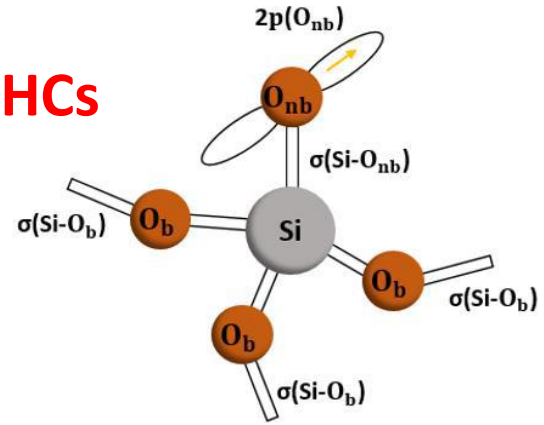

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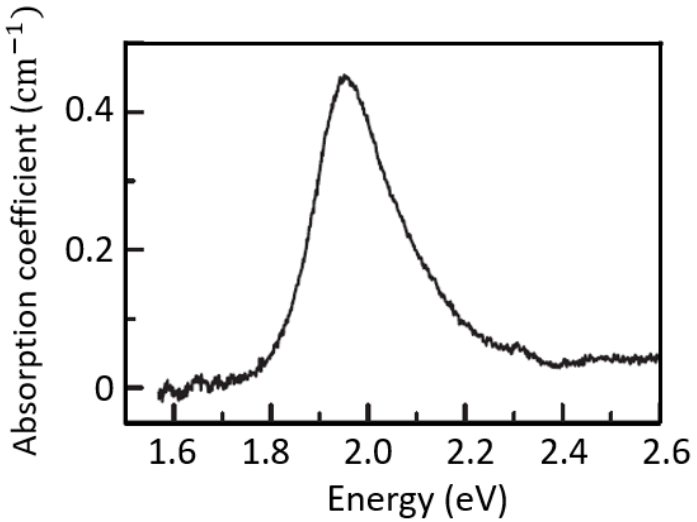
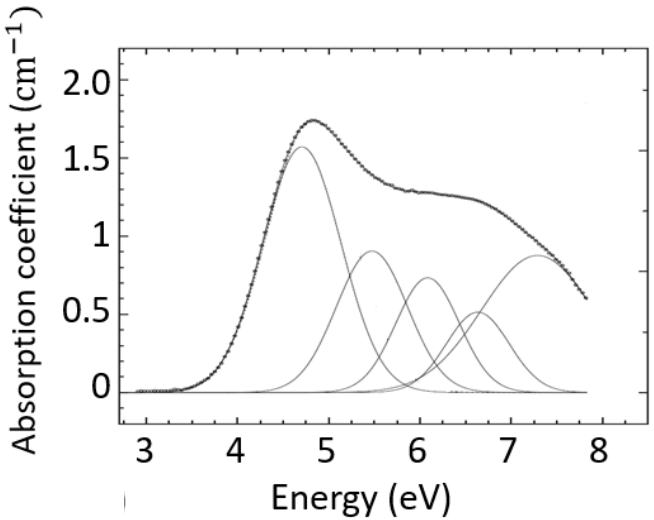
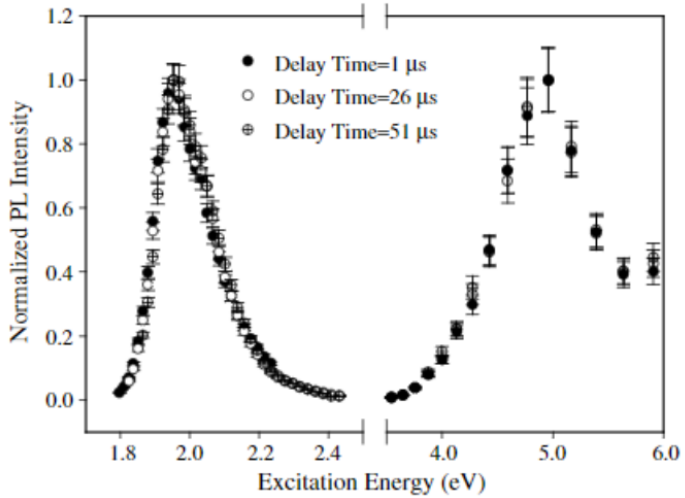
- **PL 1.9 eV excited upon the UV and 2 eV absorption bands**, with a lifetime between 15÷20 μs







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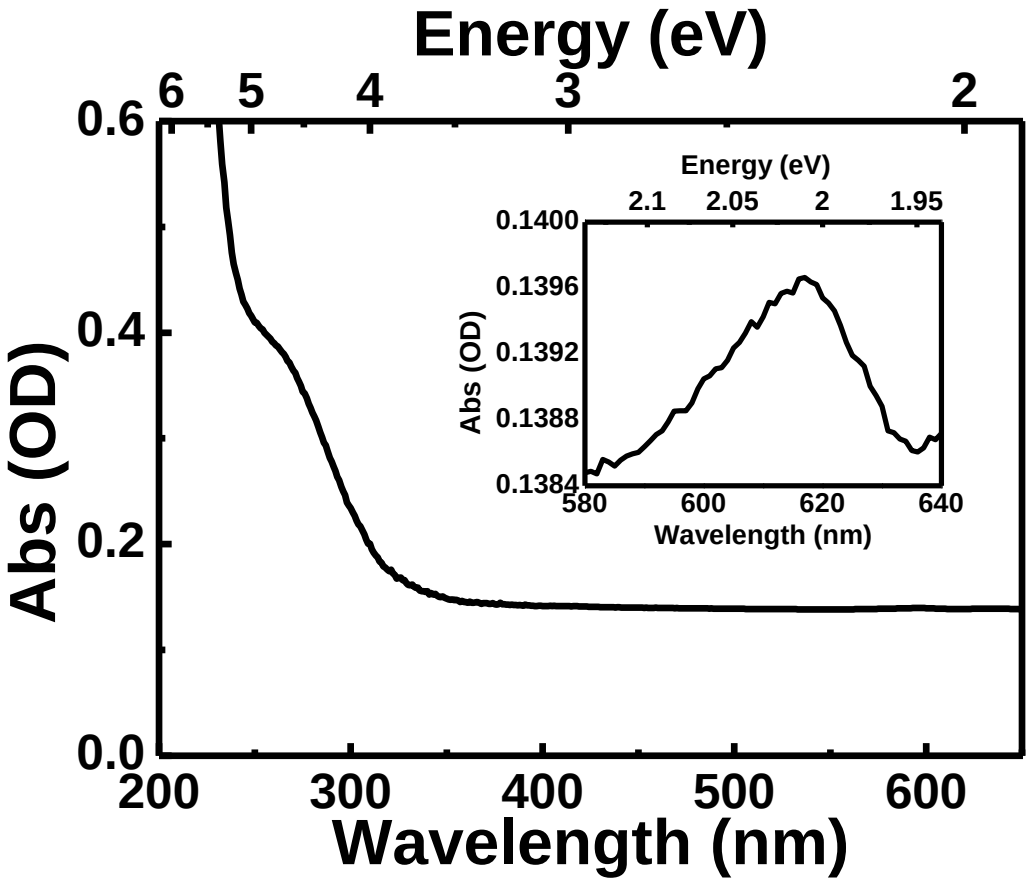
M. Cannas et al., NIMPR (2008).

β-irradiated synthetic wet silica sample



- **NBOHCs** are induced by **β-irradiation** at the dose of 5×10^9 Gy(SiO_2)

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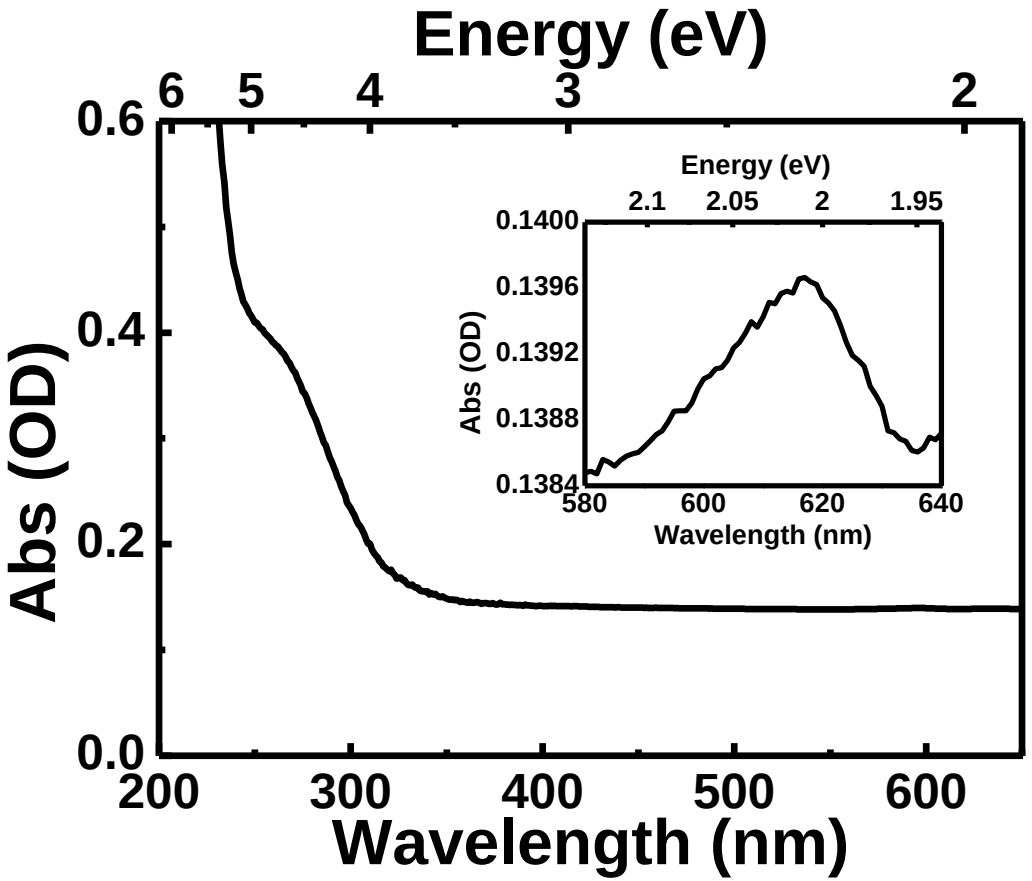

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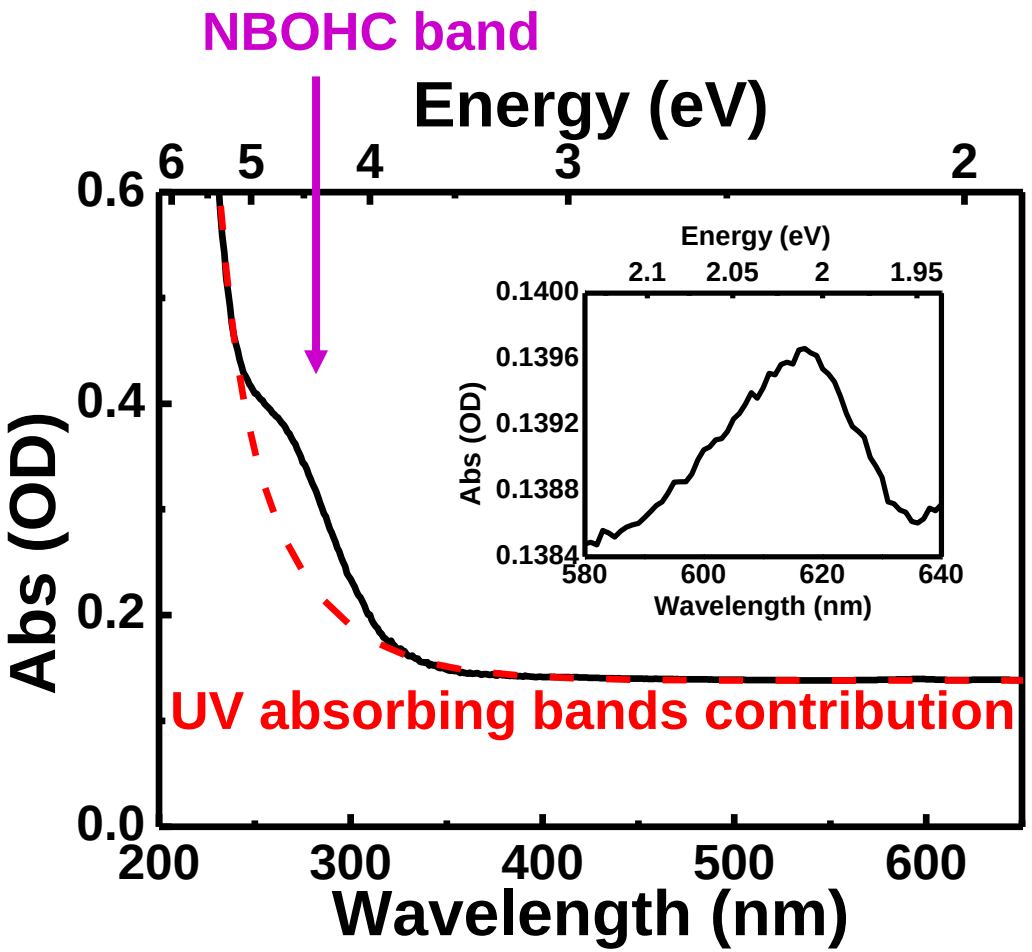

