# Adsorption & Absorption of Push-Pull Functionalized Stilbene on an Amorphous Silica Glass

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Libra Summer School 8. June 2024

universität wien

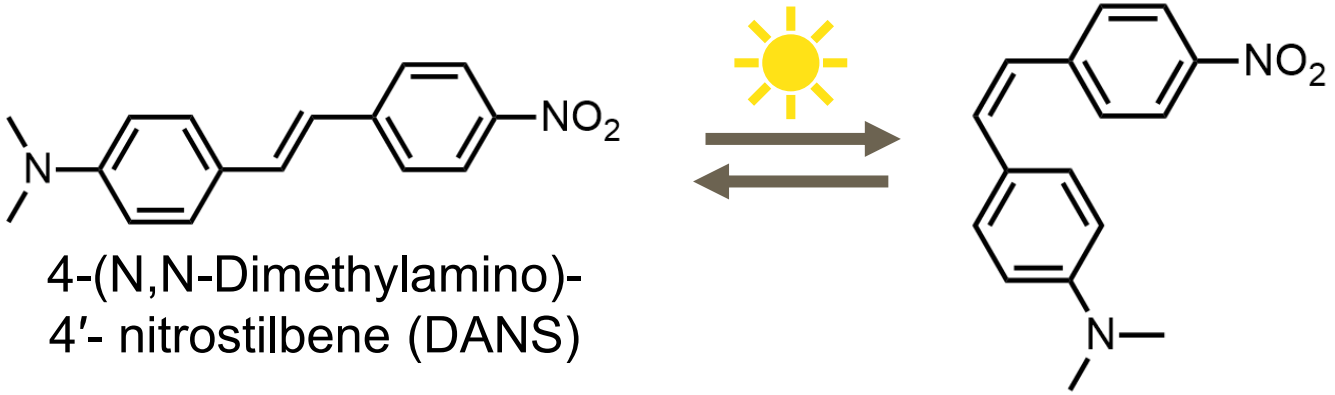
VIENNA - DOCTORAL - SCHOOL - PHYSICS

DOCTORAL COLLEGE

# My DANSers

Fluorescence

Isomerization /initial isomer

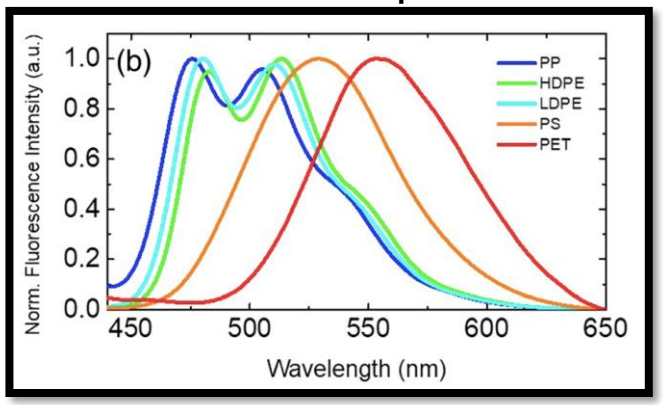



4-(N,N-Dimethylamino)-
4′- nitrostilbene (DANS)

## Fluorescence yield[1]

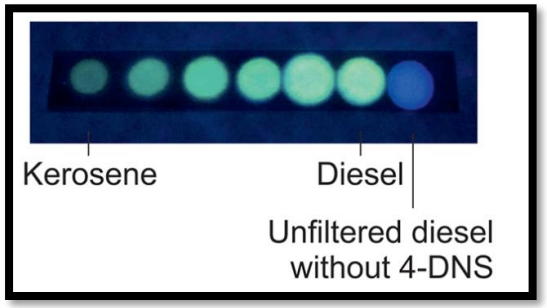
| | | |
|---|---|---|
| 4DNS | *c*-Hex | 0.33 |
| | Toluene | 0.53 |
| | THF | 0.11 |
| | $CH_2Cl_2$ | 0.008 |
| | MeCN | <0.002 |

## Detection of microplastics[2]




polypropylene (PP)
low-density polyethylene (LDPE)
high-density polyethylene
(HDPE)
polystyrene (PS)
polyethyleneterephtalate (PET)

## Detection of adulterated diesel[3]




[1]Yang, J. S., & Lin, C. J. (2015). Fate of photoexcited trans-aminostilbenes. J. Photochem. Photobiol. A, 312, 107-120.
[2]Sancataldo, G., et al., (2021). Identification of microplastics using 4-dimethylamino-4′-nitrostilbene solvatochromic fluorescence. Microsc. Res. Tech., 84(12), 2820-2831.
[3]Gotor R., et al., (2017). Detection of Adulterated Diesel Using Fluorescent Test Strips andSmartphone Readout. Energy & Fuels, 31, 11594-11600.

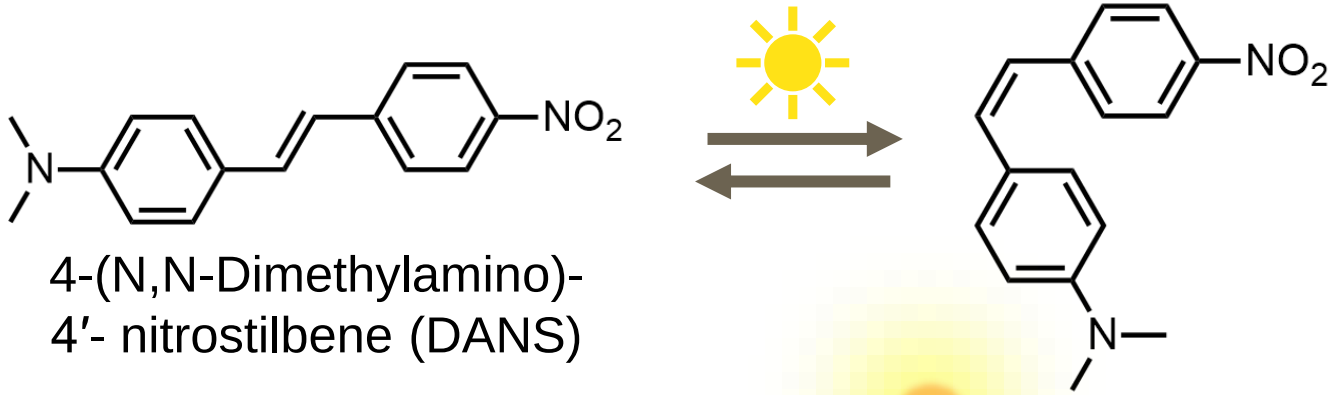
# My DANSers

Fluorescence

Isomerization /initial isomer

Prof. Markus Arndt

Ksenija Simonović

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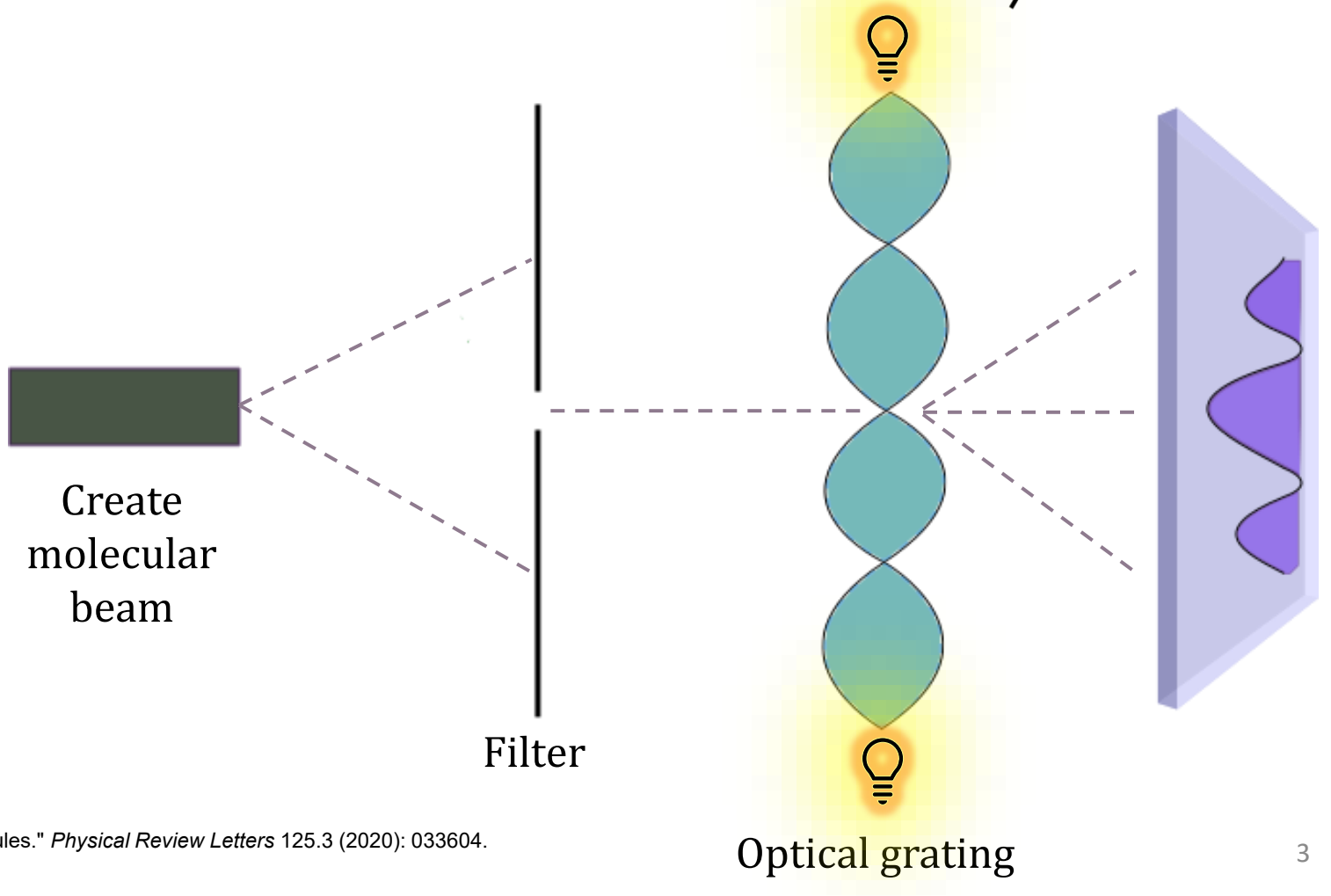
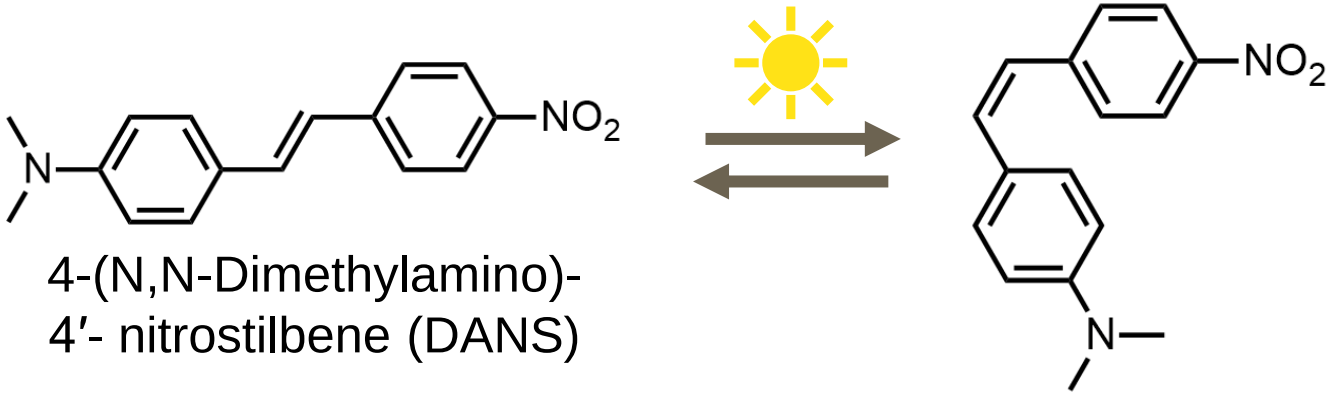



Brand, Christian, et al. "Bragg diffraction of large organic molecules." *Physical Review Letters* 125.3 (2020): 033604.

