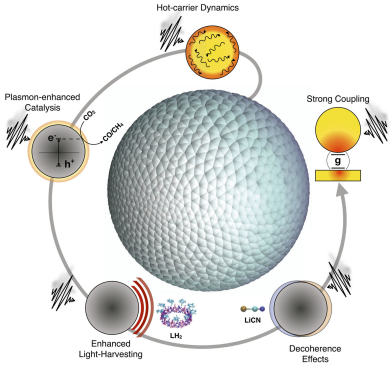
# Recent advances in modelling plasmon-assisted hot-carrier dynamics

**Emanuele Coccia**

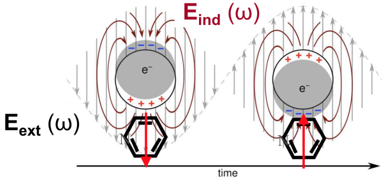
Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Giorgieri 1, 34127, Trieste

VISTA seminar

# Molecular plasmonics




- Collective electron excitations in a nanoparticle (NP)
- Au, Ag, ...
- Exceptional tunable (size, shape, material) optical properties
- Sensitivity and selectivity
- Enhancement or quenching of molecular absorption, ...



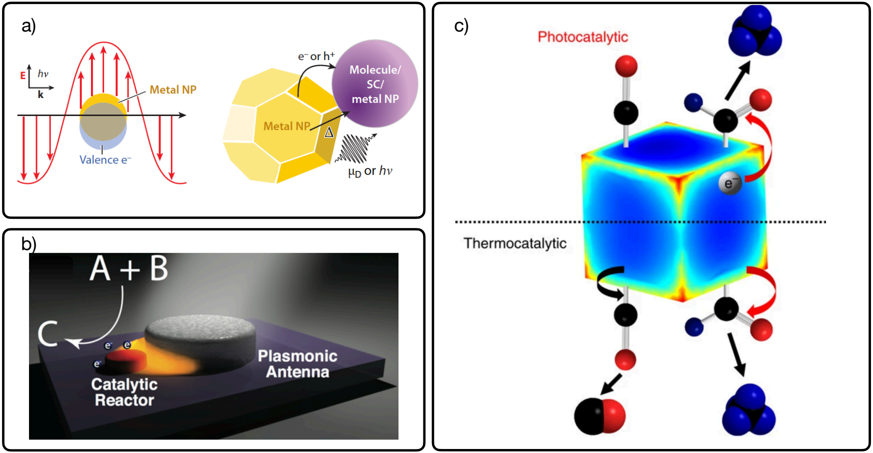

$$\mathbf{E}_{\mathbf{tot}}(\omega) = \mathbf{E}_{\mathbf{ext}}(\omega) + \mathbf{E}_{\mathbf{ind}}(\omega)$$

$$|\mathbf{E}_{\mathrm{tot}}| >> |\mathbf{E}_{\mathbf{ext}}|$$


R. P. Van Duyne, *Science*, **306**, 985 (2004)
A. Lauchner *et al.*, *Nano Lett.*, **15**, 6208 (2015)
S. Ezendam *et al.*, ACS Energy Lett., **7**, 778 (2022)