- **NBOHCs** are induced by **β-irradiation** at the dose of 5×10^9 Gy(SiO_2)
- NBOHC **concentration** around $\sim 3.2 \times 10^{18} \mathrm{cm}^{-3}$
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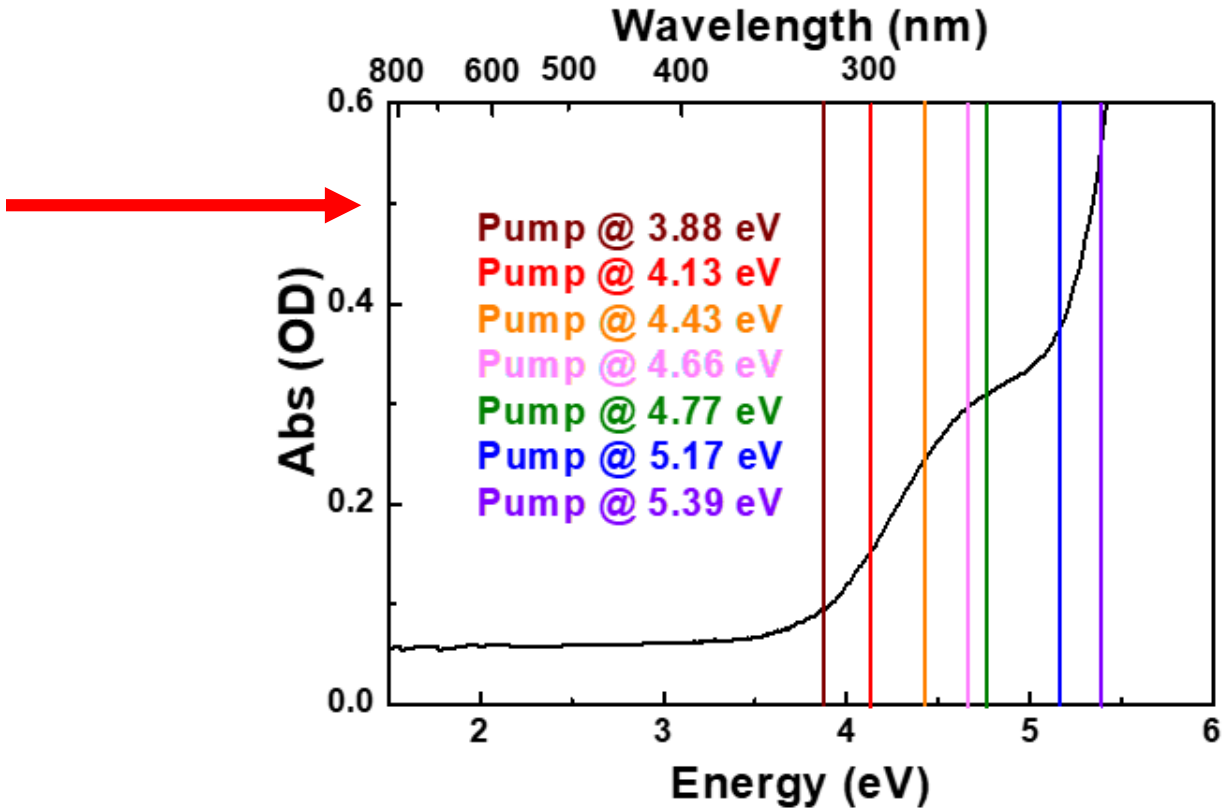
Our approach: transient absorption measurements as a function of the pumping wavelength

- The chosen **excitation wavelengths** match the sample **absorption band**



De Michele et al., Opt. Lett. (2021)

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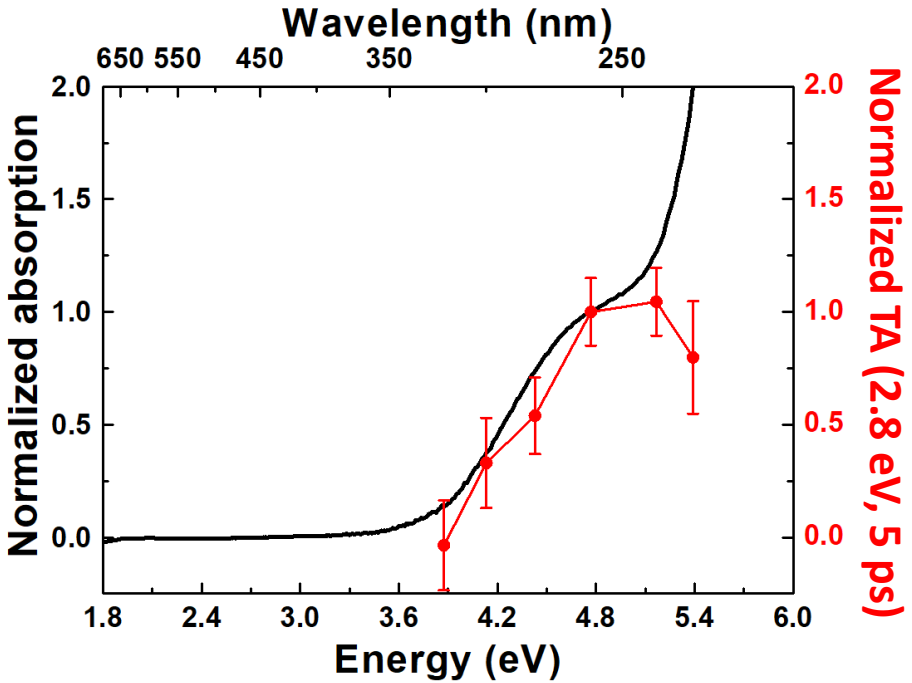

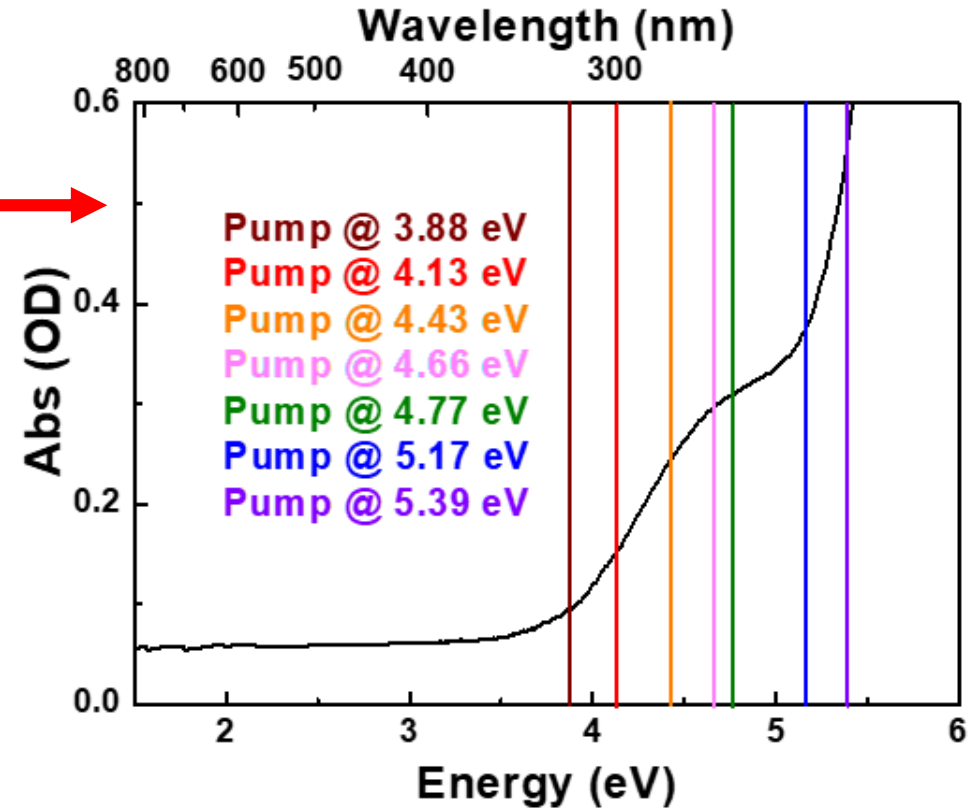

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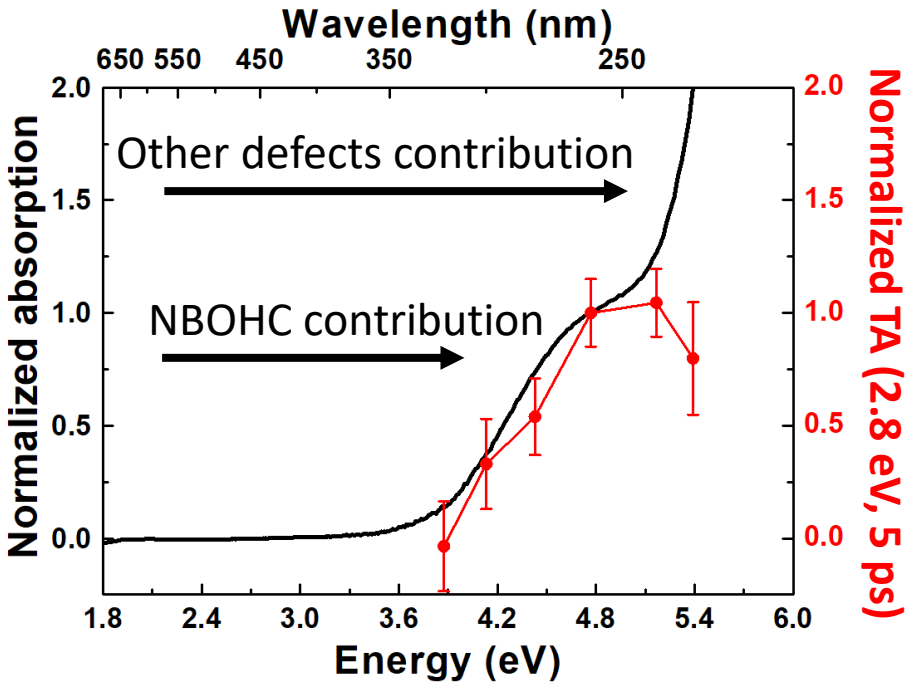

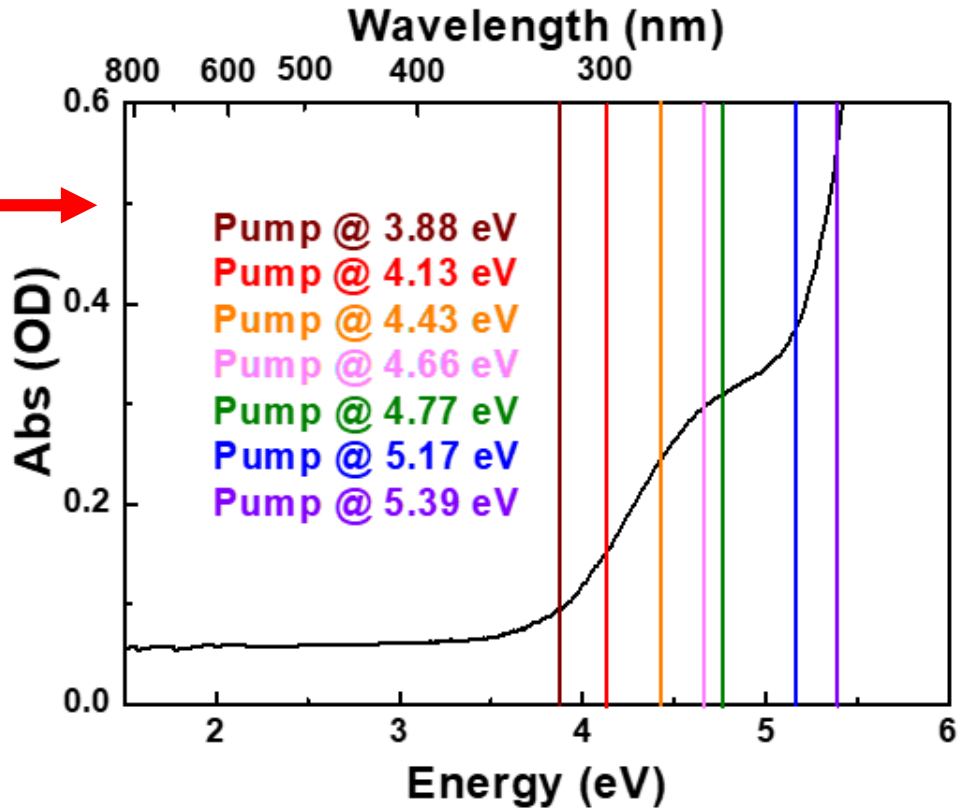

De Michele et al., Opt. Lett. (2021)