# My DANSers

Fluorescence

Isomerization /initial isomer

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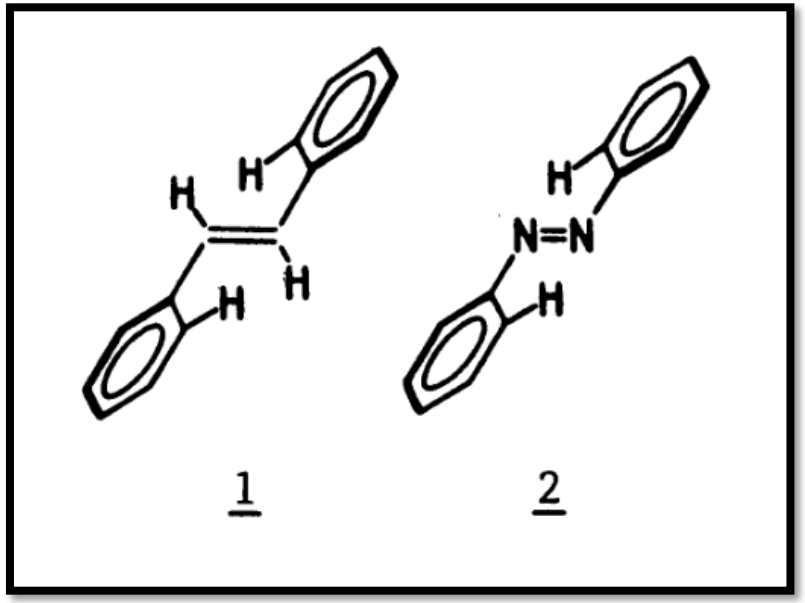
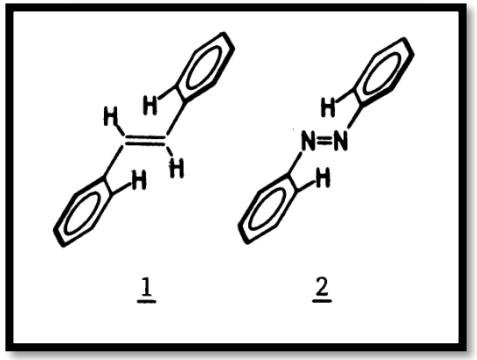



Oelkrug, D., et. Al (1986). Photochemistry on surfaces. *Pure and Applied Chemistry*, *58*(9), 1207-1218.

# My DANSers

Fluorescence

Isomerization /initial isomer

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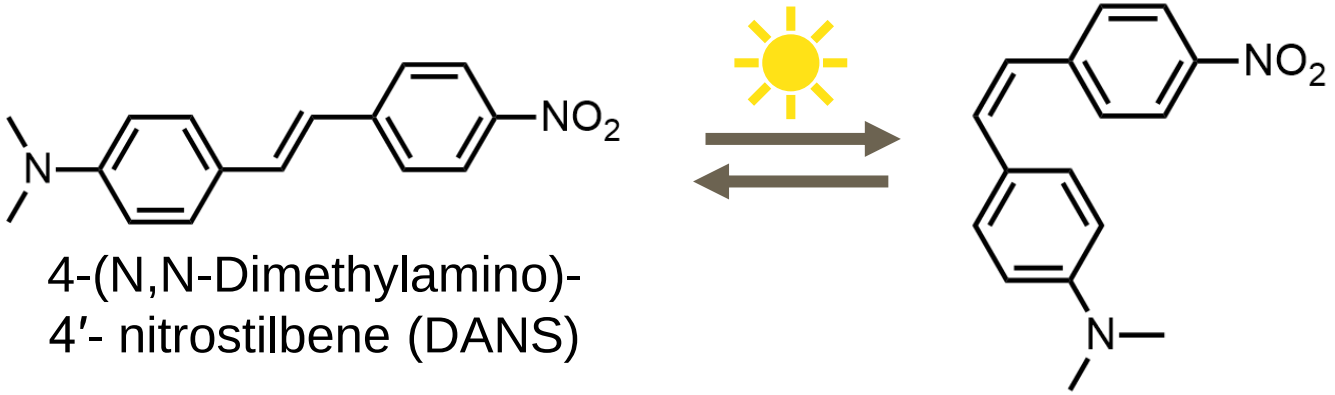



4-(N,N-Dimethylamino)-
4′- nitrostilbene (DANS)

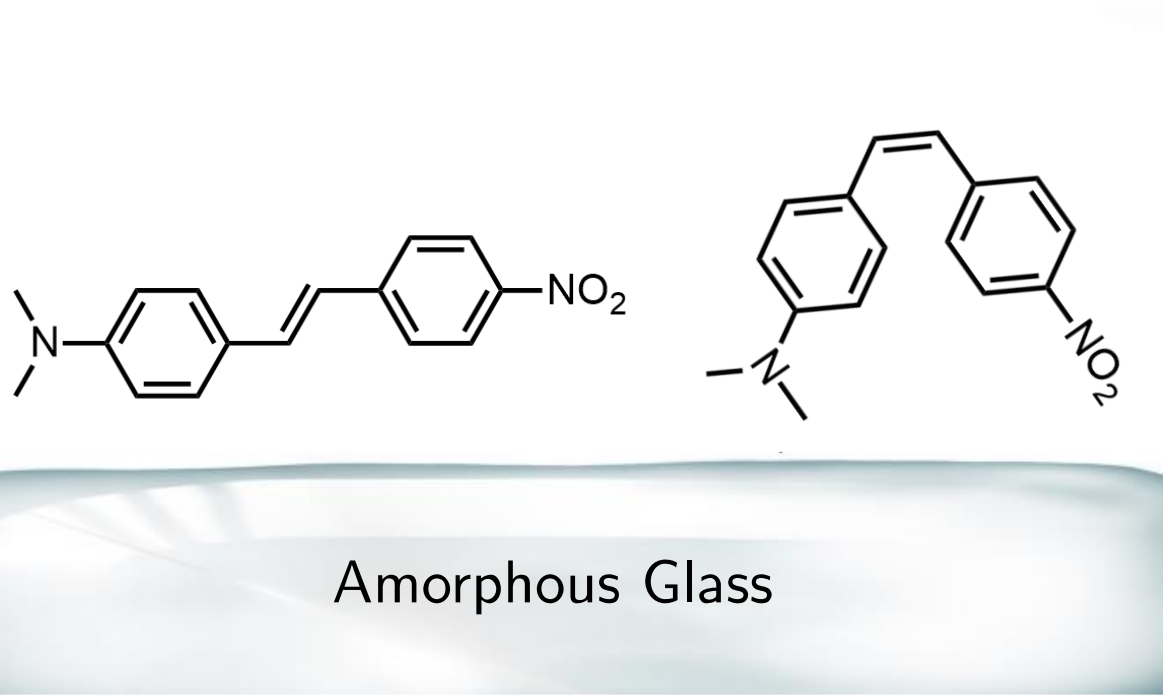
TABLE 2. Quantum yields of the photochemical trans - cis isomerization at room temperature of some organic molecules adsorbed on alumina.

| | | on alumina | | in liquid solution | |
|---|---|---|---|---|---|
| | | $S_1$-excitation | $S_2$-excitation | $S_1$-excitation | $S_2$-excitation |
| azobenzene | $\Phi_{t,c}$ | 0.35 ± 0.10 | 0.20 ± 0.05 | 0.20 ± 0.05 | 0.15 ± 0.05 |
| | $\Phi_{c,t}$ | 0.65 ± 0.05 | 0.55 ± 0.10 | 0.50 ± 0.10 | 0.30 ± 0.10 |
| stilbene | $\Phi_{t,c}$ | 0.05 ± 0.02 | | 0.50 ± 0.05 | |
| | $\Phi_{c,t}$ | 0.40 ± 0.10 | | 0.35 ± 0.05 | |
| thioindigo | $\Phi_{t,c}$ | $\simeq 10^{-5}$ | | 0.15 ± 0.05 | |
| | $\Phi_{c,t}$ | --- | | 0.40 ± 0.10 | |

Oelkrug, D., et. Al (1986). Photochemistry on surfaces. *Pure and Applied Chemistry*, *58*(9), 1207-1218.

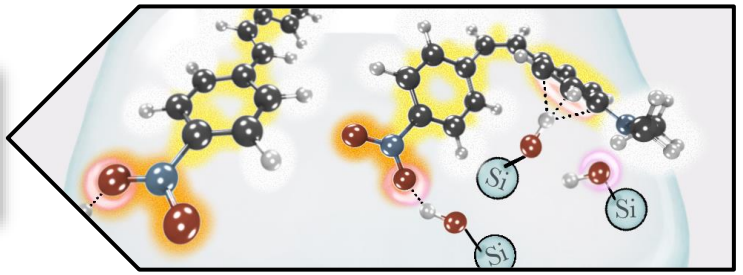
# Research Question


How the photophysics/photochemistry of DANS is influenced when it is adsorbed on glass?

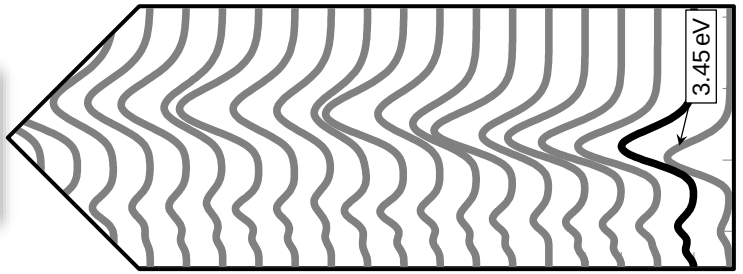


# Goals

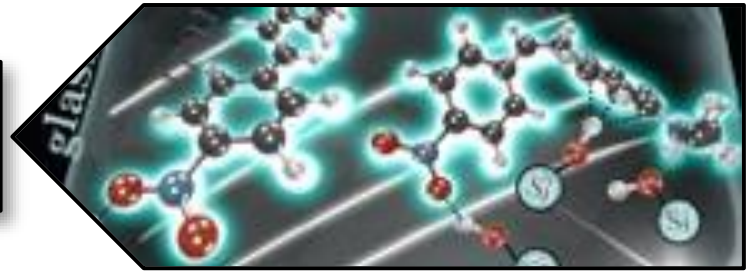
How does the molecule adsorb on the glass? Stable and unstable orientations?