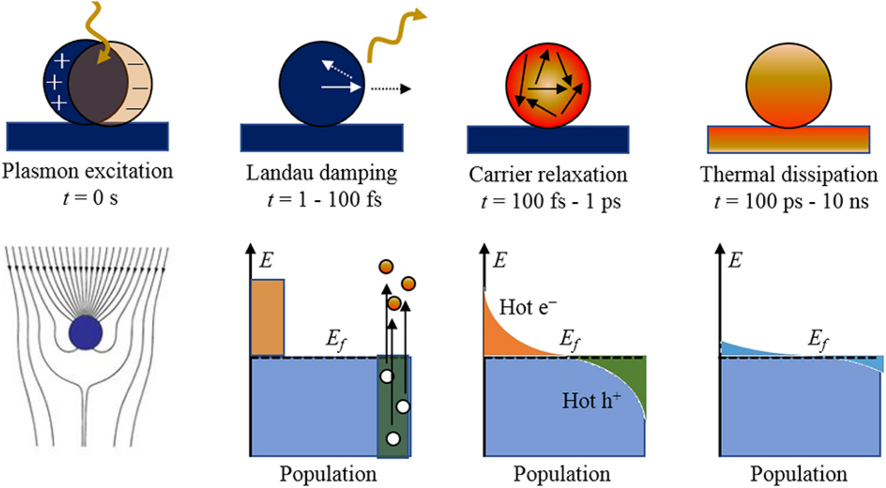
# Plasmon-mediated photocatalysis

# Plasmon-mediated photocatalysis



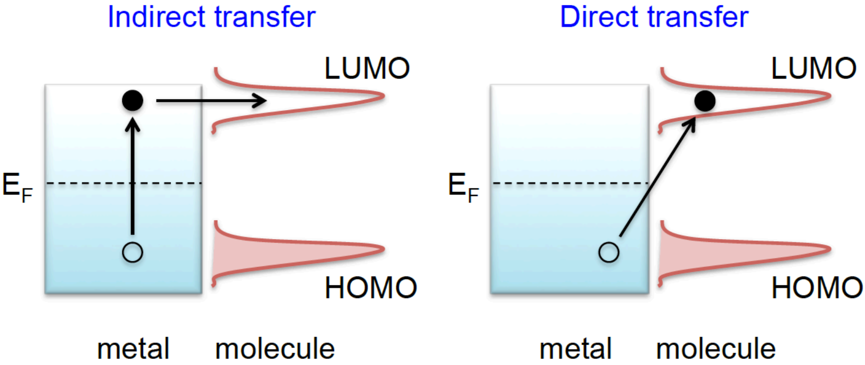

D. F. Swearer *et al.*, *PNAS*, **113**, 8916 (2016)
X. Zhang, X. Li, D. Zhang, N. Q. Su, W. Yang, H. O. Everitt and J. Liu, *Nat. Commun.*, **8**, 14542 (2017)
J. M. P. Martirez, J. L. Bao and E. A. Carter, *Annu. Rev. Phys. Chem.*, **72**, 99 (2021)

# Hot-carrier generation



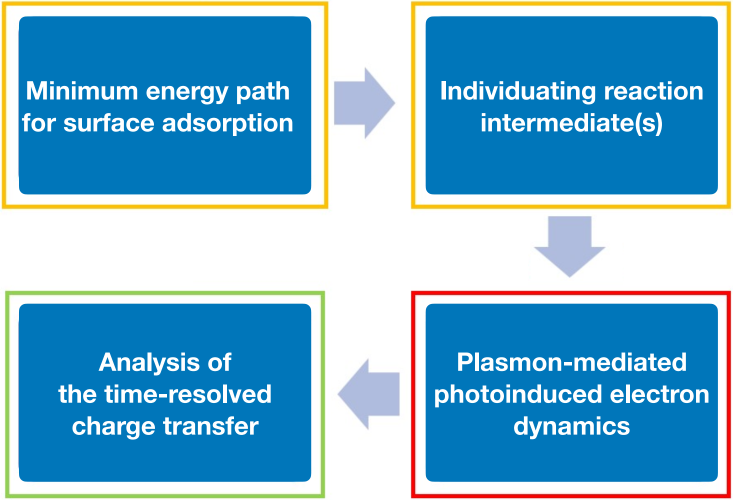

V. Kumar *et al.*, *Front. Chem.*, **7**, 299 (2019)

# Hot-carrier generation

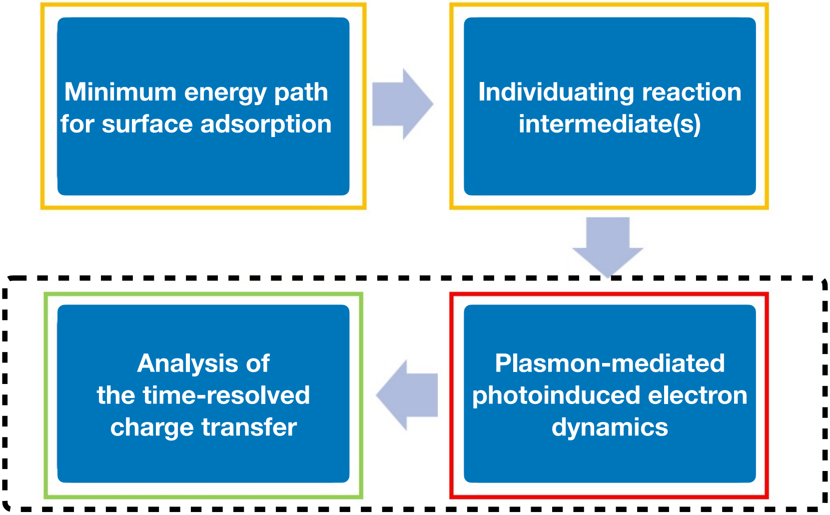



V. Kumar, T. P. Rossi, M. Kuisma, P. Erhart and D. J. Norris, *Faraday Discuss.*, **214**, 189 (2019)

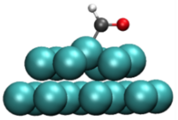
# Plasmon-mediated photocatalysis: modelling