Our approach: transient absorption measurements as a function of the pumping wavelength and in linear absorption conditions

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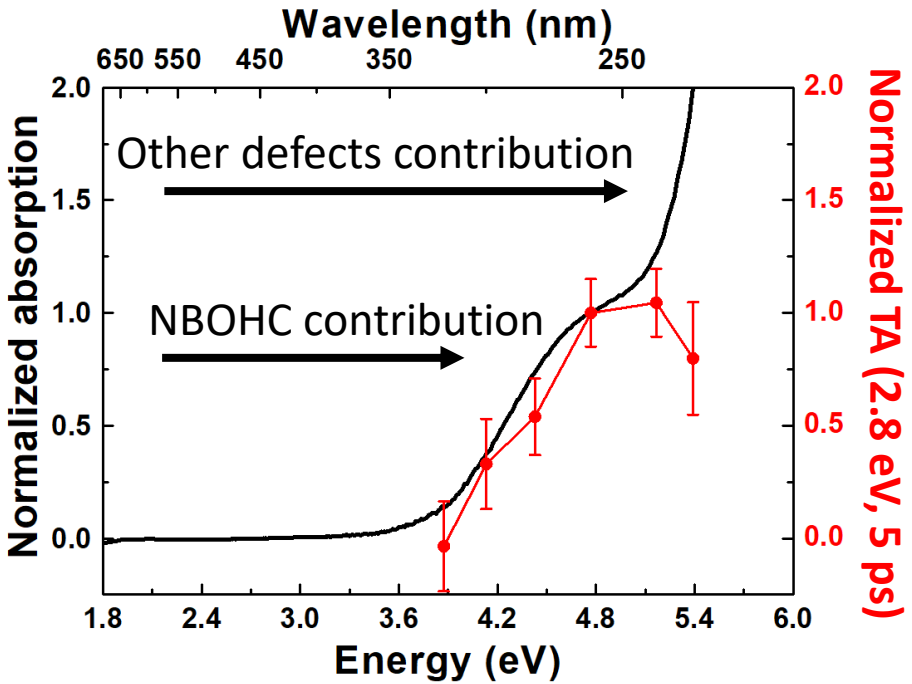

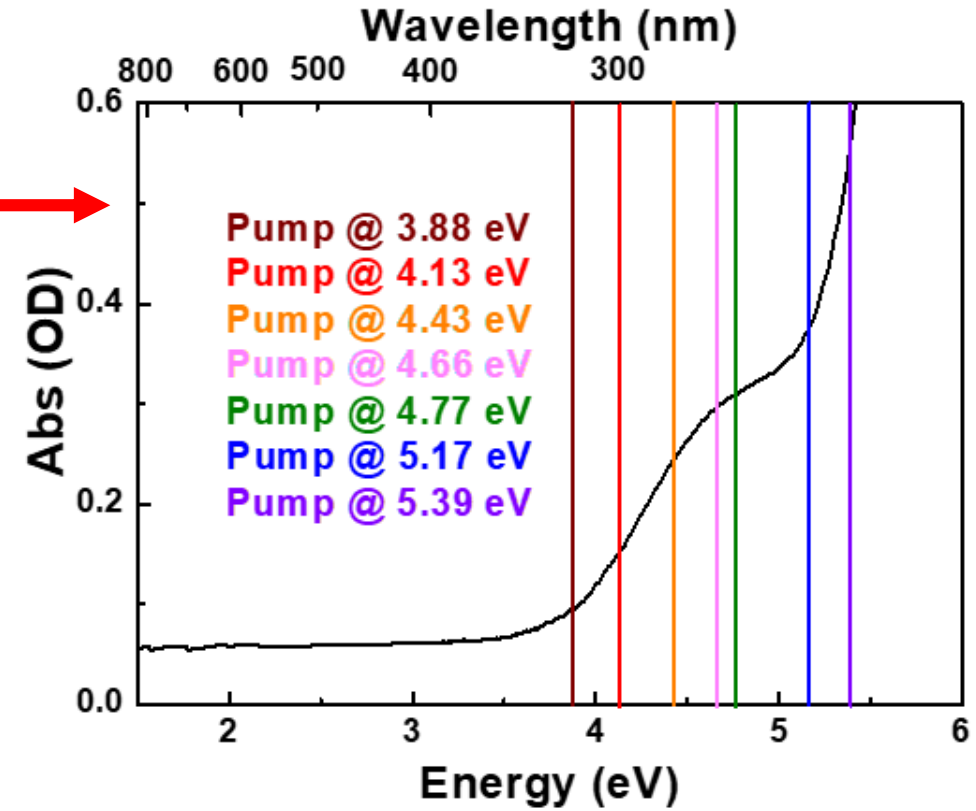

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- **No** effects involving the **whole matrix**

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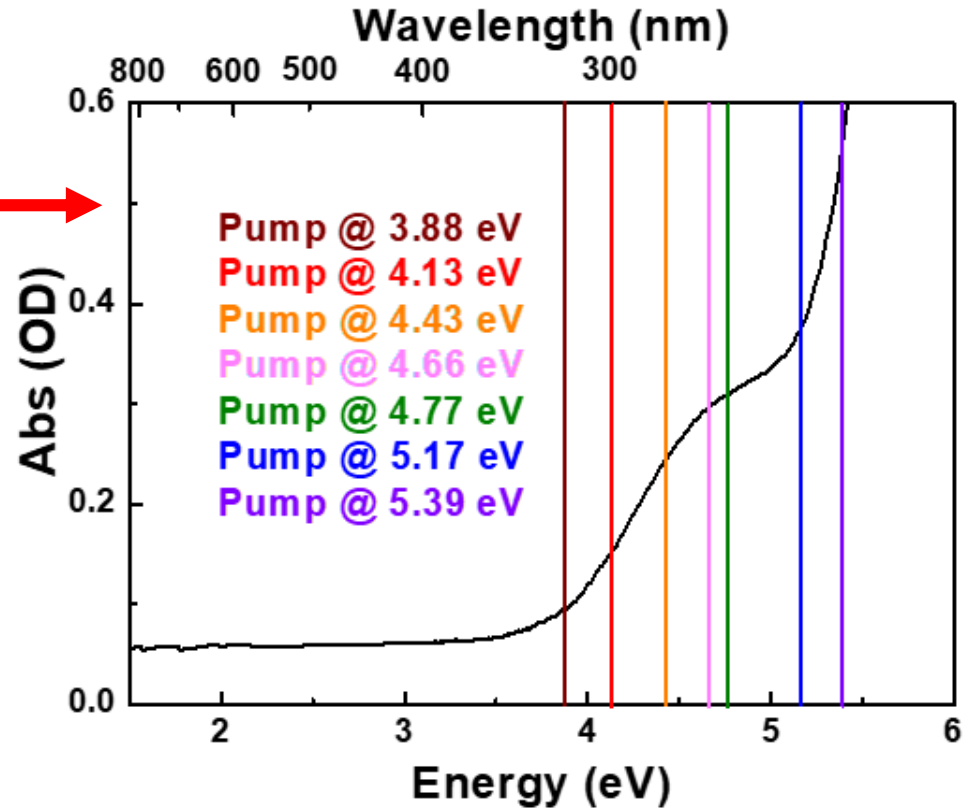

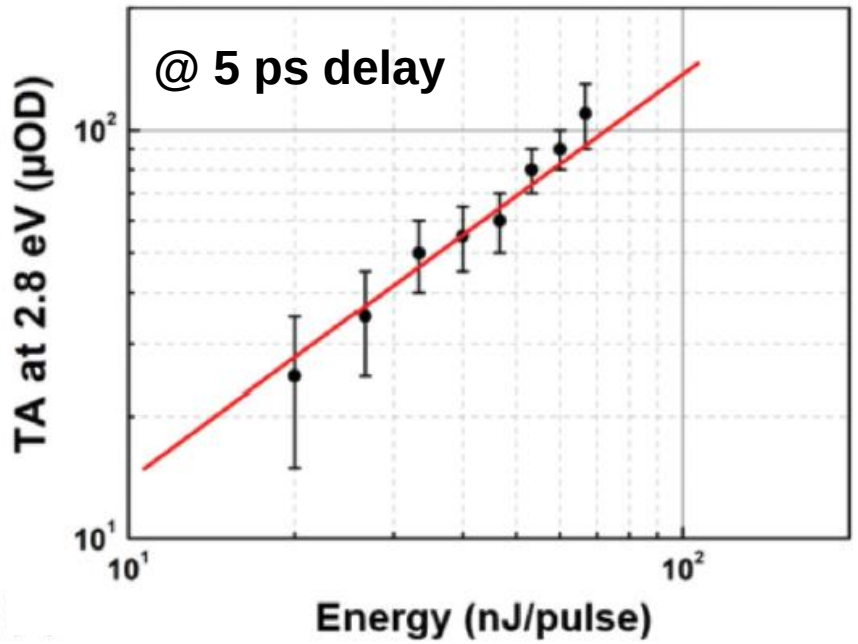

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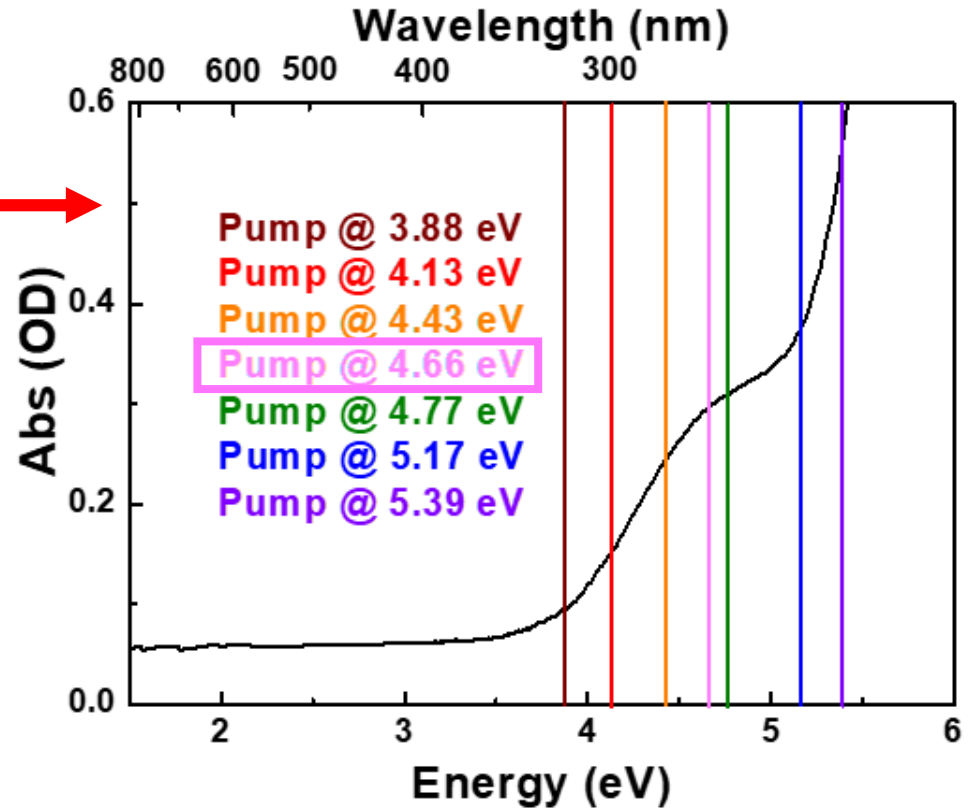