How does the absorption spectrum vary depending on the adsorption modes?




How does the nonradiative vs. radiative ratio change upon adsorption?

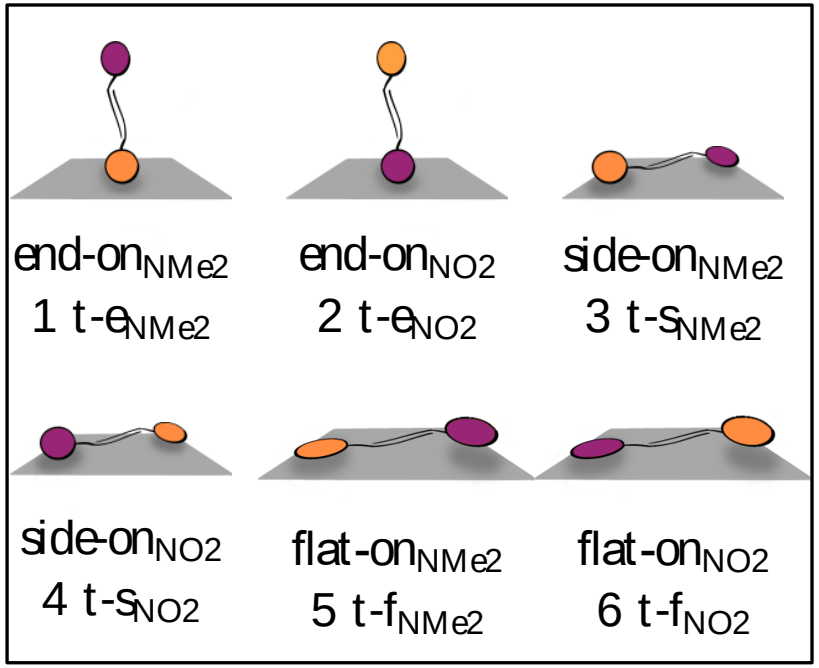


# Adsorption in the ground state

Prepare initial orientations

Relax/optimize these initial orientations within periodic boundary conditions at PBE/D3 level of theory and with plane-wave DFT

Repeat the calculations on 4 different surfaces

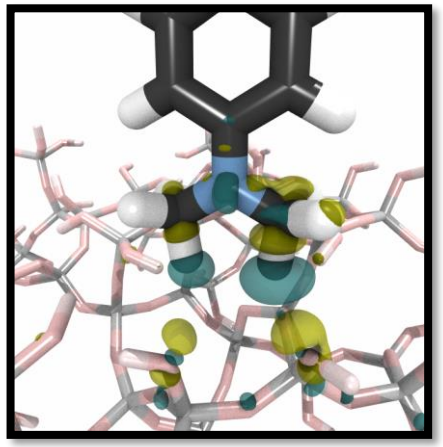
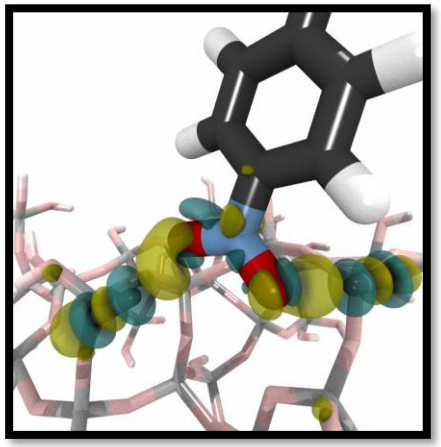
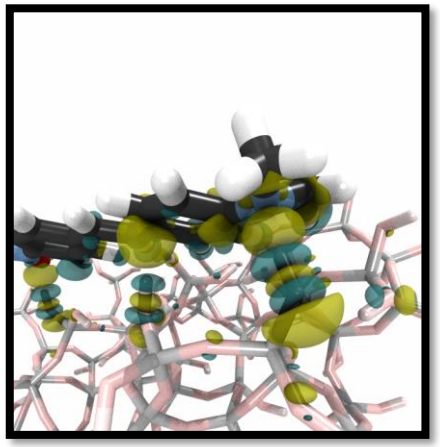
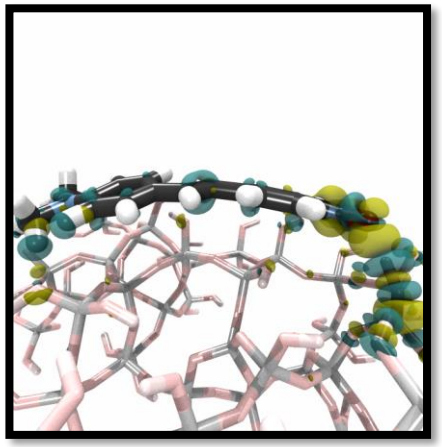
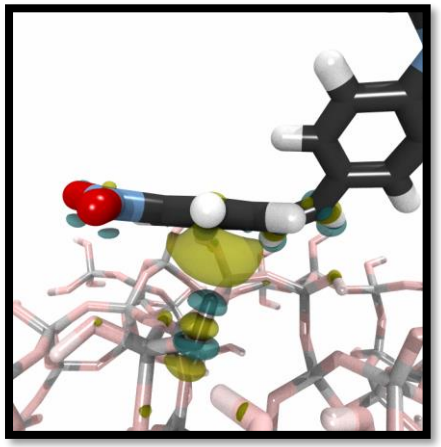



Vörös, D., Angeletti, A., Franchini, C., Mai, S., & González, L. (2023). Adsorption of 4-(N, N-Dimethylamino)-4′-nitrostilbene on an Amorphous Silica Glass Surface. *The Journal of Physical Chemistry C*, *127*(47), 22964-22974.

# Interaction examples

Interaction energy/eV: $E_{G+M} - E_G - E_M$

Charge density differences: $\rho_{G+M} - \rho_G - \rho_M$ + -

| C-H···O | O-H···O | O-H··· N | bended | O-H··· π |
|---|---|---|---|---|
|  |  |  |  |  |
| -0.38 eV | -0.85 eV | -1.77 eV | -2.18 eV | -0.69 eV |

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# Goals

https://doi.org/10.1021/acs.jpcc.3c05552

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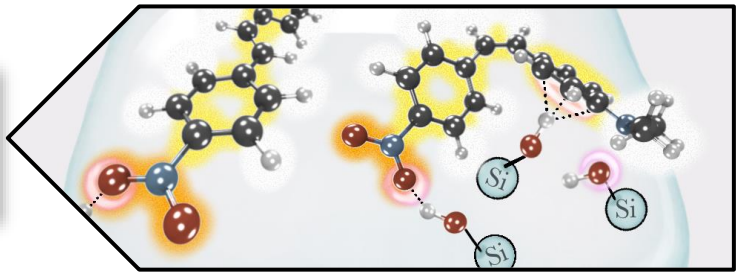


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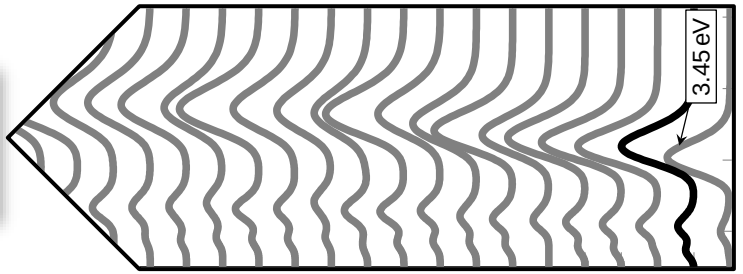


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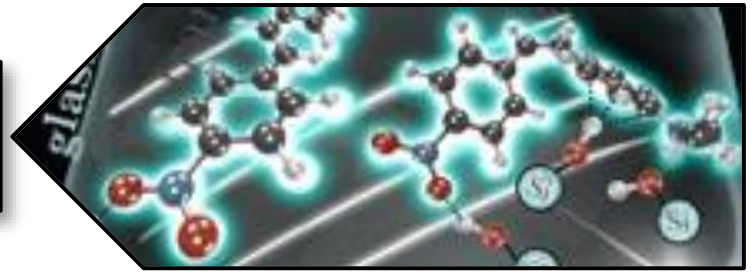
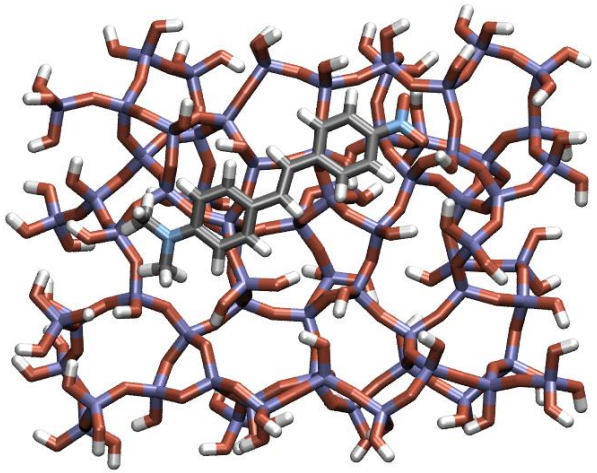


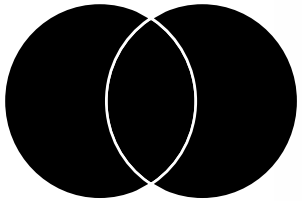
# Computational details

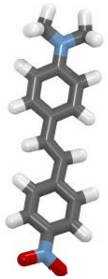
Saturate a unit cell to remove dangling bonds and to obtain cluster