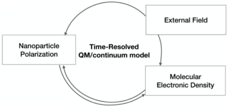


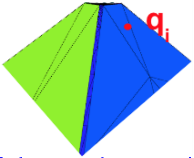
# Plasmon-mediated photocatalysis: modelling



# Time-domain QM/continuum approach






## Time-dependent Schrödinger equation

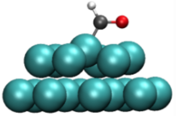
$$
\begin{aligned}
i\frac{\partial|\Psi(t)\rangle}{\partial t} &= \hat{H}(t)|\Psi(t)\rangle \\
\hat{H}(t) &= \hat{H}_0 - \vec{\hat{\mu}}\vec{E}_{ext}(t) + \mathbf{q}(t)\mathbf{V} \\
|\Psi(t)\rangle &= \sum_\lambda C_\lambda(t)|\lambda\rangle \\
|\lambda\rangle &= \sum_i \sum_a d^a_{i,\lambda}|\Phi^a_i\rangle
\end{aligned}
$$

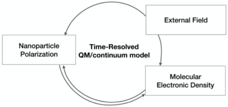
## EOM for surface charges

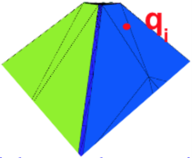
$$
\begin{aligned}
\mathbf{q}(\omega) &= \frac{1}{2\pi} f(\omega)\mathbf{F}(\omega) \\
f(\omega) &= \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} \\
\mathbf{F}(\omega) &= -[\mathbf{AD}^*\mathbf{q}(\omega) \\
&+ \mathbf{S}^{-1}(2\pi\mathbf{I}+\mathbf{DA})\mathbf{V}(\omega)] \\
\ddot{\mathbf{q}}(t) &= -\gamma\dot{\mathbf{q}}(t) - \mathbf{Q}_\omega\mathbf{q}(t) + \mathbf{Q}_f\mathbf{q}(t)
\end{aligned}
$$

Real-time simulations with polarizable continuum model (RT-PCM-NP)


S. Pipolo and S. Corni, *J. Phys. Chem. C*, **120**, 28774 (2016)
EC and S. Corni, *J. Chem. Phys.*, **151**, 044703 (2019)
G. Dall'Osto, G. Gil, S. Pipolo and S. Corni, *J. Chem. Phys.*, **153**, 184114 (2020)
EC, J. Fregoni, C. A. Guido, M. Marsili, S. Pipolo and S. Corni, *J. Chem. Phys.*, **153**, 200901 (2020)






## Time-dependent Schrödinger equation

$$
\begin{aligned}
i\frac{\partial|\Psi(t)\rangle}{\partial t} &= \hat{H}(t)|\Psi(t)\rangle \\
\hat{H}(t) &= \hat{H}_0 - \vec{\hat{\mu}}\vec{E}_{ext}(t) + \mathbf{q}(t)\mathbf{V} \\
|\Psi(t)\rangle &= \sum_\lambda C_\lambda(t)|\lambda\rangle \\
|\lambda\rangle &= \sum_i\sum_a d^a_{i,\lambda}|\Phi^a_i\rangle
\end{aligned}
$$