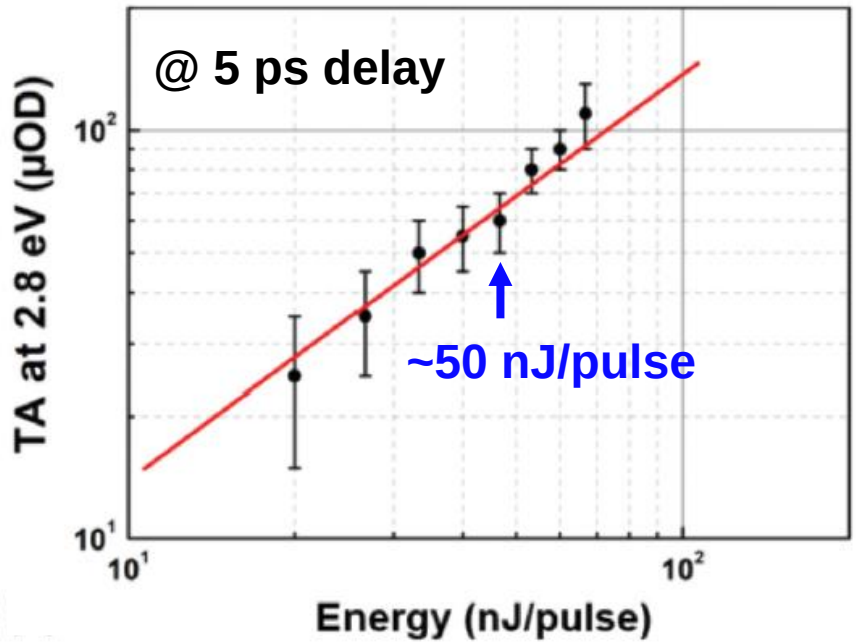

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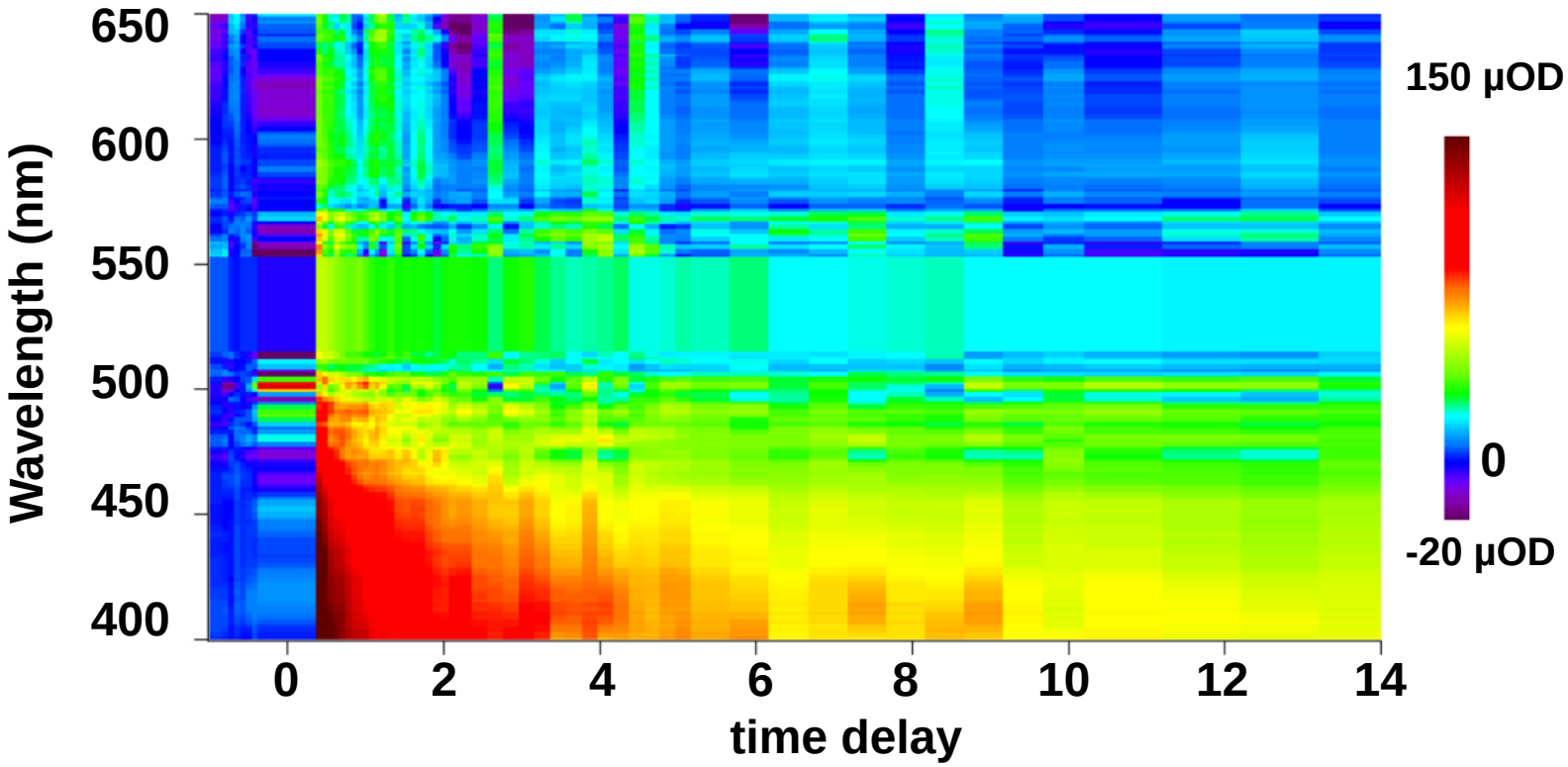
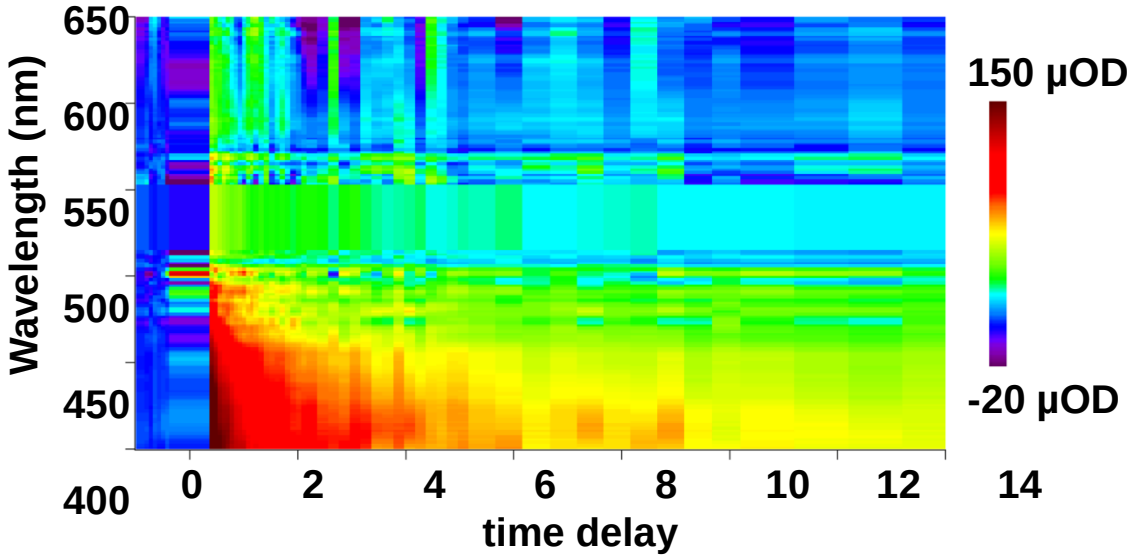
De Michele et al., Opt. Lett. (2021)

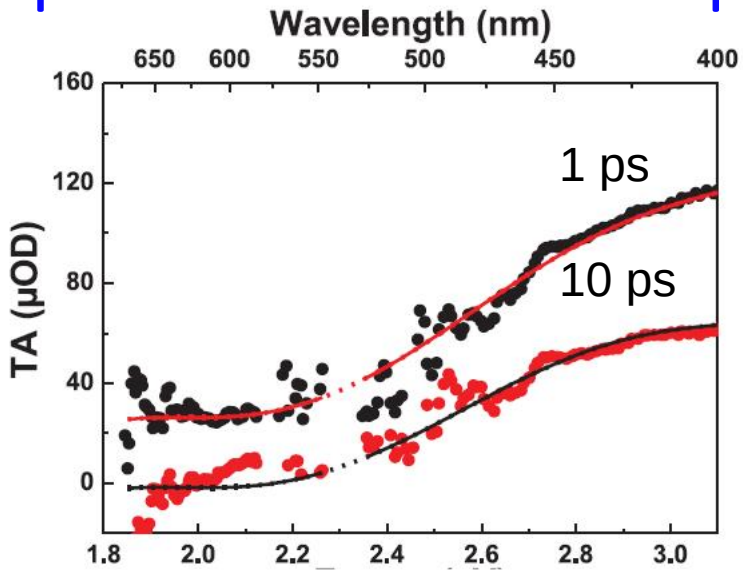
The TA spectrum exhibits a continuous wide and unstructured ESA, dominating the whole investigated spectral range



De Michele et al., Opt. Lett. (2021)

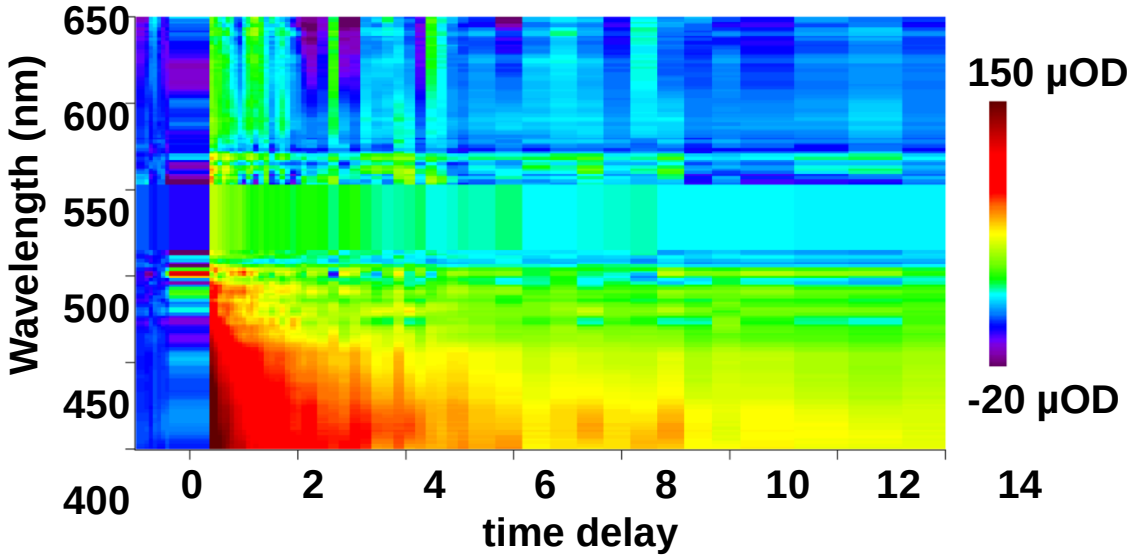
The TA spectrum doesn't change its shape as a function of the pump-probe delay

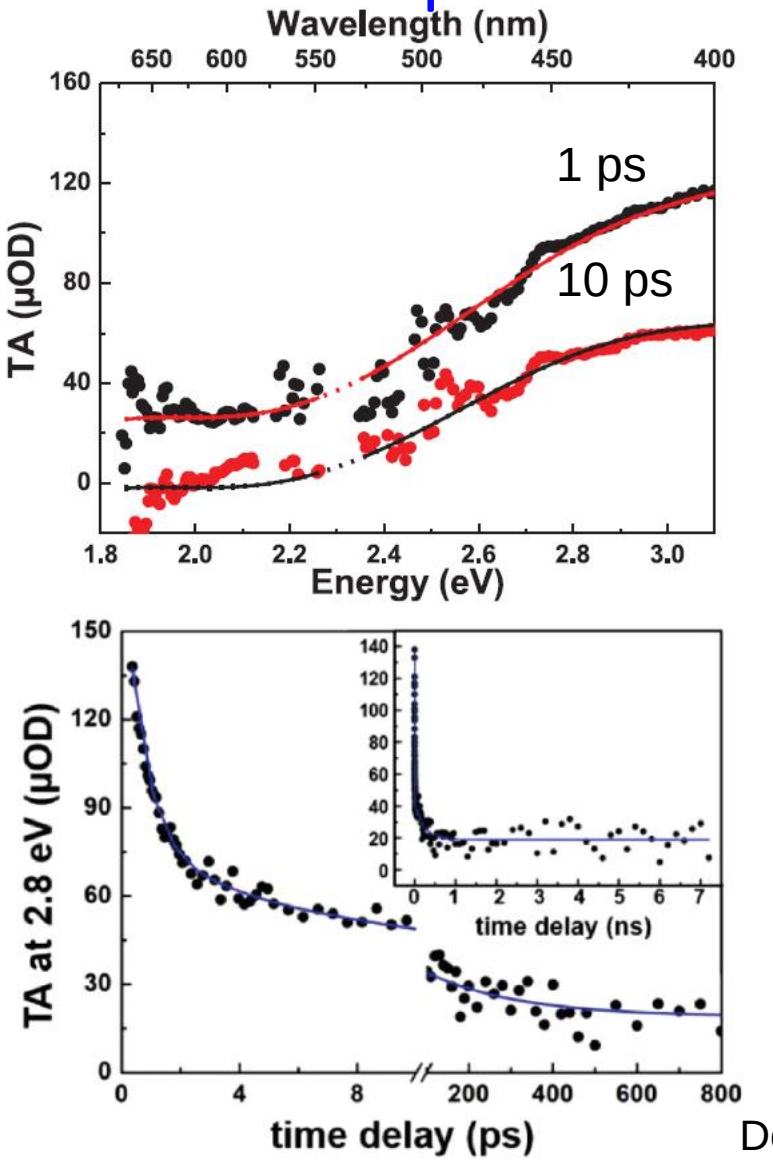




De Michele et al., Opt. Lett. (2021)