Single point calculations at TD-CAM-B3LYP/def2-SVP with TDA

Gaussian convolution to get absorption spectrum







In real space & orthonormal MO basis

One-electron transition density matrix

$$\gamma_{I0}(r_h, r_e) = \sum_{pq} \gamma_{pq}^{0I} \phi_p(r_h) \phi_q(r_e)$$

$$\langle \Psi_0 | \hat{a}_p^\dagger \hat{a}_q | \Psi_I \rangle |$$

$\hat{a}_p^\dagger$: creation operator

$\hat{a}_q$ : annihilation operator

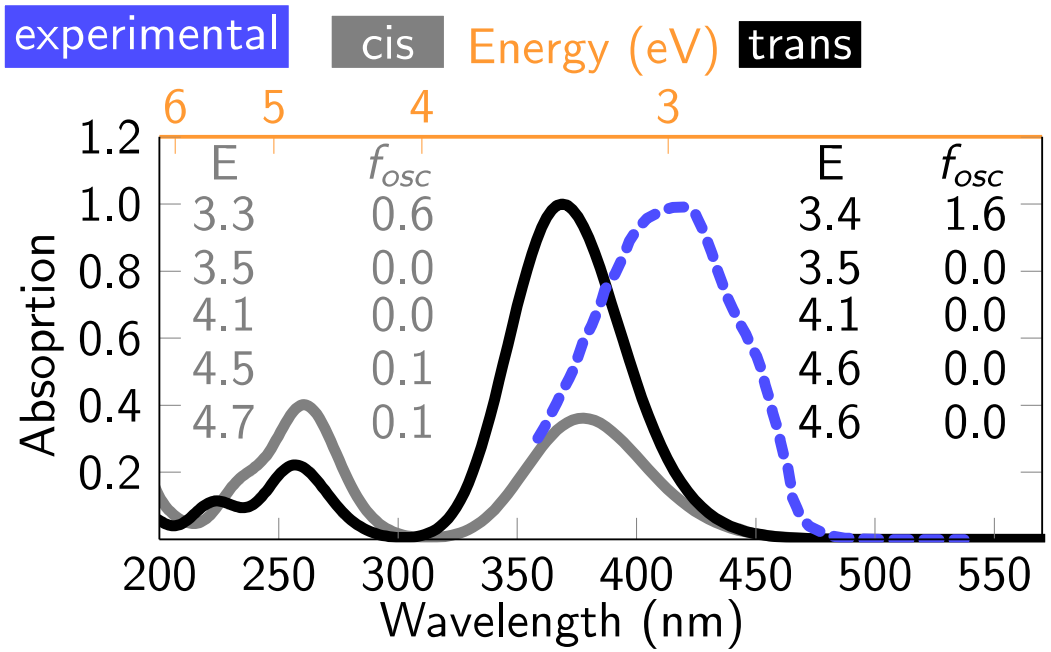
Löwdin orthogonalization

$$\Omega_{AB} = \int_A \int_B |\gamma_{0I}(r_h, r_e)|^2 dr_e dr_h$$

# Gas phase spectrum

Intense absorption band at low energy (~3.3 eV)

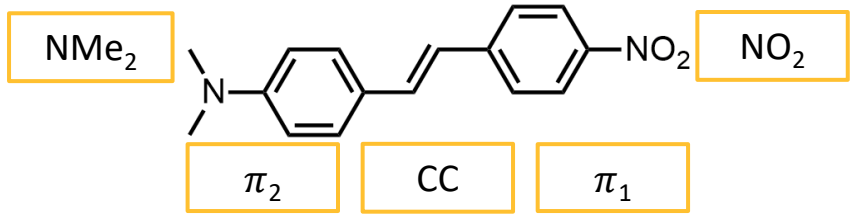
Separated from higher bands (like in experimental)

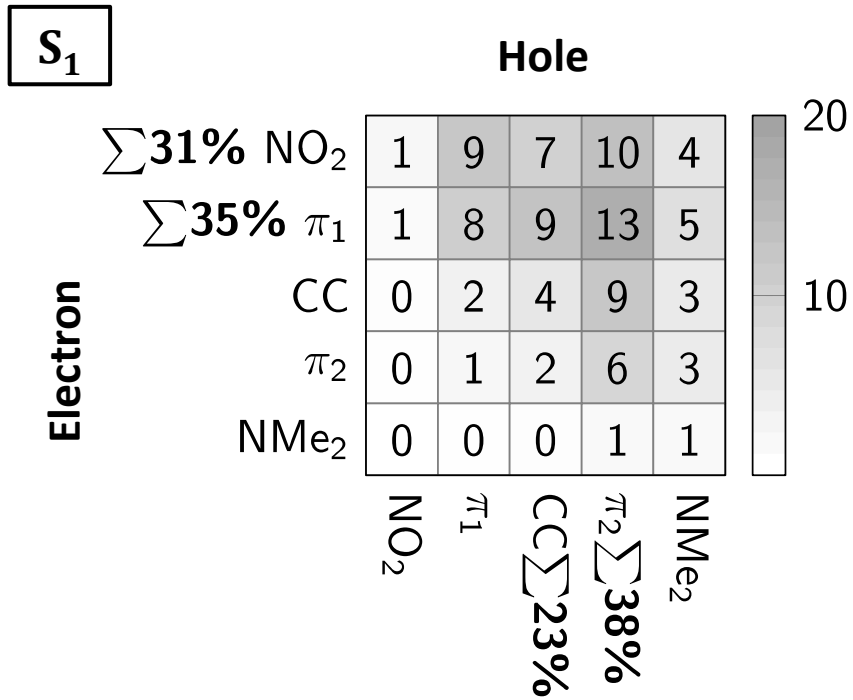


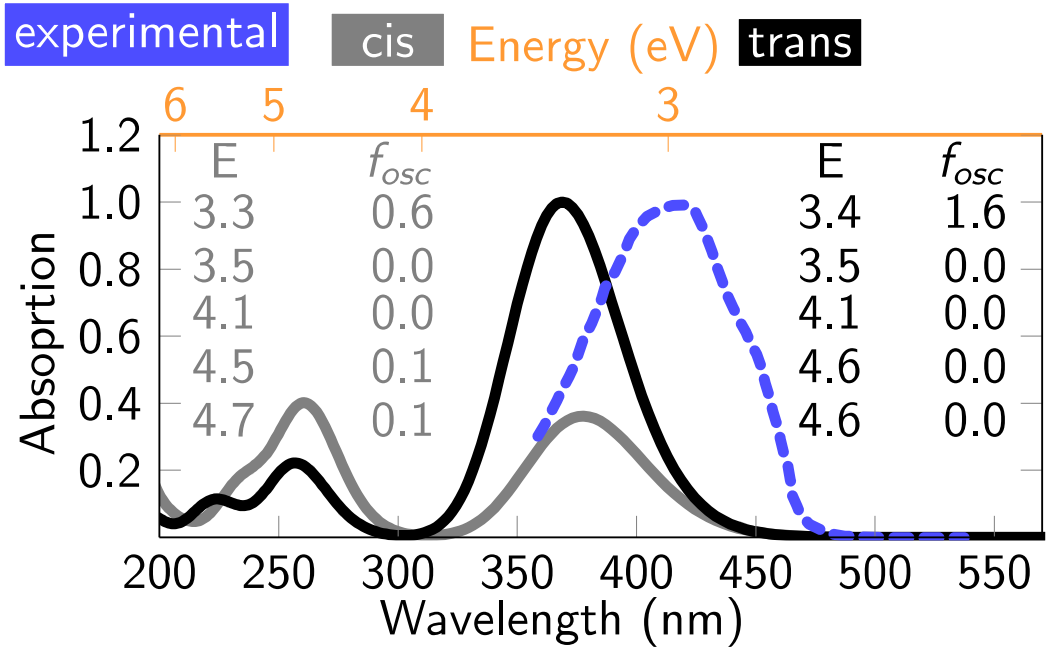

Vörös, D., F. Proché, C., Mai, S., & González, L. (2024). Hydrogen bonding to the electron accepting group controls the absorption spectrum of a push--pull stilbene adsorbed on amorphous silica. *accepted*

# Gas phase spectrum

$S_1$ highest oscillator strength: excitation from $\pi_2$ and CC to $\pi_1$ and $NO_2$ (CT=0.84)



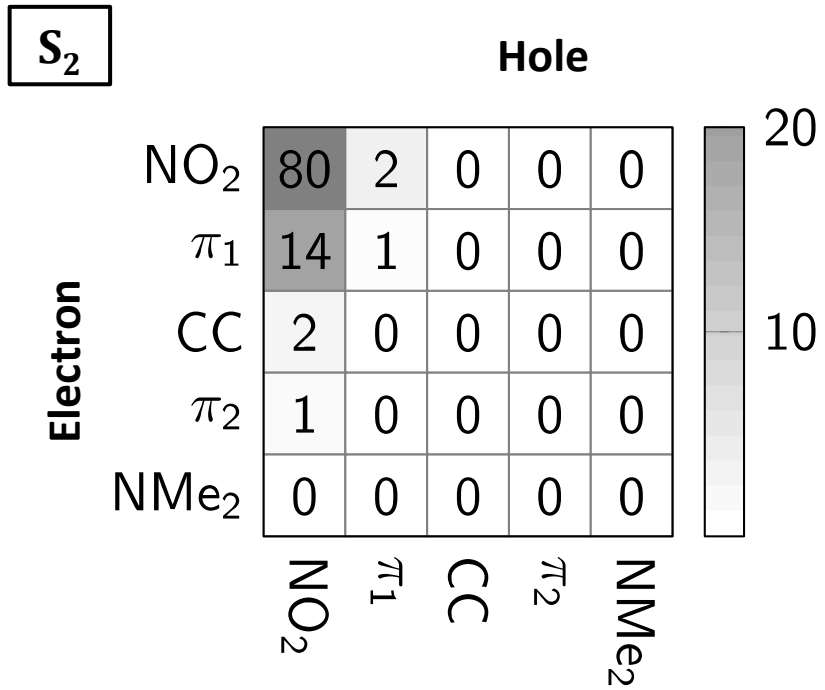



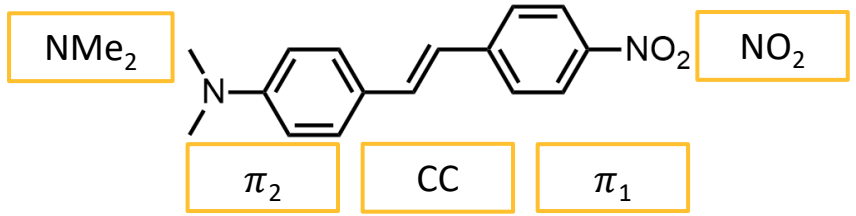



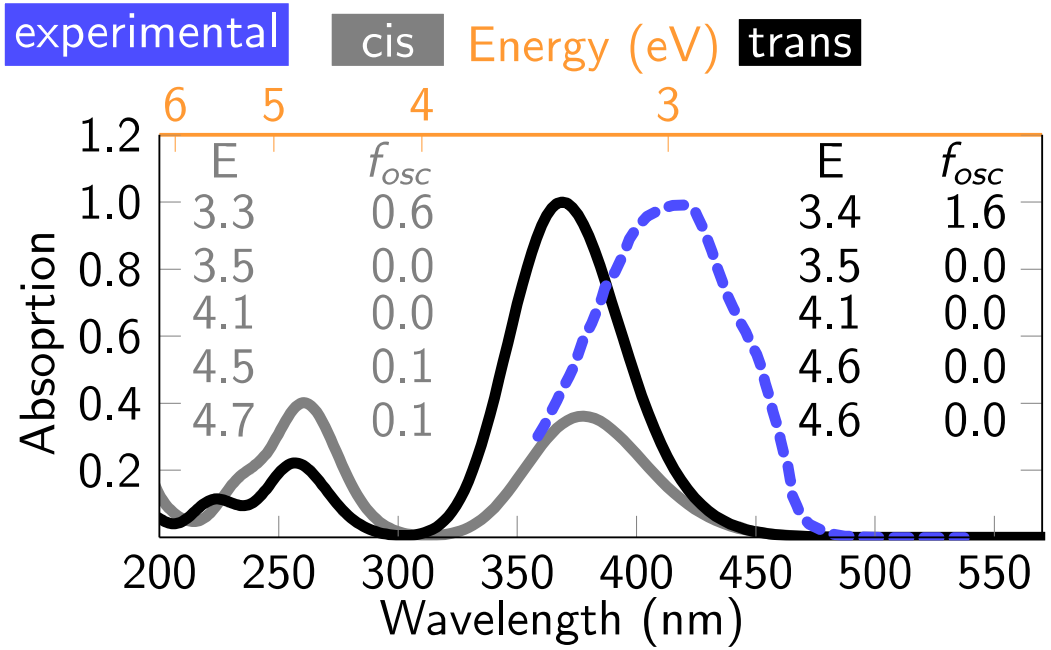
# Gas phase spectrum

$S_1$ highest oscillator strength: excitation from $\pi_2$ and CC to $\pi_1$ and $NO_2$ (CT=0.84)