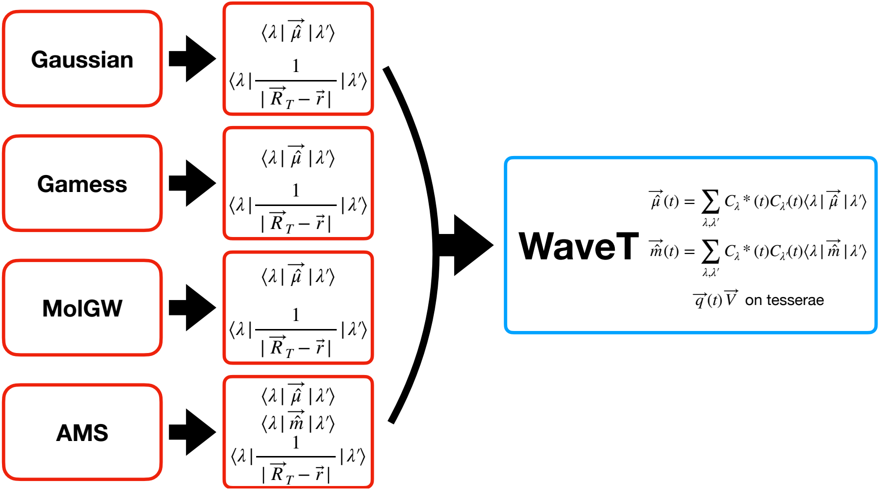
## EOM for surface charges

$$
\begin{aligned}
\mathbf{q}(\omega) &= \frac{1}{2\pi} f(\omega)\mathbf{F}(\omega) \\
f(\omega) &= \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} \\
\mathbf{F}(\omega) &= -[\mathbf{A}\mathbf{D}^*\mathbf{q}(\omega) \\
&+ \mathbf{S}^{-1}(2\pi\mathbf{I}+\mathbf{D}\mathbf{A})\mathbf{V}(\omega)] \\
\ddot{\mathbf{q}}(t) &= -\gamma\dot{\mathbf{q}}(t) - \mathbf{Q}_\omega\mathbf{q}(t) + \mathbf{Q}_f\mathbf{q}(t)
\end{aligned}
$$

Real-time simulations with polarizable continuum model (RT-PCM-NP)

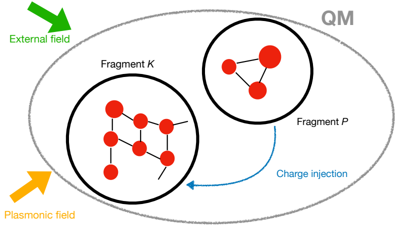
S. Pipolo and S. Corni, *J. Phys. Chem. C*, **120**, 28774 (2016)
**EC** and S. Corni, *J. Chem. Phys.*, **151**, 044703 (2019)
G. Dall'Osto, G. Gil, S. Pipolo and S. Corni, *J. Chem. Phys.*, **153**, 184114 (2020)
**EC**, J. Fregoni, C. A. Guido, M. Marsili, S. Pipolo and S. Corni, *J. Chem. Phys.*, **153**, 200901 (2020)

# Time-domain QM/continuum model




**WaveT**: https://github.com/stefano-corni/WaveT_TDPlas

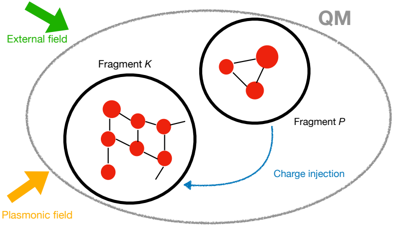
# Time-domain QM/continuum model




- $\Delta\text{PDOS}_K(t,\epsilon) \equiv \text{PDOS}_K(t,\epsilon) - \text{PDOS}(0,\epsilon)$

$$\begin{aligned}\Delta\text{PDOS}_K(t,\epsilon) &= -\sum_i^{occ} w_i^K \text{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_a^{vir} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L(\epsilon-\epsilon_i) \\ &+ \sum_a^{vir} w_a^K \text{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_i^{occ} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i)\end{aligned}$$

# Time-domain QM/continuum model




- $\Delta \mathrm{PDOS}_K(t,\epsilon) \equiv \mathrm{PDOS}_K(t,\epsilon) - \mathrm{PDOS}(0,\epsilon)$

$$\Delta \mathrm{PDOS}_K(t,\epsilon) = -\sum_i^{occ} w_i^K \mathrm{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_a^{vir} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L(\epsilon-\epsilon_i)$$
$$+ \sum_a^{vir} w_a^K \mathrm{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_i^{occ} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i)$$

- Charge population

electron/hole: $\frac{1}{2}\int_{-\infty}^{\infty} \left[\Delta \mathrm{PDOS}(t,\epsilon) \pm |\Delta \mathrm{PDOS}(t,\epsilon)|\right] d\epsilon$