Almost 60% of the TA spectrum decays in less than 1 ps





Experimental decay

$$\sum_{i=1}^{3} A_i e^{-t/\tau_i} + C$$

Parameters	Value
C	20 µOD
A_1	100 µOD
τ_1	0.67 ps
A_2	40 µOD
τ_2	6.5 ps
A_3	20 µOD
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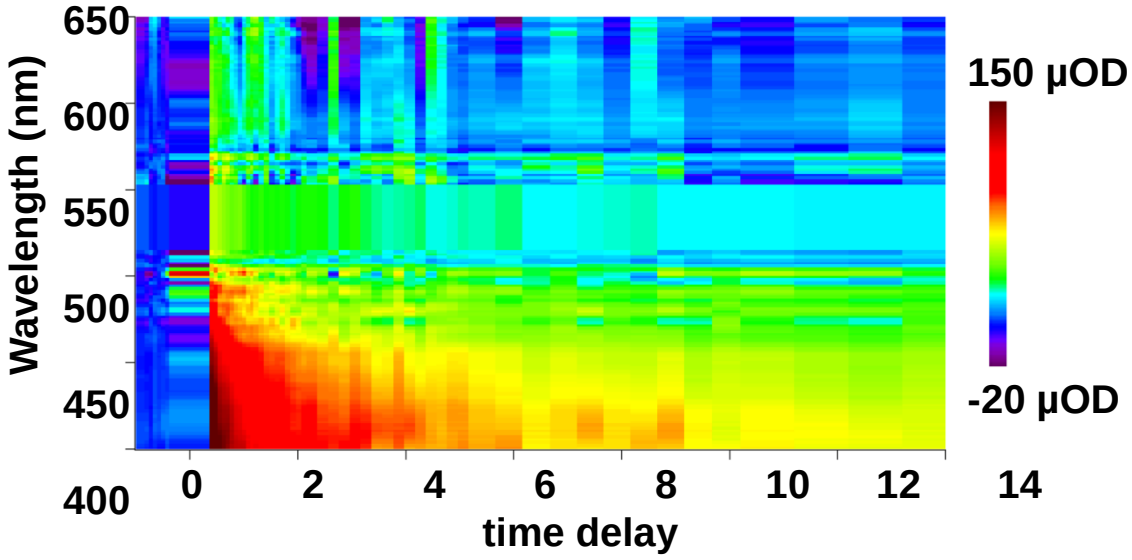

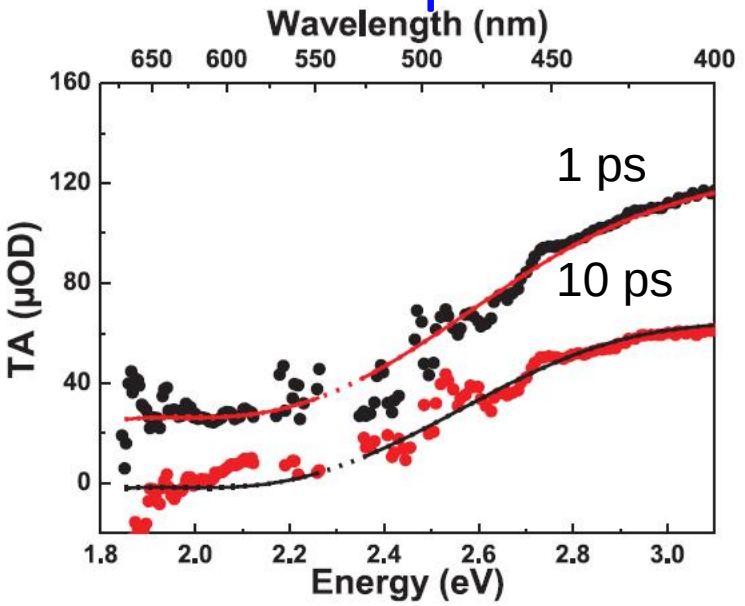

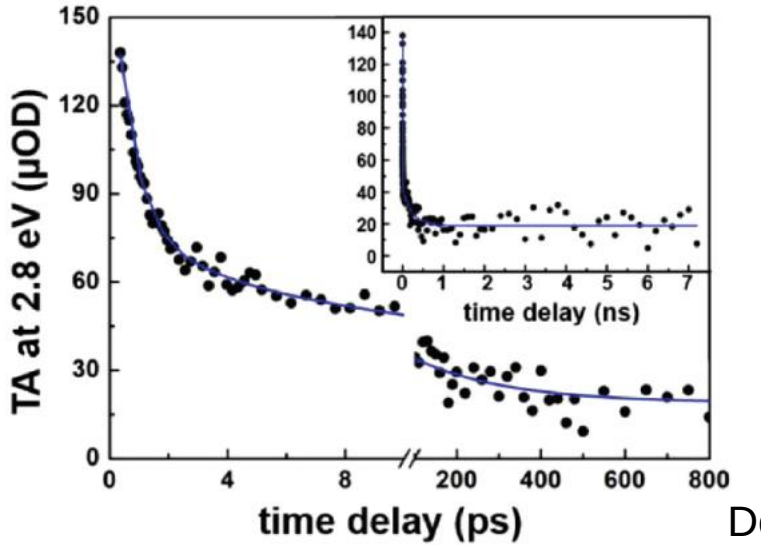

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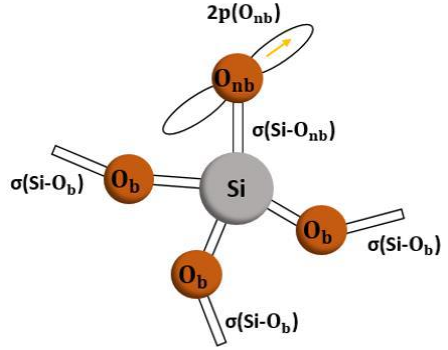
The NBOHC excitation and relaxation



NBOHC's ground state

De Michele et al., Opt. Lett. (2021)

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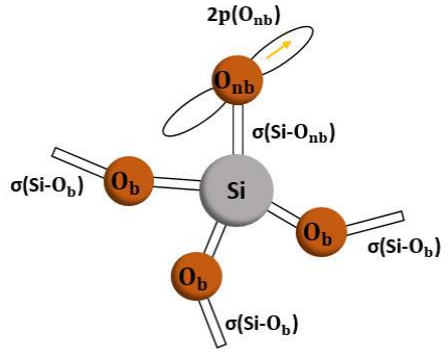

NBOHC's ground state

p(Onb) ⟶ **Available state**

σ(Si-Onb) ⟶ **Full orbital**

VB

De Michele et al., Opt. Lett. (2021)

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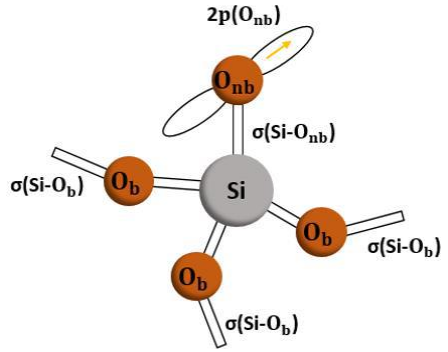
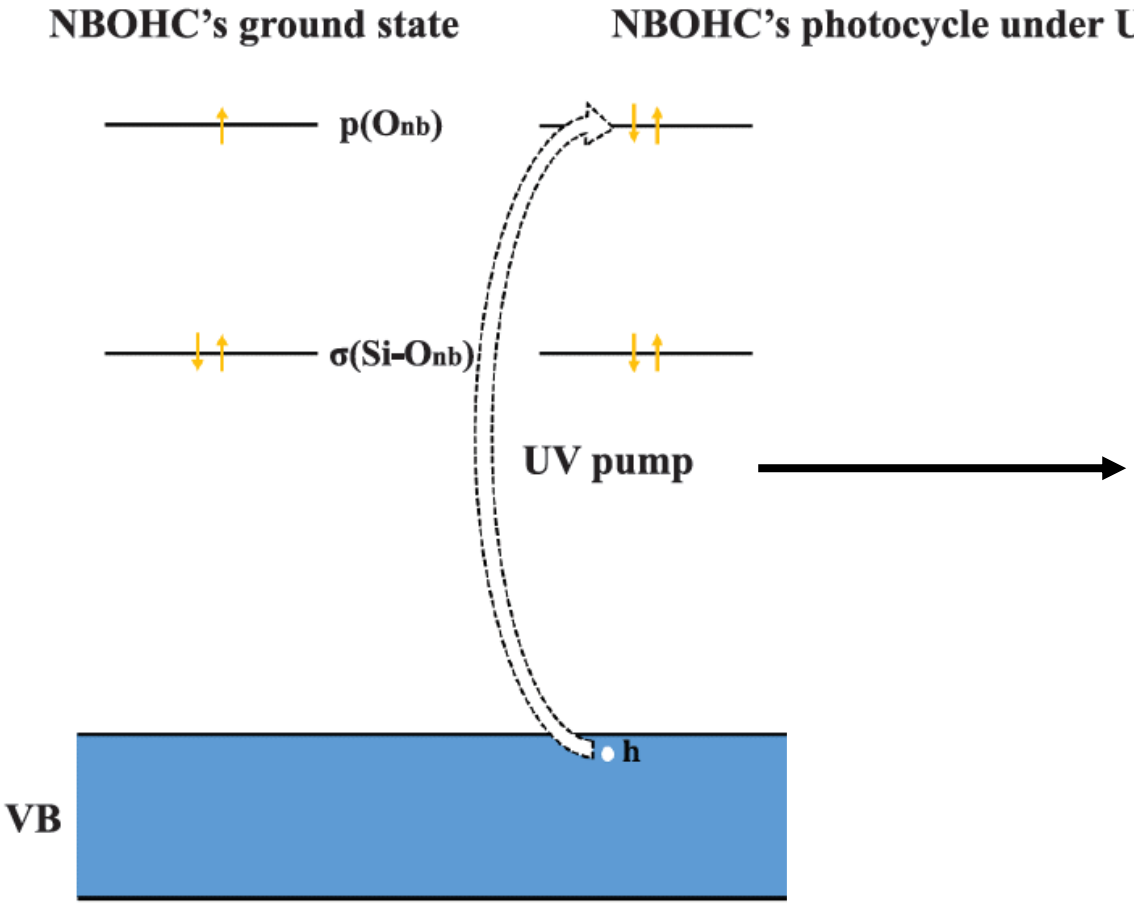


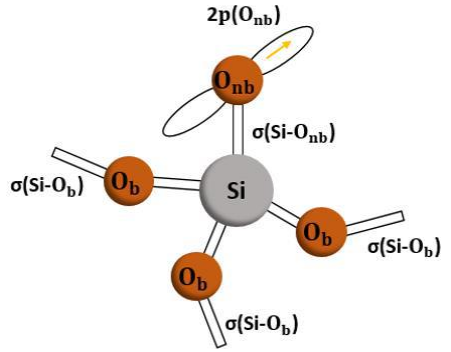


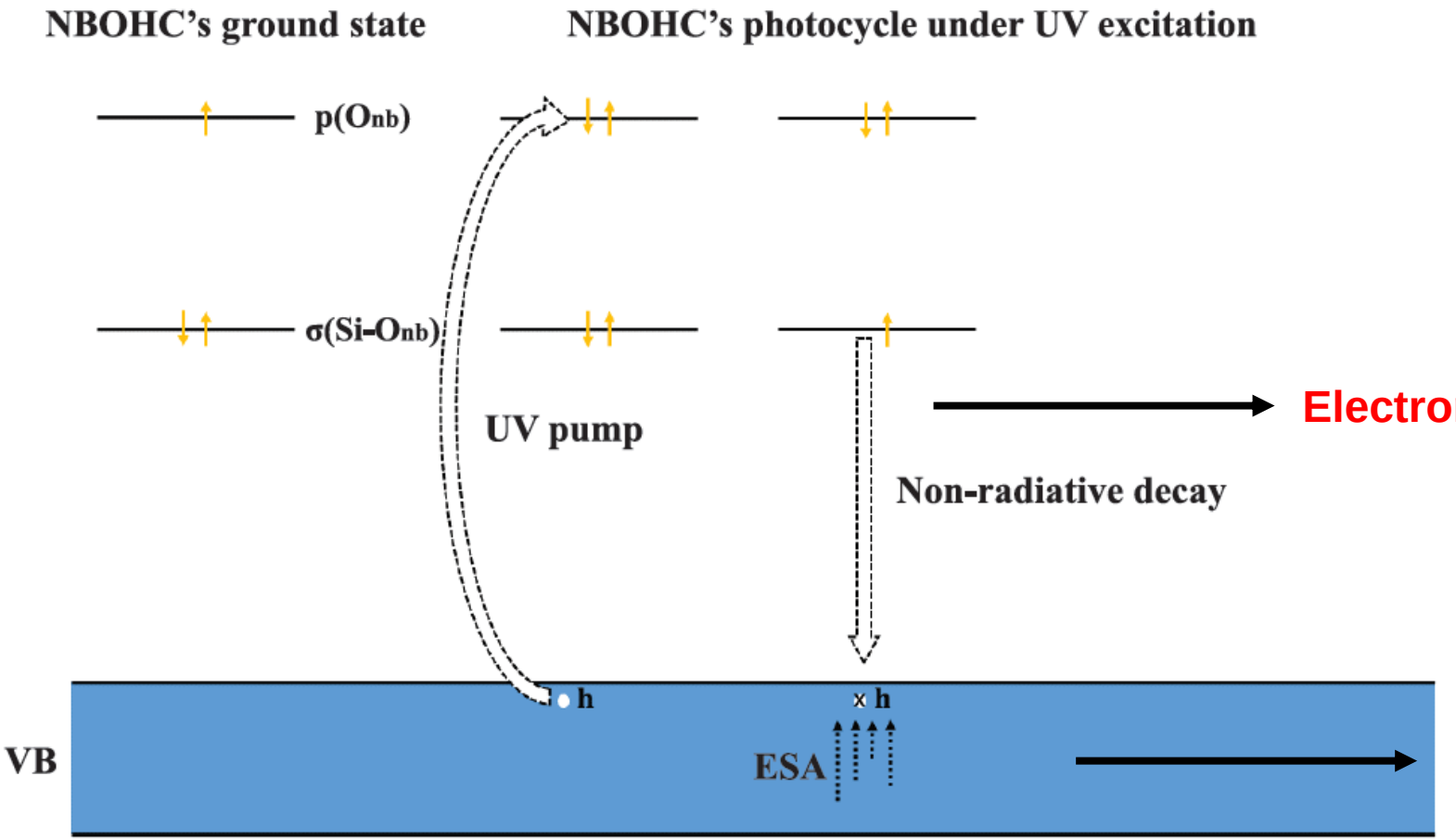
UV excitation

promotion of the electron from VB to the p(Onb) orbital

De Michele et al., Opt. Lett. (2021)