$S_2$ and $S_3$ are dark $n\pi^*$ localized excitations (CT=0.19)



# Variety in the spectra

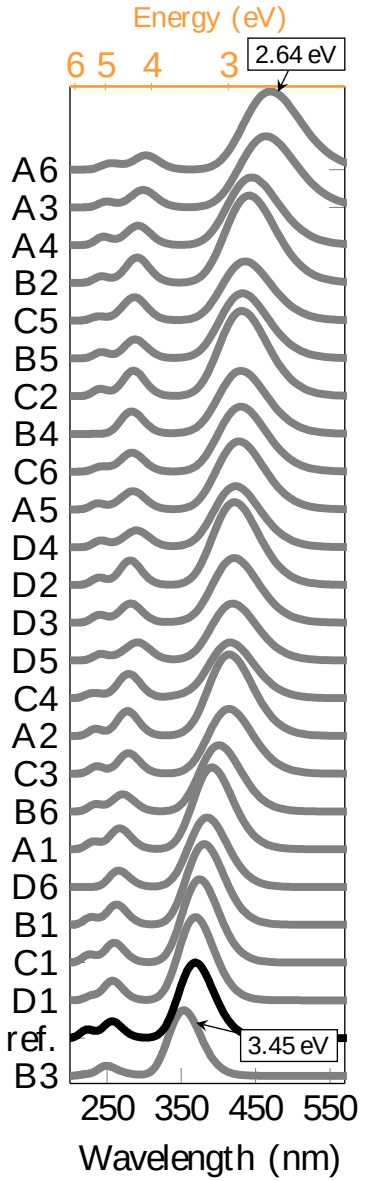
Bride range of spectral shifts

Position of first bright CT state varies ~0.8 eV (trans) and 1.2 eV (cis)

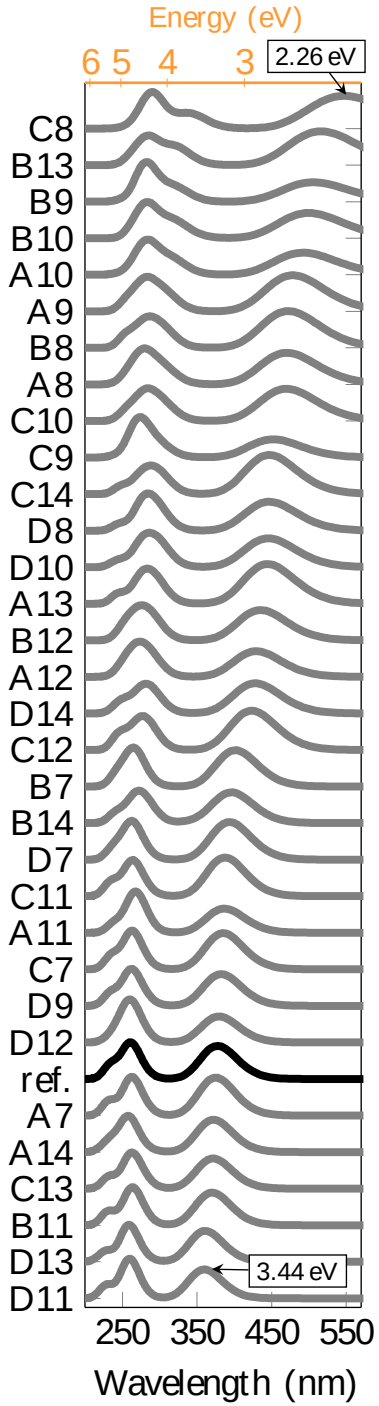
Intensity of bands varies

Significant effect on electronic excitation

trans-DANS

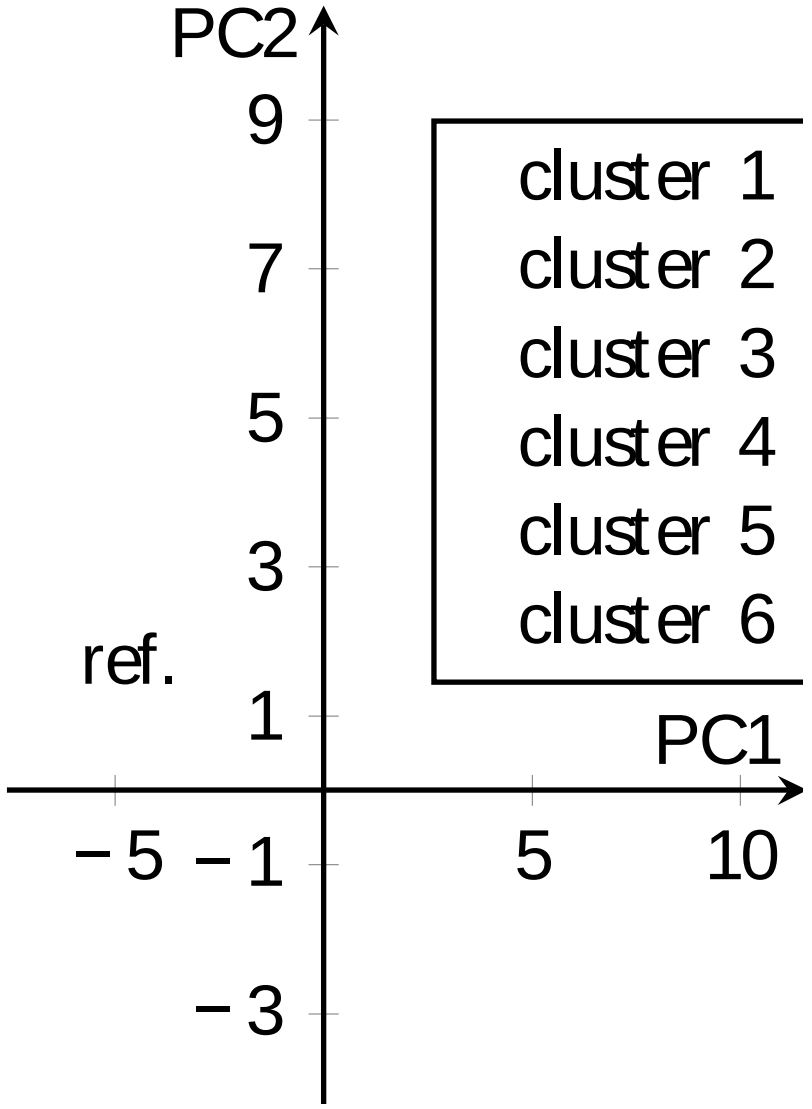



cis-DANS



# K-Means clustering ONLY with electron-hole correlation matrix

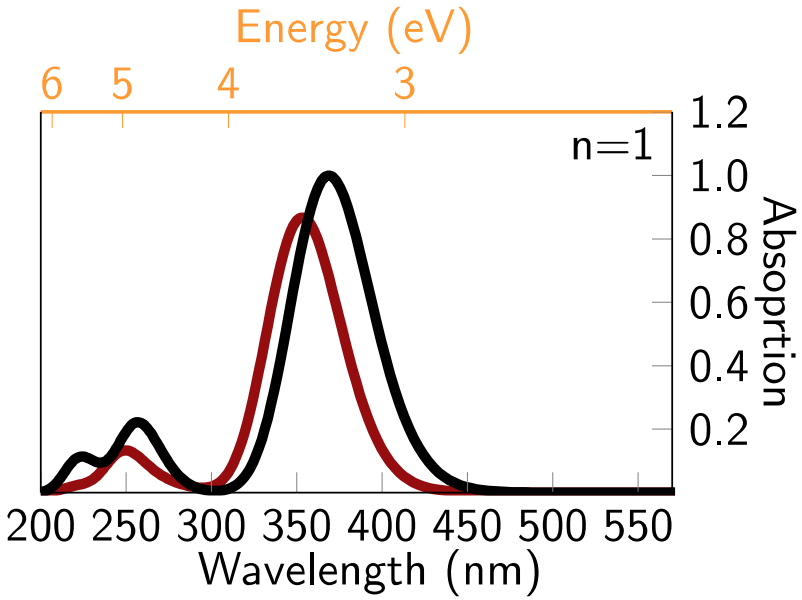
K-Means clustering → principal component analysis

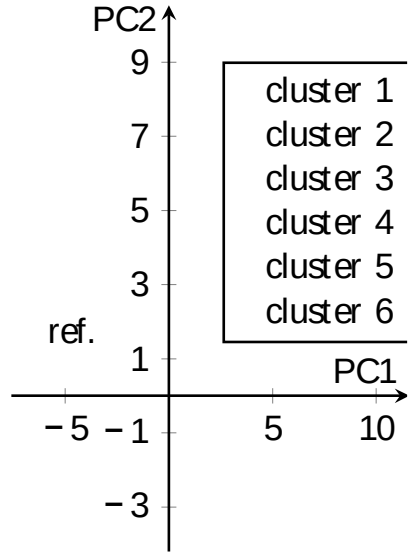


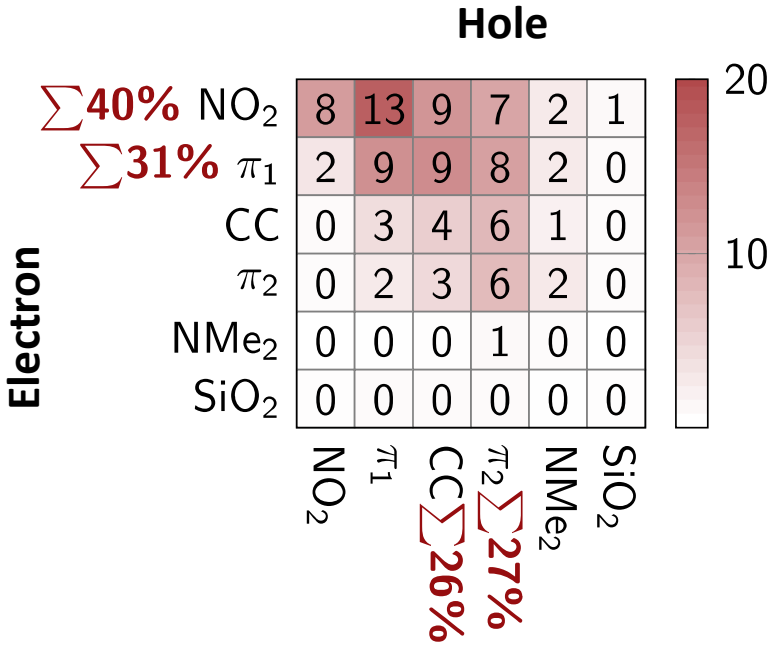
# K-Means clustering with electron-hole correlation matrix