P. Grobas Illobre, M. Marsili, S. Corni, M. Stener, D. Toffoli and **EC**, *J. Chem. Theory Comput.*, **17**, 6314 (2021)

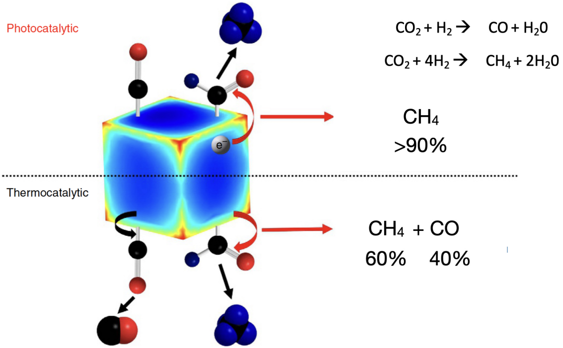
# Carbon dioxide hydrogenation

ARTICLE

Received 28 Sep 2016 | Accepted 11 Jan 2017 | Published 23 Feb 2017 DOI: 10.1038/ncomms14542 OPEN

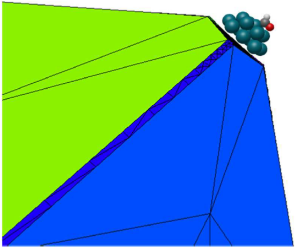
## Product selectivity in plasmonic photocatalysis for carbon dioxide hydrogenation

Xiao Zhang[1], Xueqian Li[1], Du Zhang[1], Neil Qiang Su[1], Weitao Yang[1], Henry O. Everitt[2,3] & Jie Liu[1]



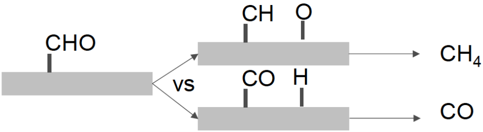

Selectivity enhancement due to hot carriers?

X. Zhang, X. Li, D. Zhang, N. Q. Su, W. Yang, H. O. Everitt and J. Liu, *Nat. Commun.*, **8**, 14542 (2017)



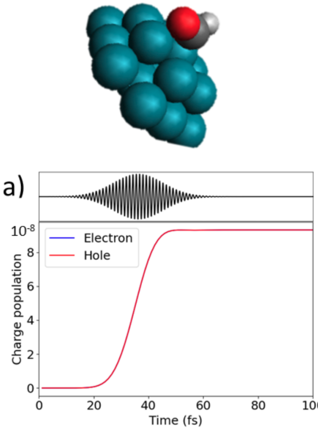
- QM portion
  - Two Rh layers from Rh(111) slab
  - CHO-$Rh_{19}$ optimized at DFT (PBE/DZ) level (AMS)
- Classical portion
  - Rh nanocube 37 nm in side (as in exp.)
  - $\epsilon(\omega)$ from exp.

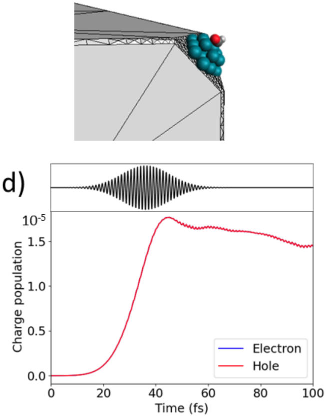
CHO dissociation is the rate-determining step




M. Vanzan, M. Marsili and S. Corni, *Catalysts*, **11**, 538 (2021)
G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# Results: nanocube effect on carrier injection




enhancement of $10^3$ with NP

change of the time profile

WaveT code for 100-fs

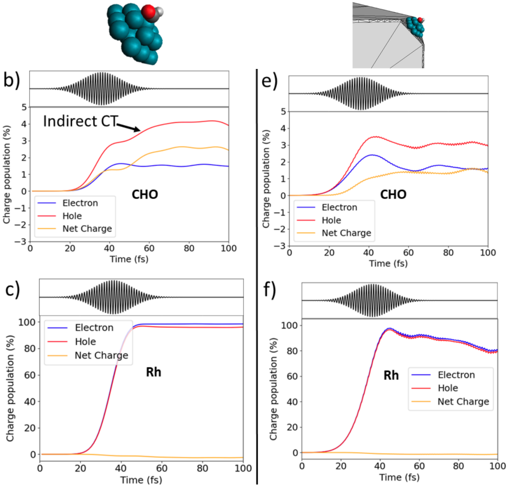
Pulse wavelength: 365 (FWHM 21 fs), weak field, linear polarization $\perp$ to the vertex