The NBOHC excitation and relaxation



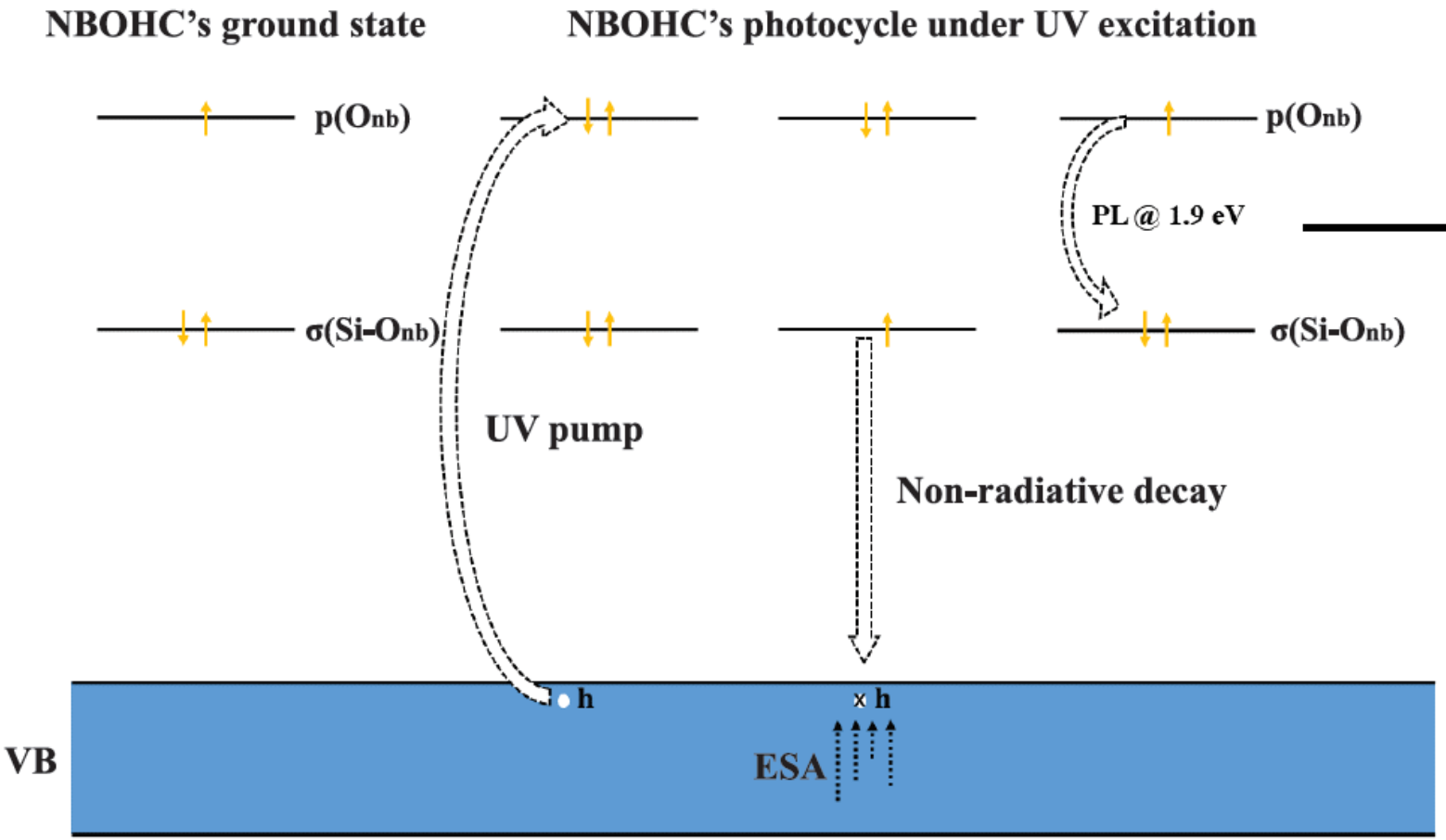


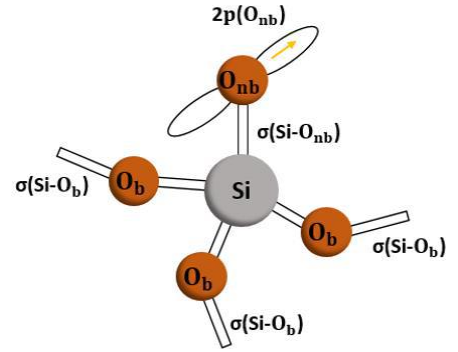
Electron relaxation: Charge transfer

ESA in the VB:
In agreement with the continuous and unstructured TA spectrum

De Michele et al., Opt. Lett. (2021)

The NBOHC excitation and relaxation





After the charge transfer

Available state in the σ(Si-Onb) orbital

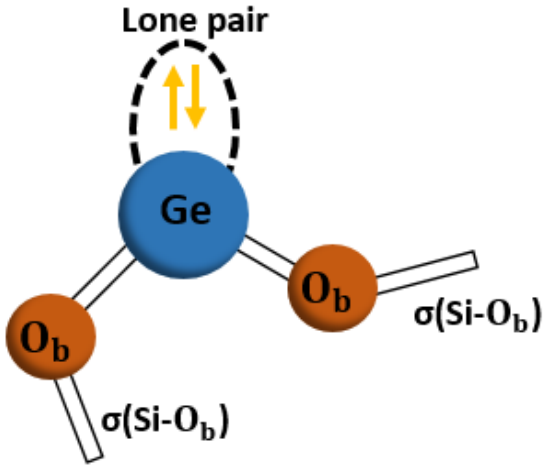
PL @ 1.9 eV

NBOHC in the ground state

De Michele et al., Opt. Lett. (2021)

The next step

The GLPC: a model defect to study the photocycle of basic molecular systems embedded in solids.



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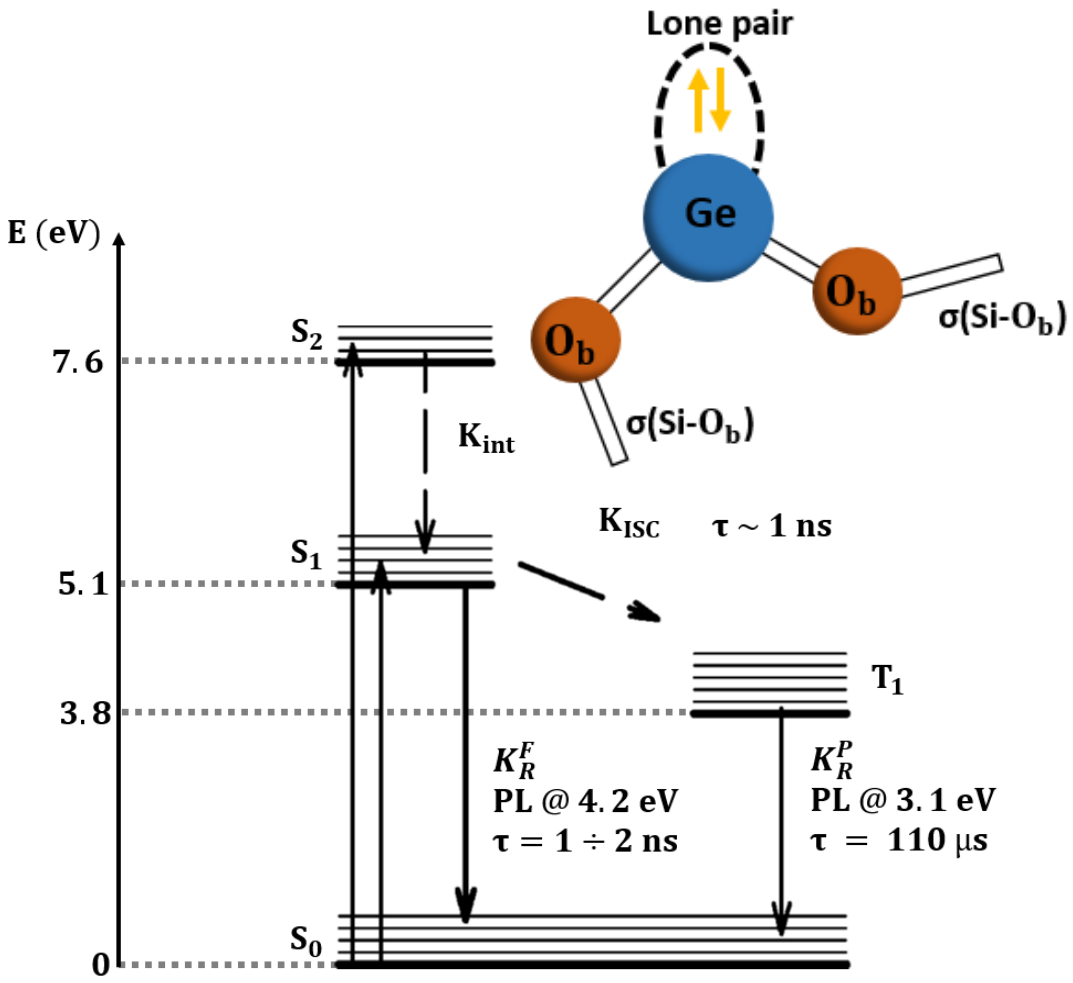