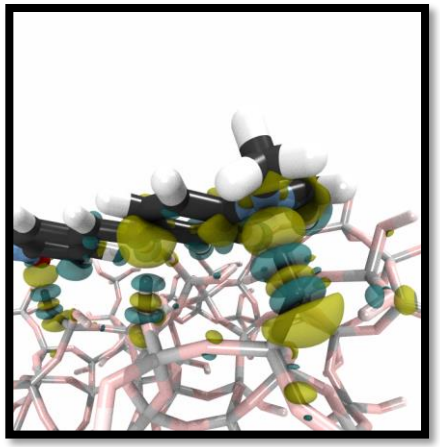
Clustering → principal component analysis

- Small blueshift
- Bright CT switches with n$\pi^*$ state → mixes with local excitation
- Decreased oscillator strength
- Parallel to surface
- O-H···N HB with $NMe_2$



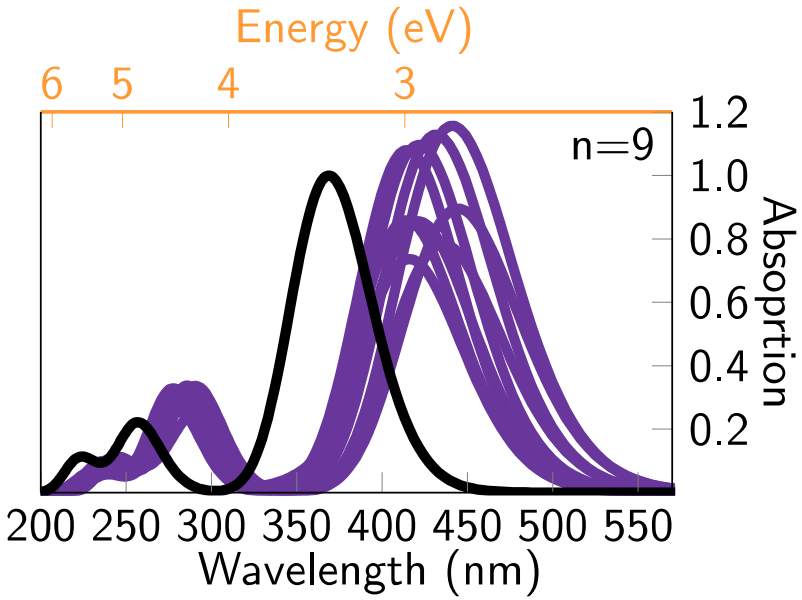



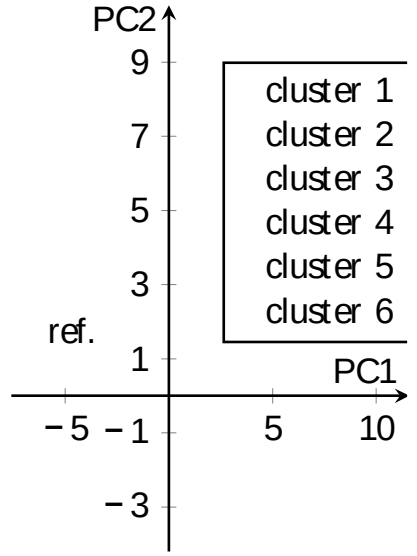



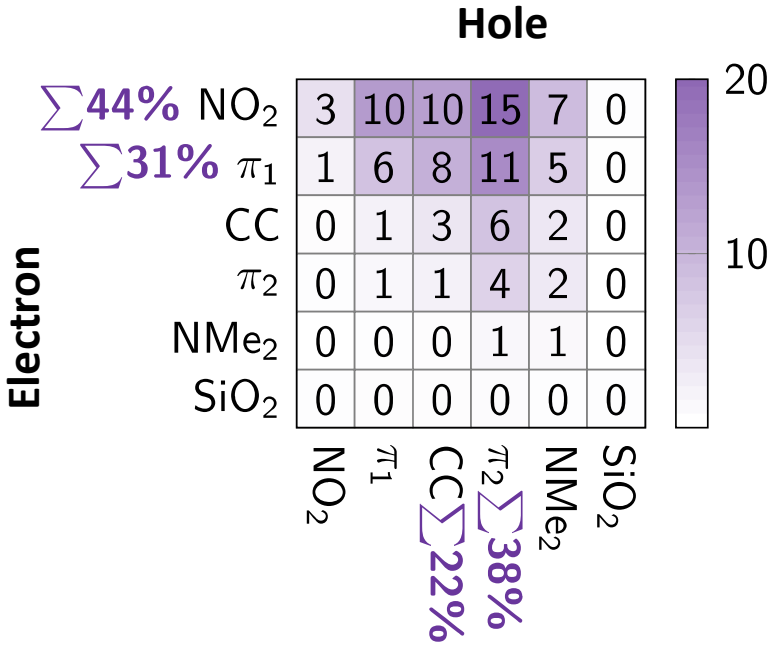
# K-Means clustering with electron-hole correlation matrix

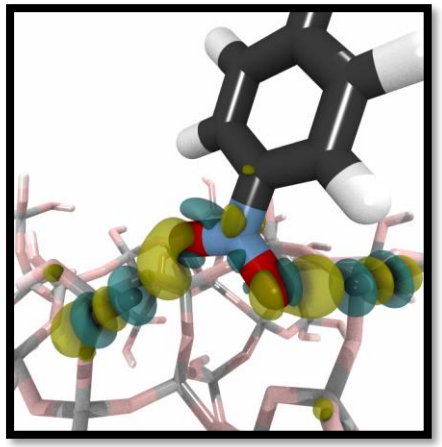
Clustering → principal component analysis

- Strong redshift
- Excited electrons drawn more to $NO_2$
- Decreased/increased oscillator strength
- Perpendicular (only $NO_2$) and side-on
- O-H···O HB with $NO_2$



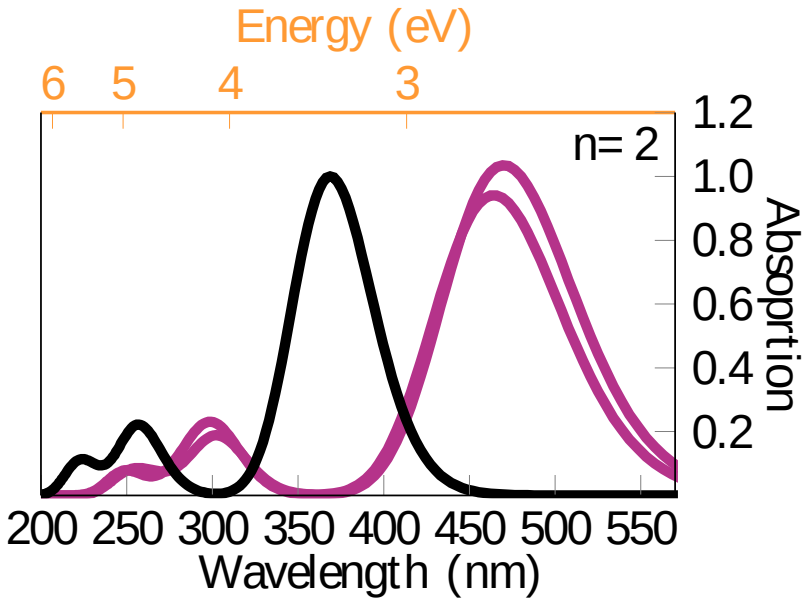



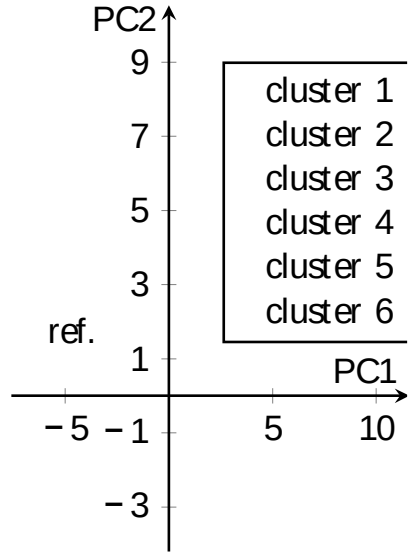



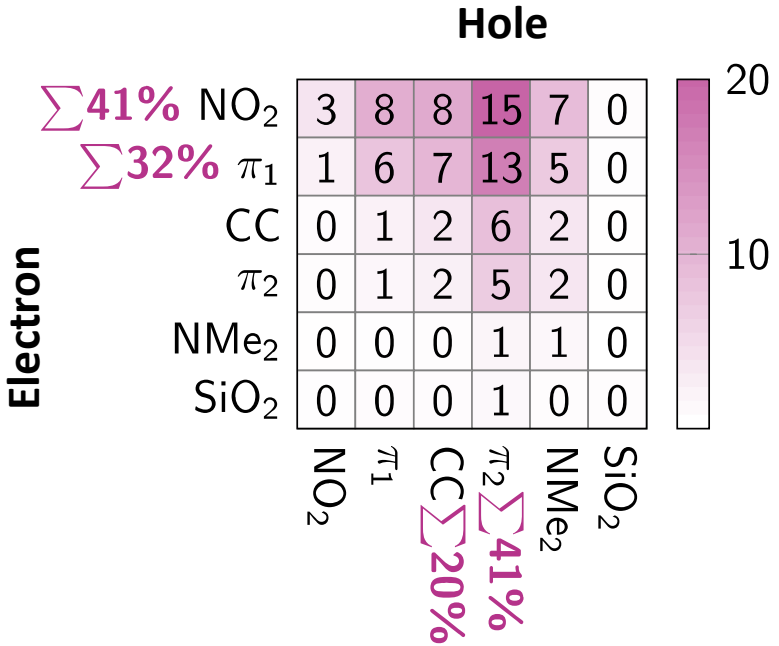
# K-Means clustering with electron-hole correlation matrix

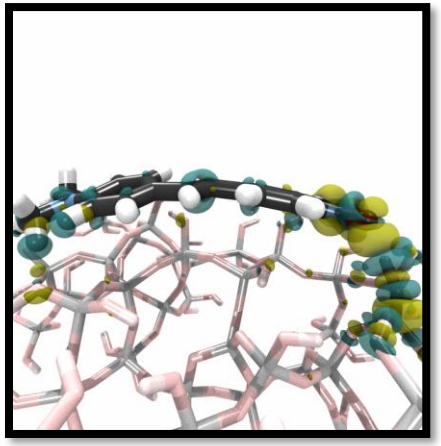
Clustering → principal component analysis

- Strongest redshift
- Excited electrons drawn more to $NO_2$
- Decreased oscillator strength
- Parallel & bended
- O-H···O HB with $NO_2$
- strong involvement of glass



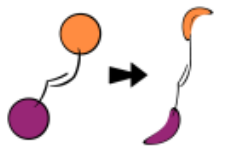
# Decomposition analysis

Molecule optimized in gas phase and spectrum in gas phase

Molecule optimized with glass and glass removed

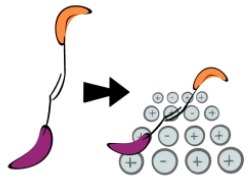
Molecule optimized with glass and glass replaced by point charges