DFT+GW/BSE: PBE0/def-TZVP, $G_n W_n$ (4 iter.), static BSE kernel (455 states)

1000 td charges, clamped nuclei

G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# Results: nanocube effect on carrier injection

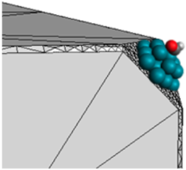


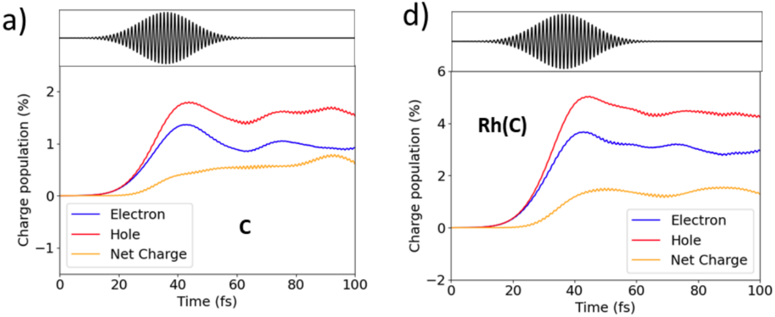

w/o NP: direct and delayed plasmon-assisted charge transfer

w NP: direct charge transfer ($10^{10}$ s$^{-1}$ hot-carrier generation)

G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

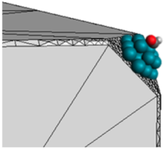
# Results: charge population on CHO

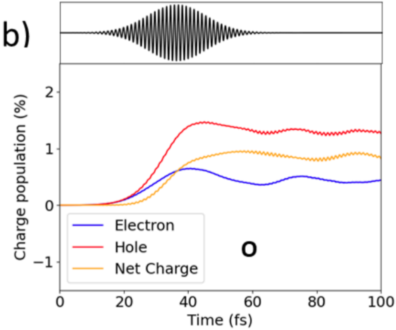


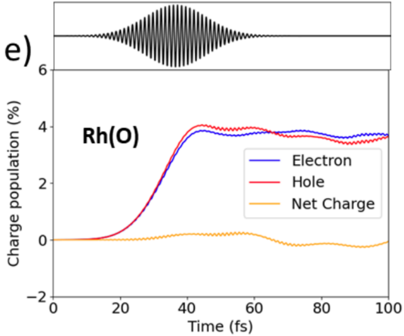



G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

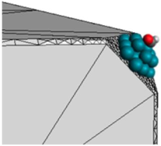
# Results: charge population on CHO



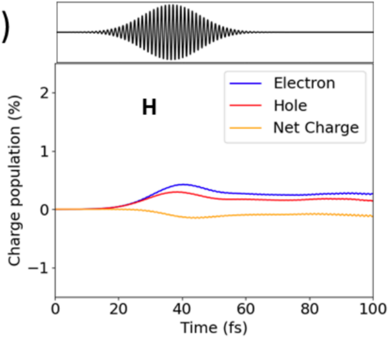



G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted



c)



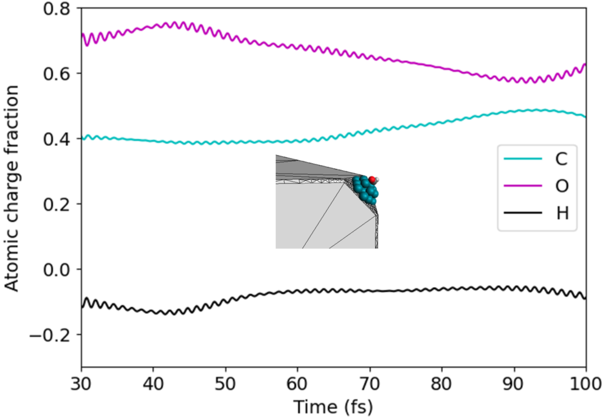

f)

| Atom | Net Charge |
| --- | --- |
| C | ↗ |
| O | ↗ |
| H | ↘ |
| Rh(C) | ↗ |
| Rh(O) | = |