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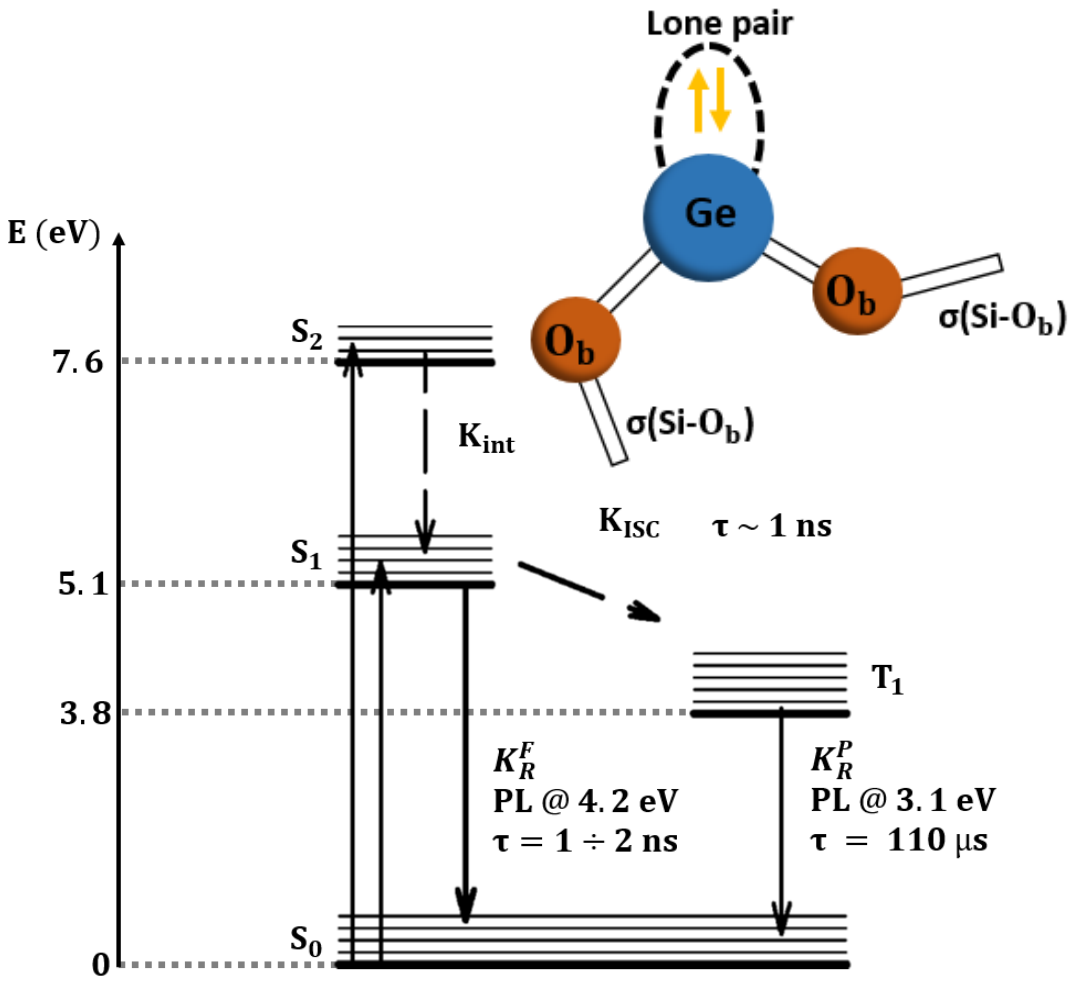
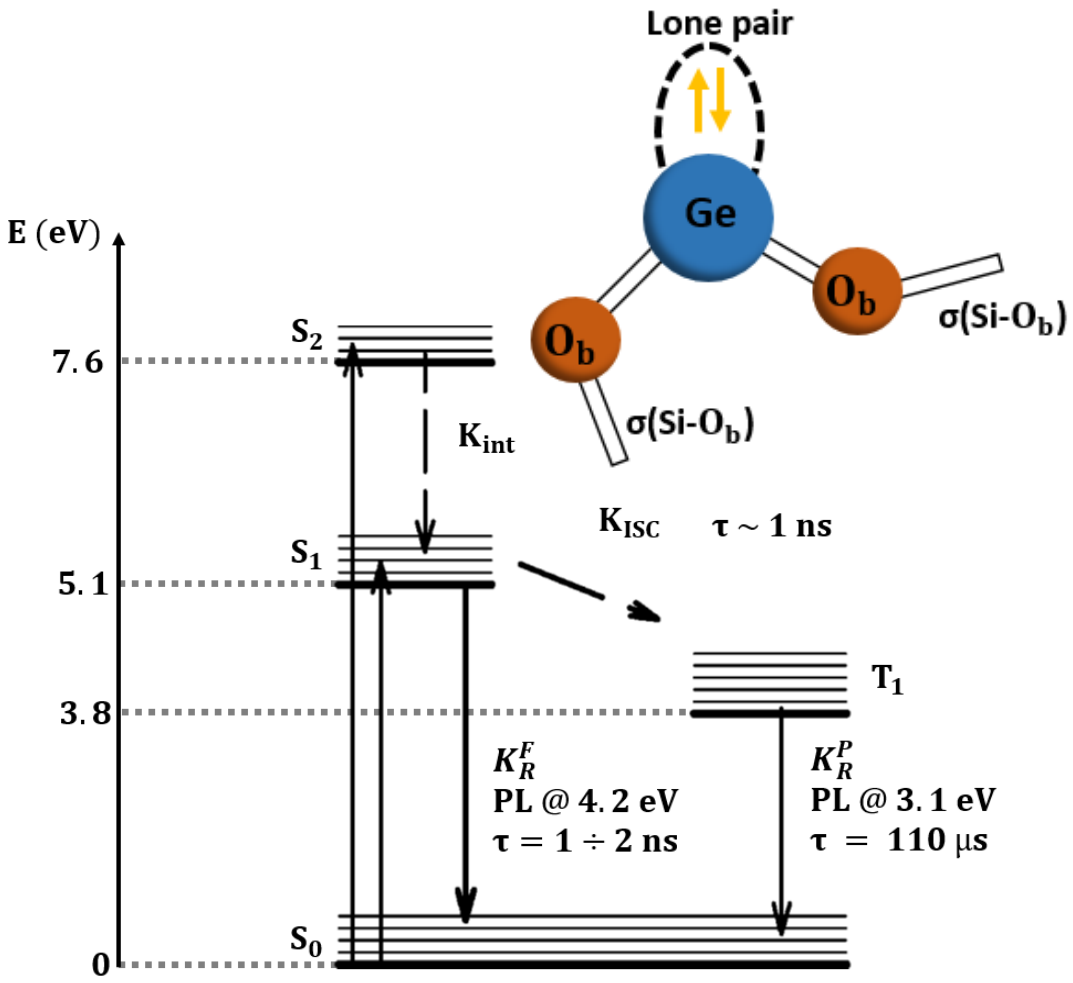


GLPC relaxation mechanisms upon UV excitation are still questionable:

- the contribution of **non-radiative** $S_1 \rightarrow S_0$ depopulation VS the **radiative** one and the **intersystem crossing (ISC)**
- the **nature of the ISC process itself**, characterized by a non-Arrhenius behavior as a function of the temperature

The GLPC: a model defect to study the photocycle of basic molecular systems embedded in solids.



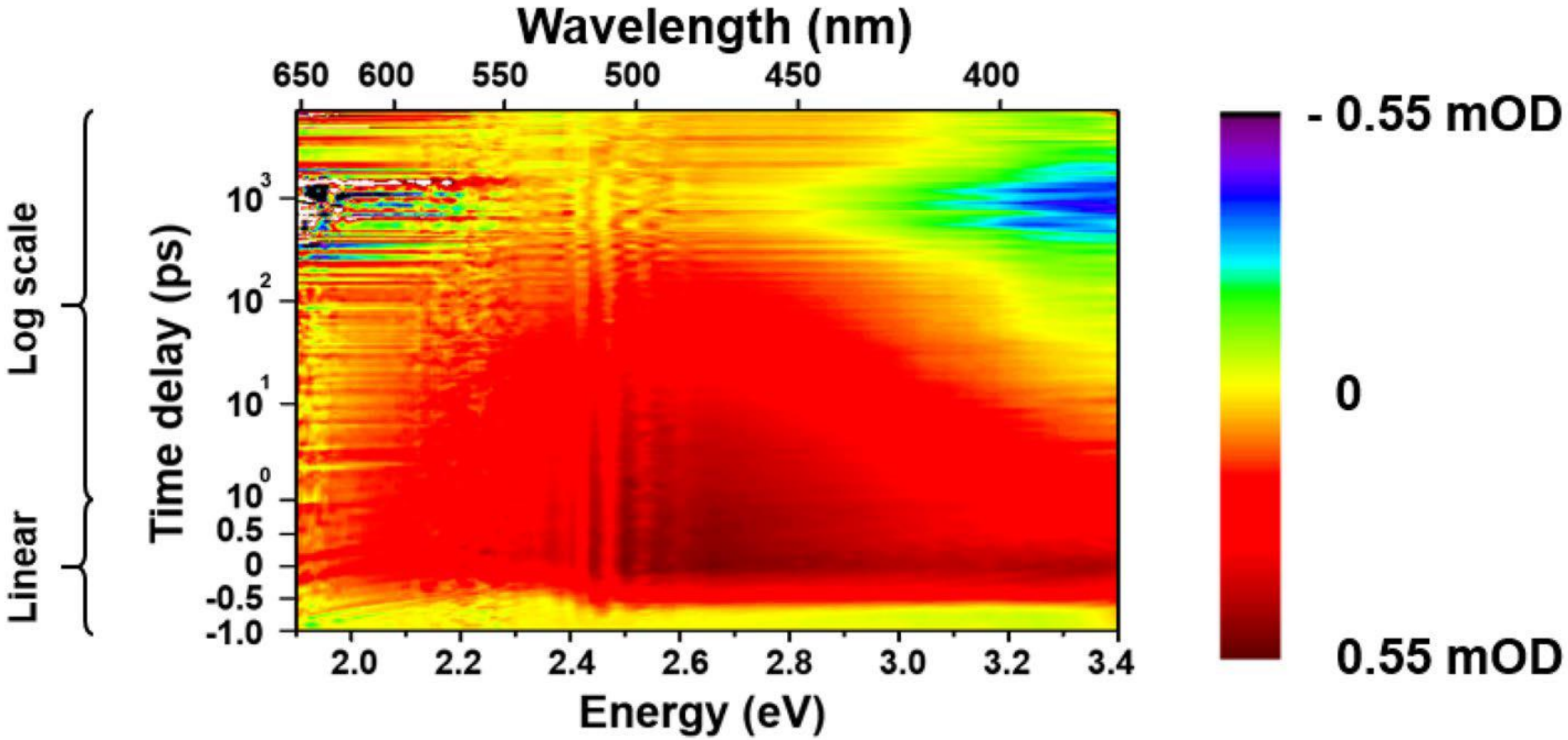
GLPC relaxation mechanisms upon UV excitation are still questionable:

- the contribution of **non-radiative** $S_1 \rightarrow S_0$ depopulation VS the **radiative** one and the **intersystem crossing (ISC)**
- the **nature of the ISC process itself**, characterized by a non-Arrhenius behavior as a function of the temperature

Our approach:

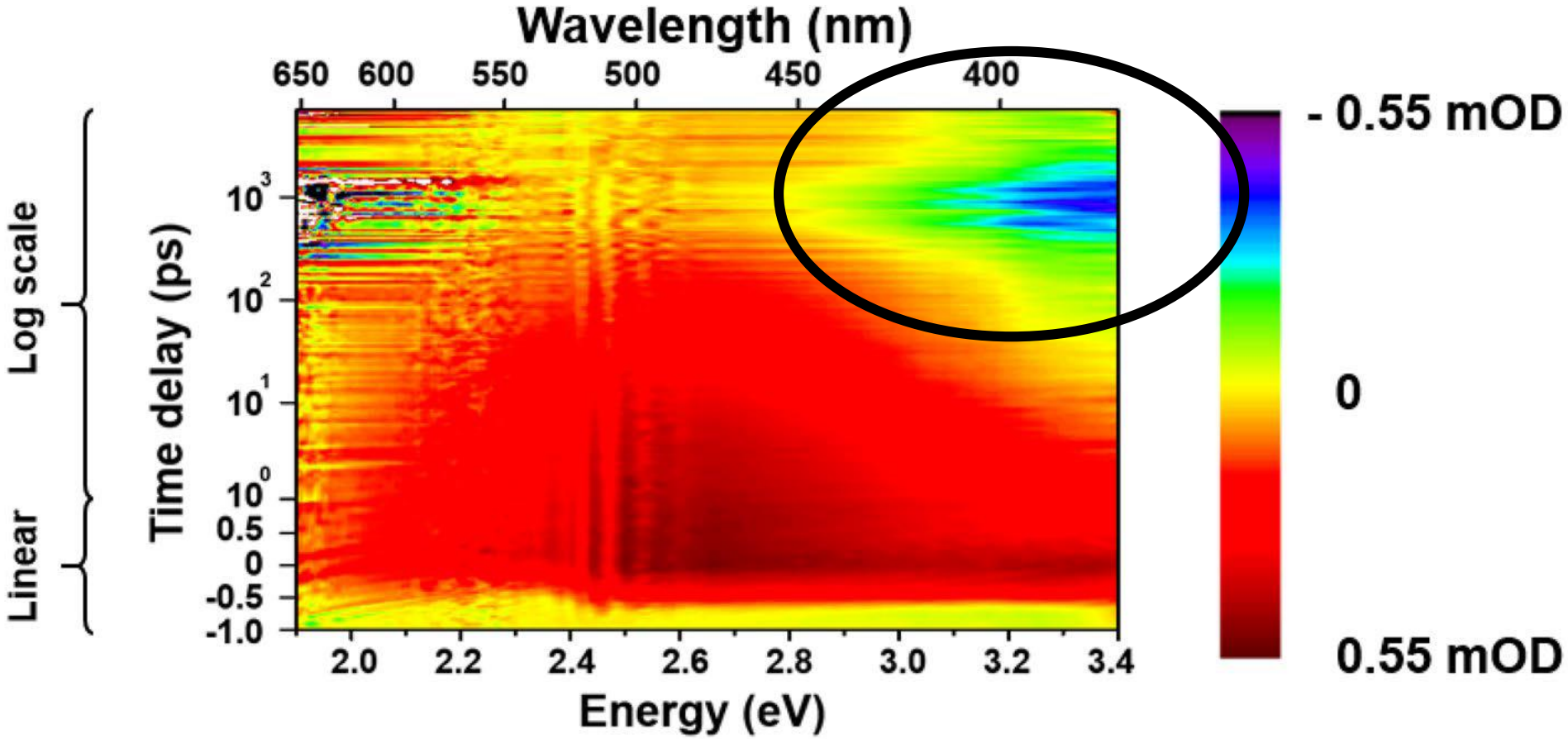
- TA measurements in **linear absorption conditions**
- TA as a function of the **excitation wavelength**