Molecule optimized with glass and full QM



deformed − reference

" deformation"



charges − deformed

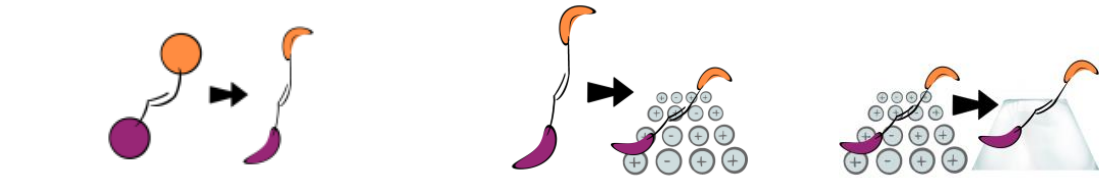
" electrostatic"

full − charges

" polarization"

# Decomposition analysis

+ -



deformed − reference

" deformation"

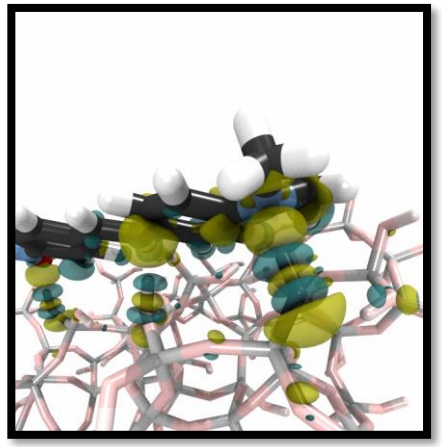
charges − deformed

" electrostatic"

full − charges

" polarization"

O-H··· N



Reduced the electron donor capacity of $NMe_2$

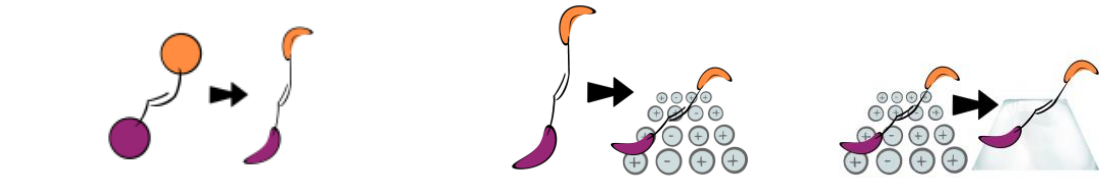
Reduces CT character (increased localization on the nitrophenyl)

Larger part of interaction is from electrostatic part

Blueshift

# Decomposition analysis

+ -



deformed − reference

" deformation"

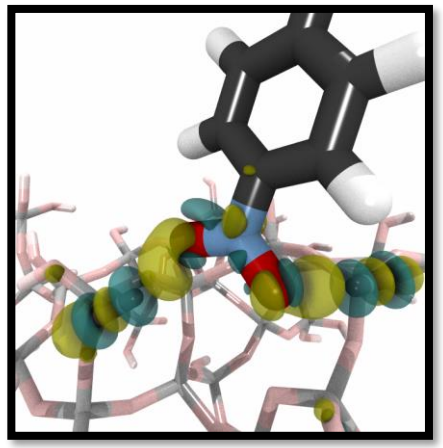
charges − deformed

" electrostatic"

full − charges

" polarization"

O-H···O



Stabilizing the excited electron on $NO_2$

Enhances push-pull properties (increased CT)

Large part of interaction is from electrostatic part

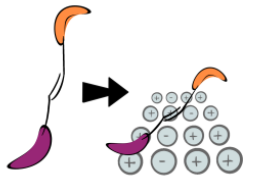
Strong redshift

# Decomposition analysis

+ -

deformed − reference

" deformation"



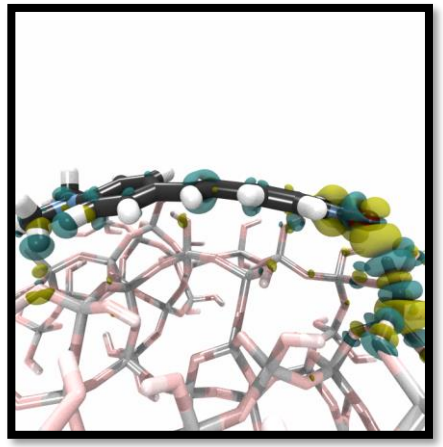
charges − deformed

" electrostatic"

full − charges

" polarization"

Parallel



Can lead to even stronger redshift

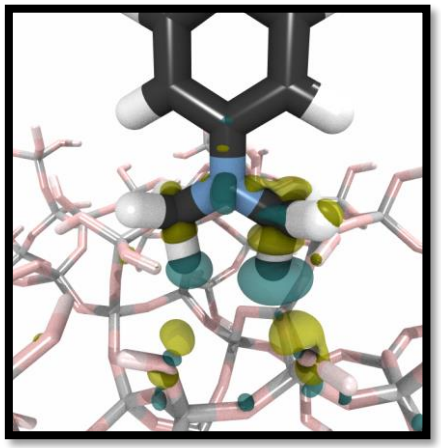
Deformation leads to mixing of bright $\pi\pi^*$ state and dark $n\pi^*$

Electrostatic interaction leads to again demixing

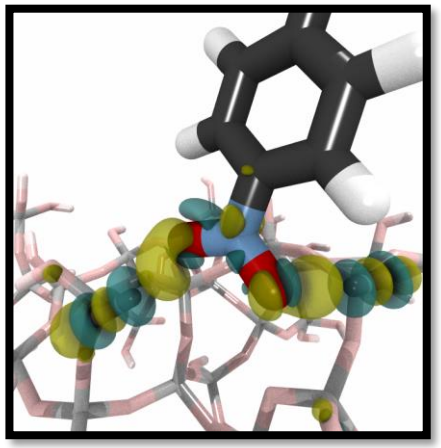
Parallel orientation leads to decreased oscillator strength (- polarization)

# Conclusion

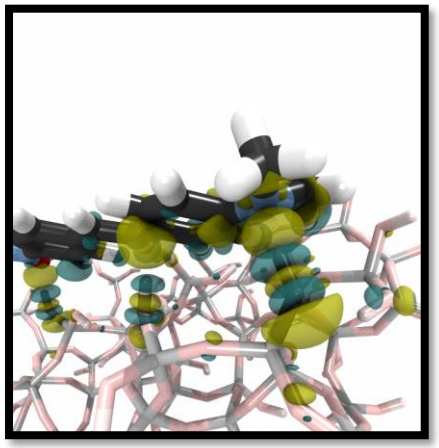
C-H···O



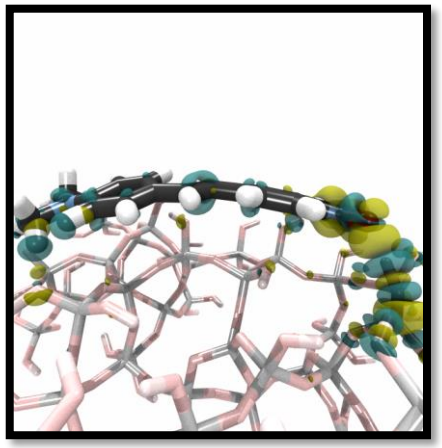
O-H···O



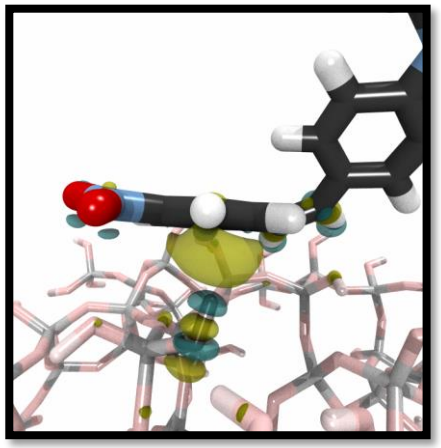
O-H··· N



bended



O-H··· π



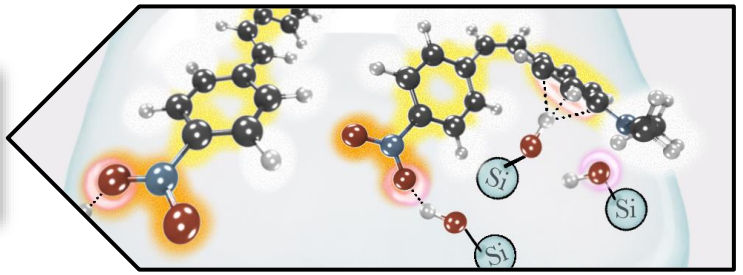
The strongest interaction, HB to $NO_2$ has the largest effect

HB reinforces the push-pull effect → redshift

# Goals

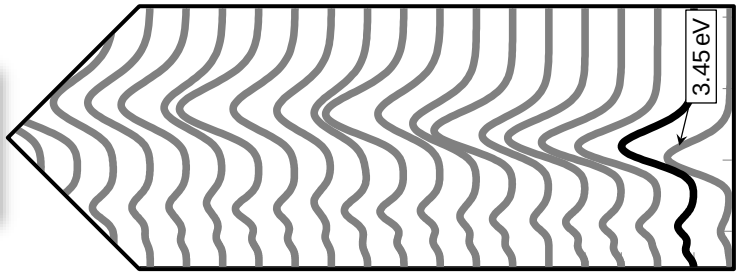
https://doi.org/10.1021/acs.jpcc.3c05552

How does the molecule adsorb on the glass? Stable and unstable orientations?