Hole injection into C and O

G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

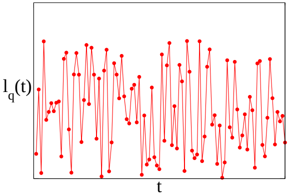
# Results: $CH_4$ favoured over CO




Electron-poor oxygen atom: CH + O

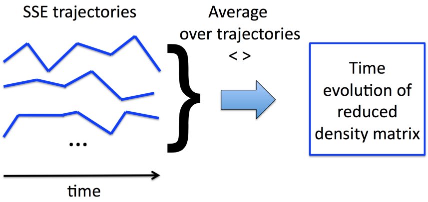
G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

$$
\begin{aligned}
i\frac{\partial}{\partial t}|\Psi(t)\rangle &= \hat{H}(t)|\Psi(t)\rangle + \sum_q l_q(t)\hat{S}_q|\Psi(t)\rangle - \frac{i}{2}\sum_q \hat{S}_q^\dagger \hat{S}_q|\Psi(t)\rangle \\
|\Psi(t)\rangle &= \sum_\lambda C_\lambda(t)|\lambda\rangle
\end{aligned}
$$



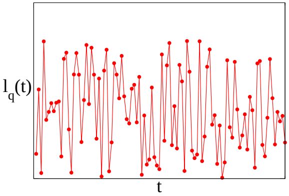

- SSE in Markovian limit

R. Biele and R. D'Agosta, *J. Phys.: Condens. Matter*, **24** 273201(2012)



# Stochastic Schrödinger equation (SSE)

$$
\begin{aligned}
i\frac{\partial}{\partial t}|\Psi(t)\rangle &= \hat{H}(t)|\Psi(t)\rangle + \sum_q l_q(t)\hat{S}_q|\Psi(t)\rangle - \frac{i}{2}\sum_q \hat{S}_q^\dagger \hat{S}_q|\Psi(t)\rangle \\
|\Psi(t)\rangle &= \sum_\lambda C_\lambda(t)|\lambda\rangle
\end{aligned}
$$

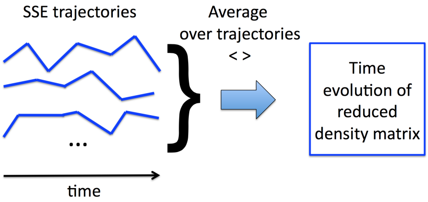



- Interaction channels $\hat{S}_q$:
  - Dephasing ($T_2$)

EC, F. Troiani and S. Corni, *J. Chem. Phys.*, **148**, 204112 (2018)
EC and S. Corni, *J. Chem. Phys.*, **151**, 044703 (2019)

- SSE in Markovian limit

R. Biele and R. D'Agosta, *J. Phys.: Condens. Matter*, **24** 273201(2012)



# SSE for analysis

Pure dephasing operator

$$
\begin{aligned}
\hat{S}_q^{\text{dep}} &= \sqrt{\gamma_q/2}\sum_p P(\lambda,\lambda')|\lambda\rangle\langle\lambda'| \\
T_2 &= \frac{1}{\gamma_q} \\
P(\lambda,\lambda') &= -1 \quad \text{if} \quad \lambda = \lambda' \\
&= 1 \quad \text{otherwise}
\end{aligned}
$$

$\Delta$PDOS applied to the SSE

$$
\begin{aligned}
\Delta\text{PDOS}_K^{\text{SSE}}(t,\epsilon) &= -\sum_i^{occ} w_i^K \text{Re}\left[\sum_{\lambda,\lambda'} \overline{C_\lambda^*(t)C_{\lambda'}(t)} \sum_a^{vir} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i) \\
&+ \sum_a^{vir} w_a^K \text{Re}\left[\sum_{\lambda,\lambda'} \overline{C_\lambda^*(t)C_{\lambda'}(t)} \sum_i^{occ} (d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i).
\end{aligned}
$$

SSE version of charge population is defined by using $\Delta\text{PDOS}_K^{\text{SSE}}(t,\epsilon)$

**EC**, F. Troiani and S. Corni, *J. Chem. Phys.*, 148, 204112 (2018)
G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# SSE for analysis

Pure dephasing operator

$$
\begin{aligned}
\hat{S}_q^{\text{dep}} &= \sqrt{\gamma_q/2}\sum_p P(\lambda,\lambda')|\lambda\rangle\langle\lambda'| \\
T_2 &= \frac{1}{\gamma_q} \\
P(\lambda,\lambda') &= -1 \quad \text{if} \quad \lambda=\lambda' \\
&= 1 \quad \text{otherwise}
\end{aligned}
$$