6% Ge-doped sample TA response upon UV excitation



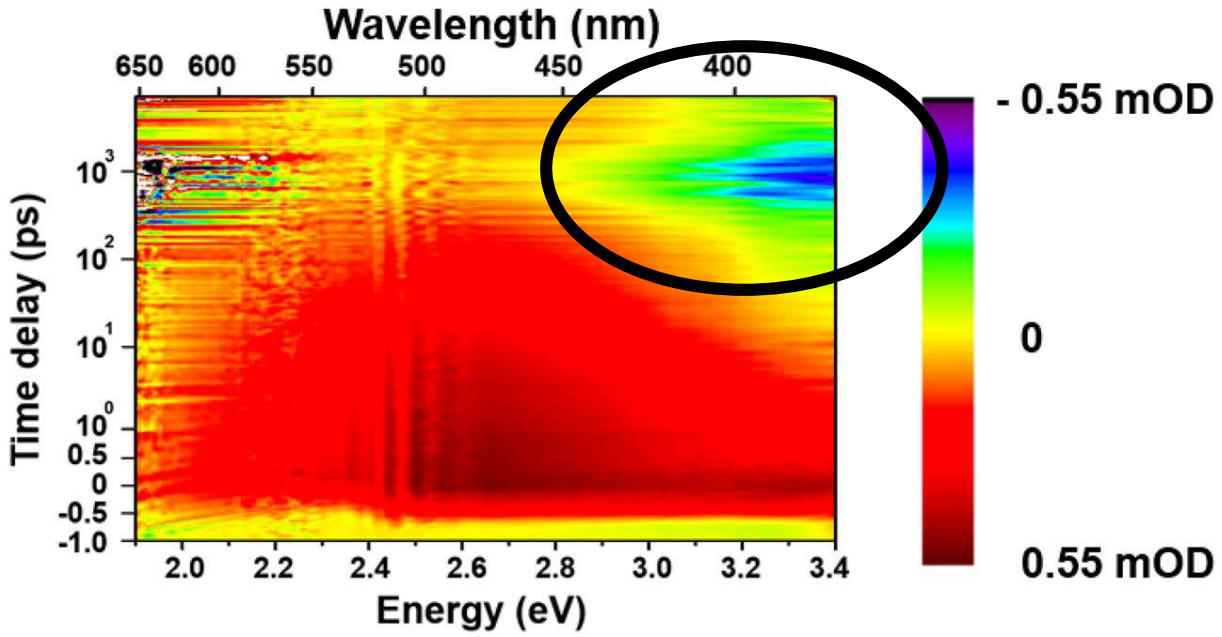
De Michele et al., Sci. Rep. (2022)

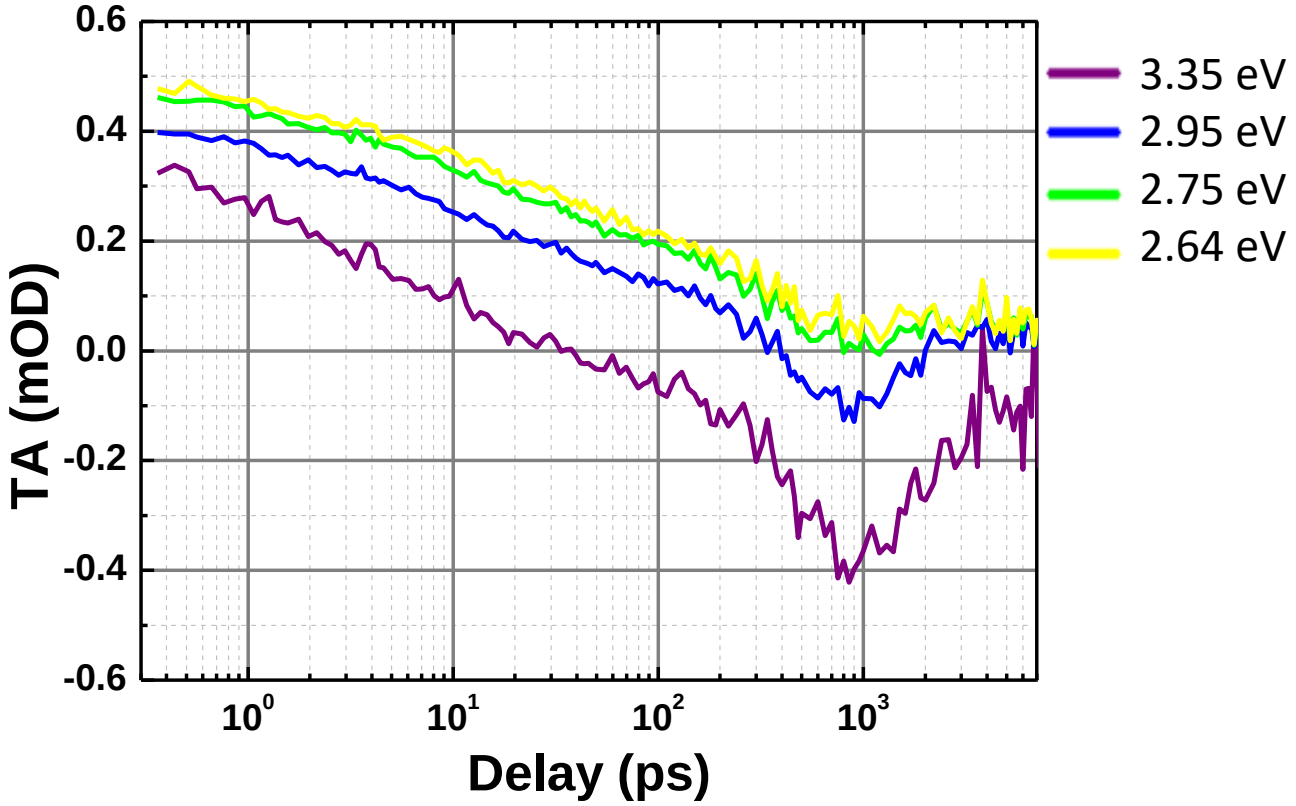
6% Ge-doped sample TA response upon UV excitation



De Michele et al., Sci. Rep. (2022)

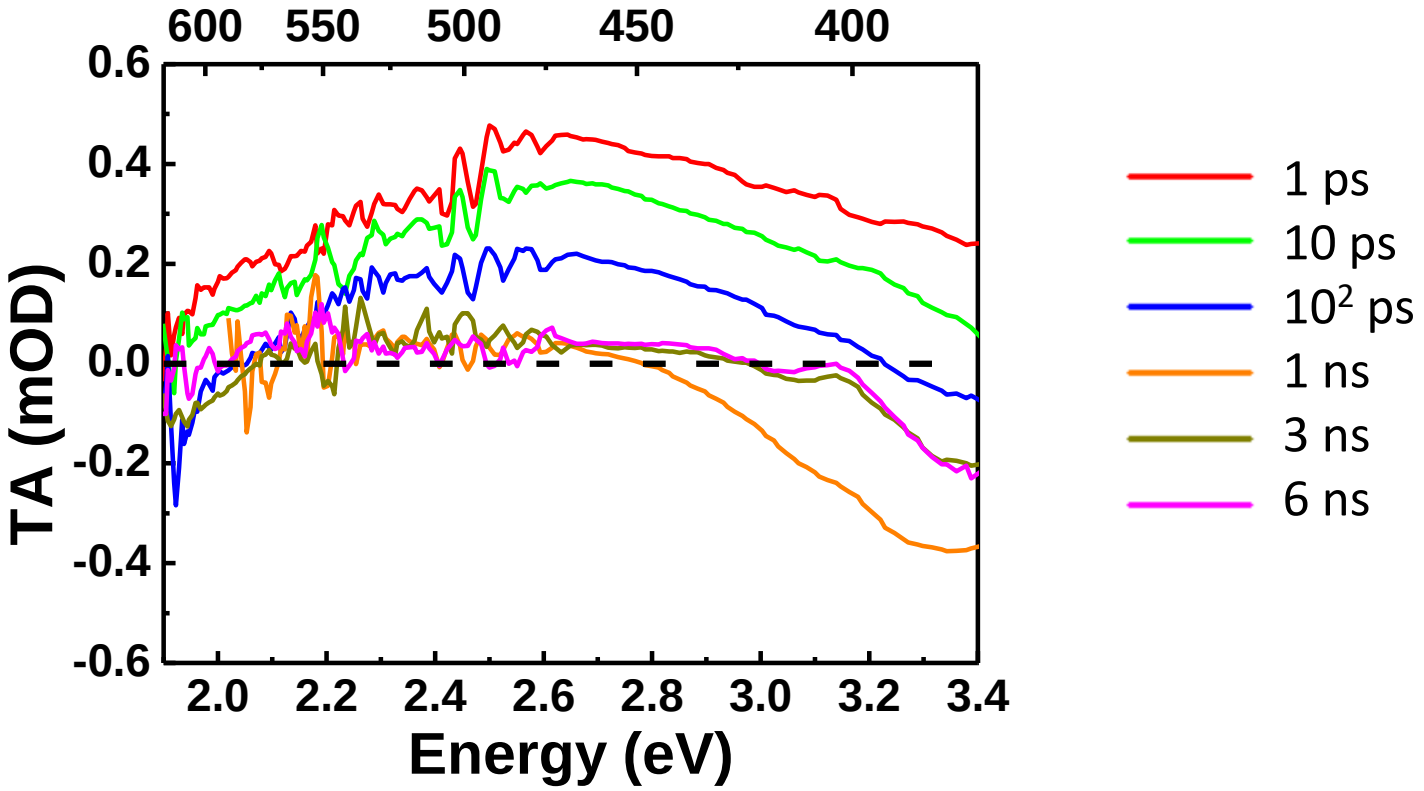
6% Ge-doped sample TA response upon UV excitation

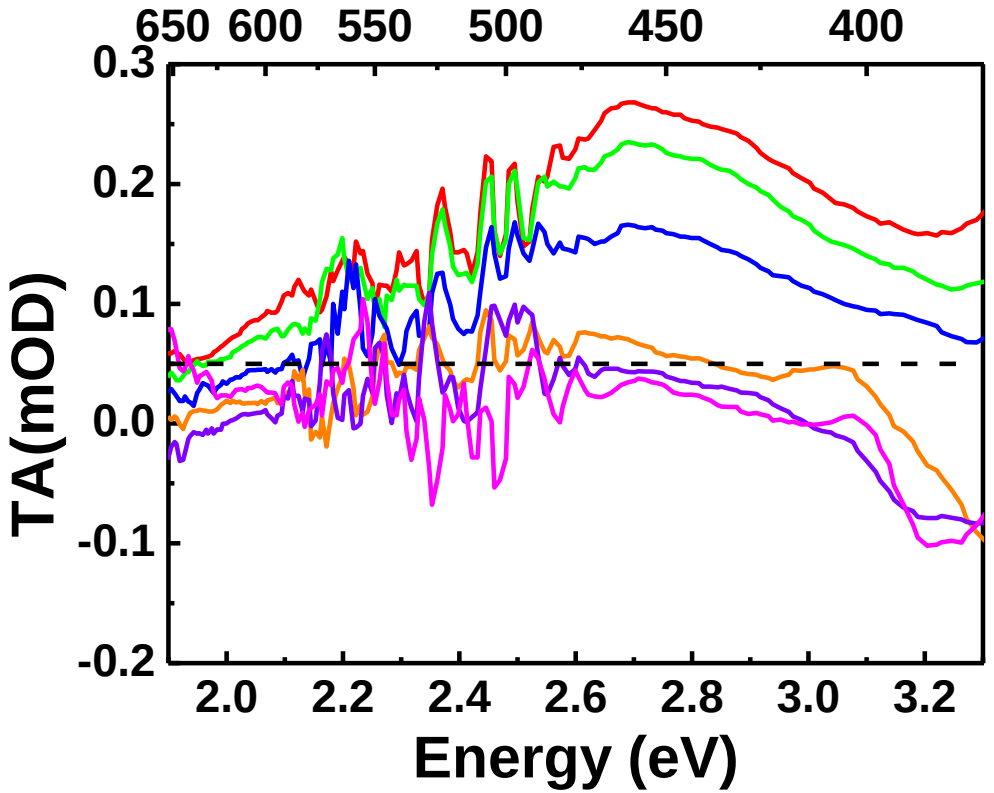




De Michele et al., Sci. Rep. (2022)

6% VS 0.1 % Ge-doped sample: the role of the high doping





6% Ge-doped sample

0.1 Ge-doped sample

De Michele et al., Sci. Rep. (2022)

Conclusions

- ❑ We presented a **new promising experimental approach** to investigate the **pump-probe response of color centers:**

- Possibility to excite in **linear absorption conditions**

- Possibility to excite at **different pumping wavelengths**

- ❑ For the first time, **we characterized the NBOHC TA dynamics** in **single photon absorption conditions** with an **unprecedented time resolution**

- ❑ Work is in progress: the Ge-lone pair center (GLPC)

Thank you for your attention