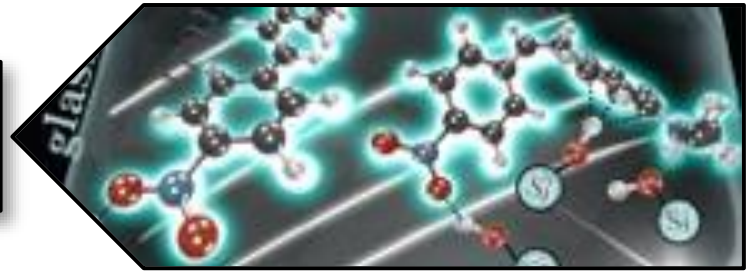



Accepted and soon online

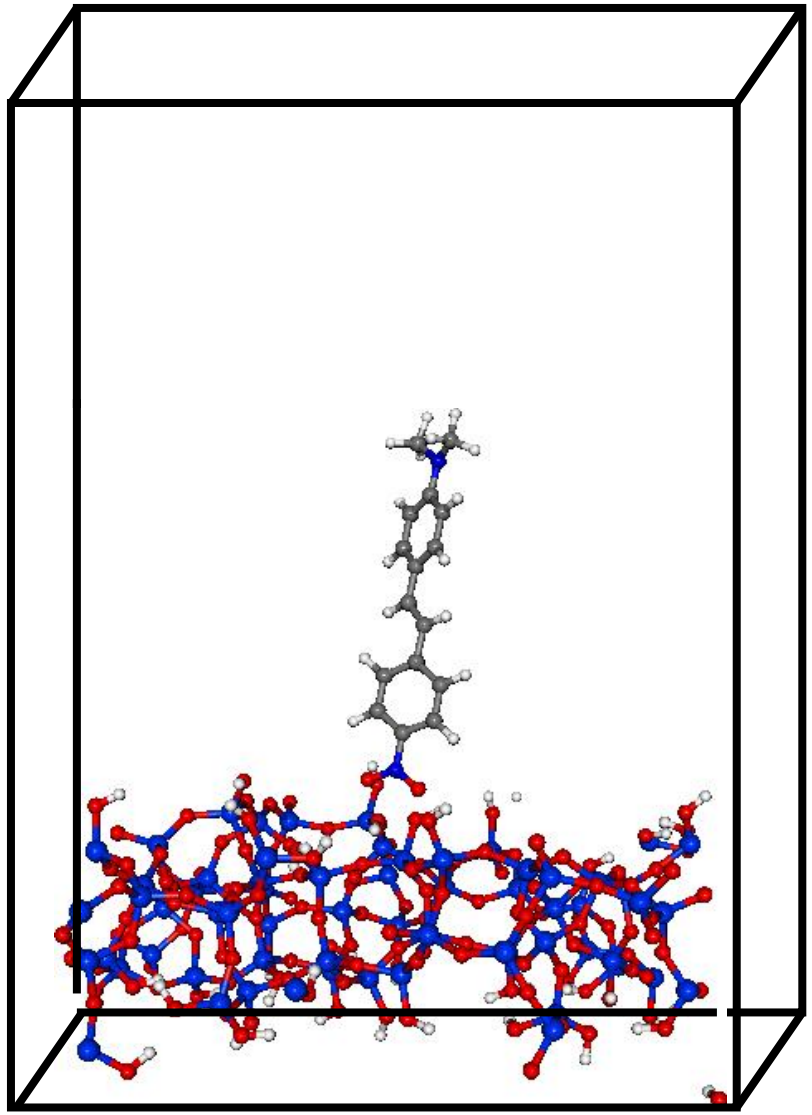
How does the absorption spectrum vary depending on the adsorption modes?




How does the nonradiative vs. radiative ratio change upon adsorption?

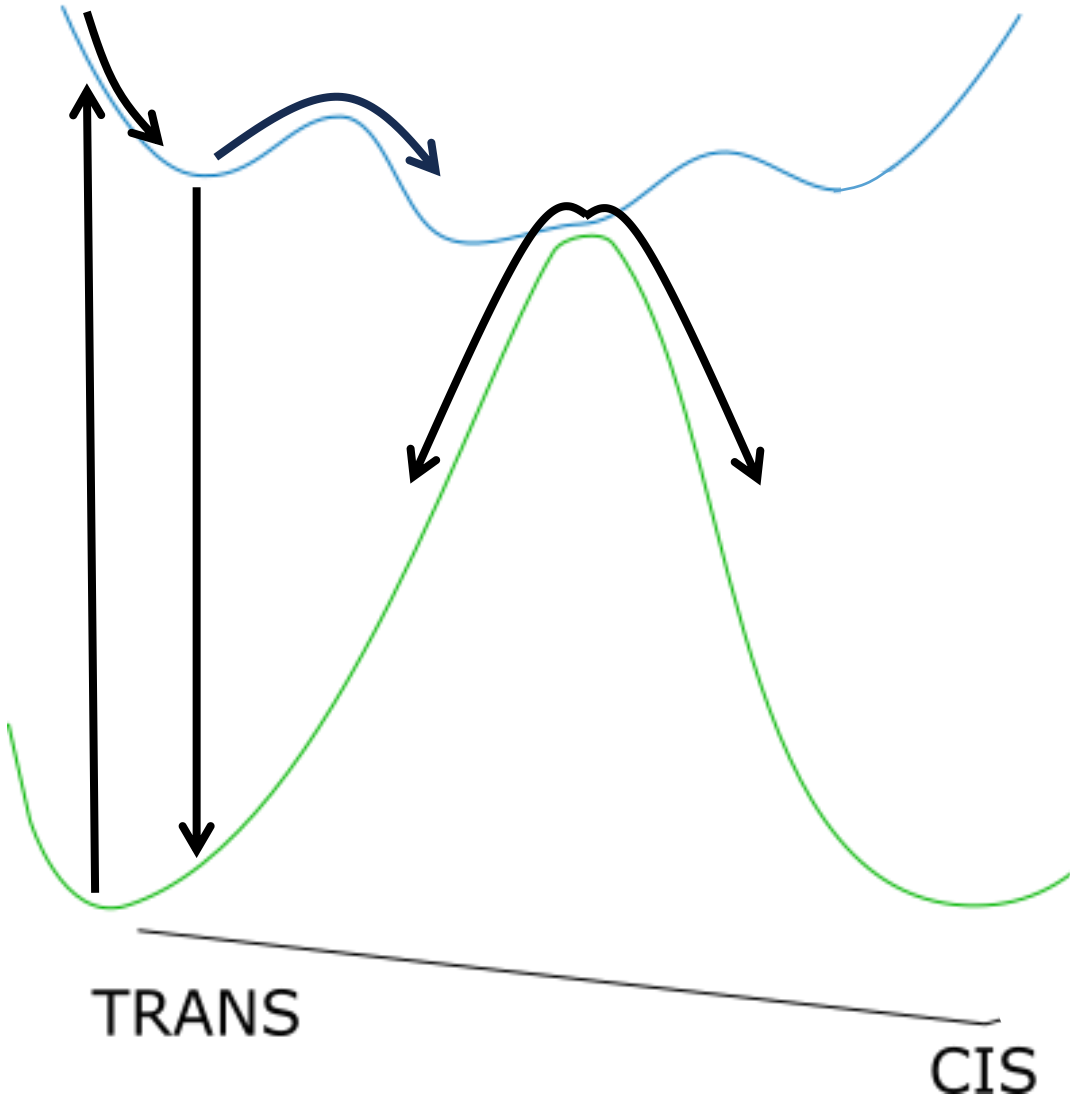


# 1st Challenge: Solid state with big unit cell

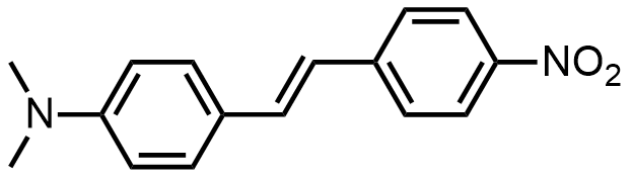


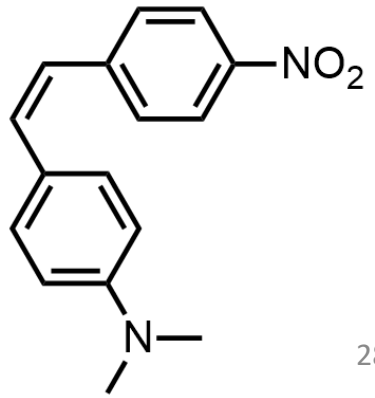
- Can we do periodic system for the excited state dynamics?
- What alternatives are?

# 2nd Challenge: Conical intersection with ground state




- We need multireference method
- But it should not be to expensive



# Thank you for your attention!

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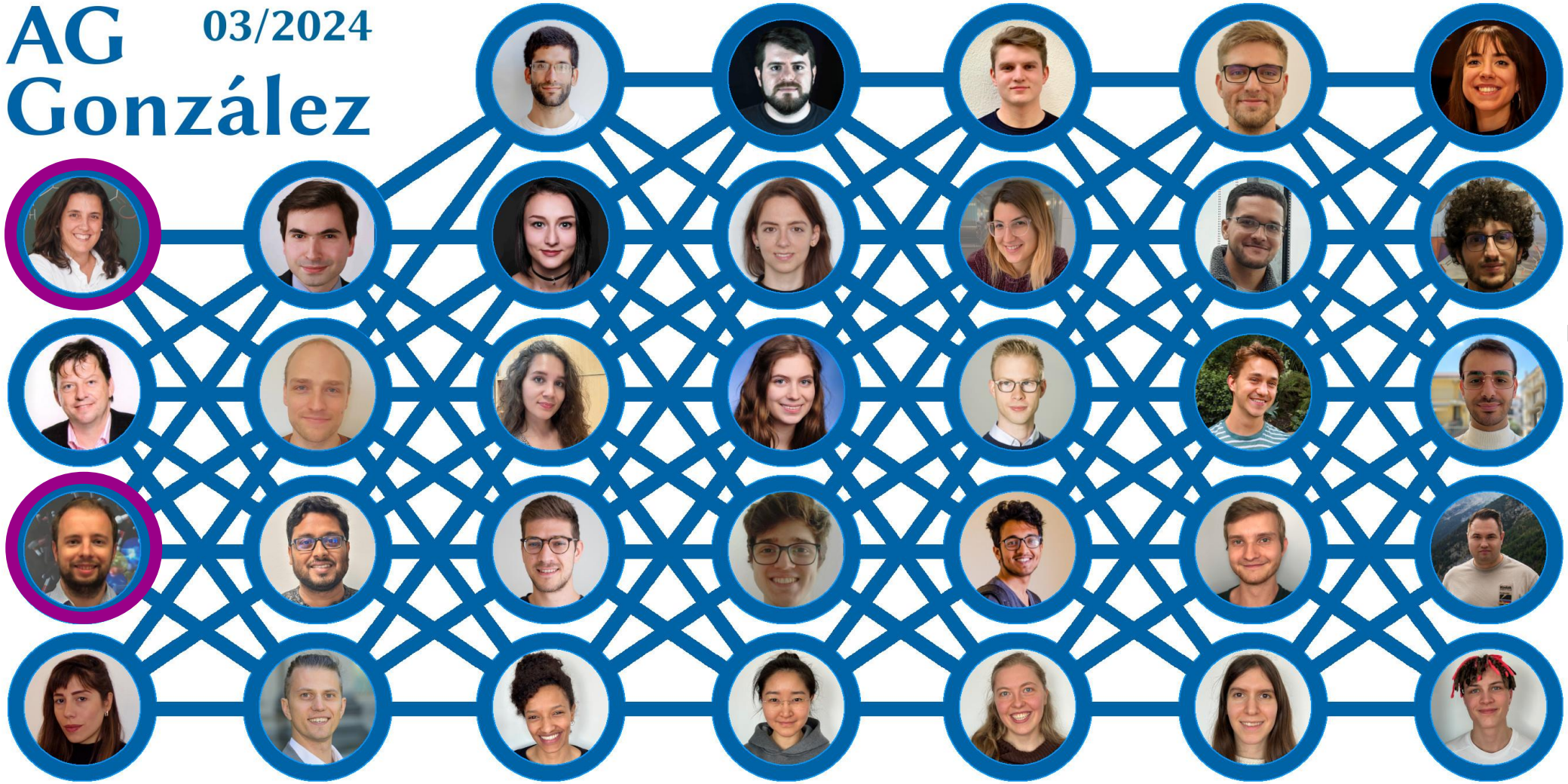


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