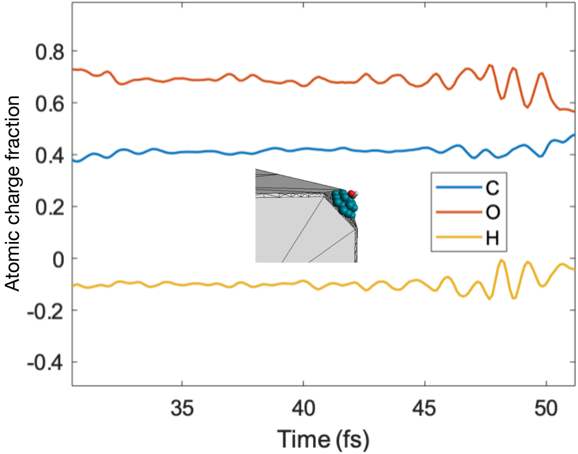
$\Delta$PDOS applied to the SSE

$$
\begin{aligned}
\Delta\text{PDOS}_K^{\text{SSE}}(t,\epsilon) &= -\sum_i^{occ} w_i^K \text{Re}\left[\sum_{\lambda,\lambda'}\overline{C_\lambda^*(t)C_{\lambda'}(t)}\sum_a^{vir}(d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i) \\
&+ \sum_a^{vir} w_a^K \text{Re}\left[\sum_{\lambda,\lambda'}\overline{C_\lambda^*(t)C_{\lambda'}(t)}\sum_i^{occ}(d_{i,\lambda}^a)^* d_{i,\lambda'}^a\right] L_\eta(\epsilon-\epsilon_i).
\end{aligned}
$$

SSE version of charge population is defined by using $\Delta\text{PDOS}_K^{\text{SSE}}(t,\epsilon)$

**EC**, F. Troiani and S. Corni, *J. Chem. Phys.*, **148**, 204112 (2018)
G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# Results: $T_2$ = 5 fs



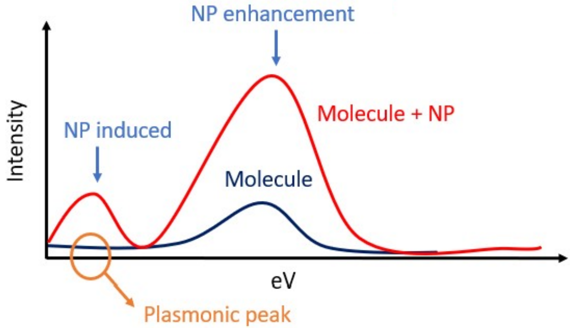

Same picture as in coherent dynamics

G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# Plasmon-enhanced circular dichroism

# Plasmon-enhanced circular dichroism

- Plasmonic systems with intrinsic chirality
- **Achiral plasmonic NPs coupled to a chiral molecule**
- Chiral arrangement of achiral plasmonic NPs

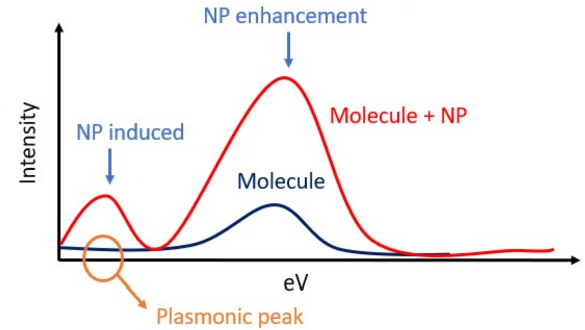



**Only electronic circular dichroism (ECD) is considered here**


A. O. Govorov, Z. Fan, P. Hernandez, J. M. Slocik and R. R. Naik, *Nano Lett.*, 10, 1374 (2010)
M. Hentschel, M. Schaferling, X. Duan, H. Giessen and N. Liu, *Sci. Adv.*, 3, e1602735 (2017)
N. S. Shahana Nizar, M. Sujith, K. Swathi, C. Sissa, A. Painelli and K. G. Thomas, *Chem. Soc. Rev.*, 50, 11208 (2021)

# Plasmon-enhanced circular dichroism

- Plasmonic systems with intrinsic chirality
- **Achiral plasmonic NPs coupled to a chiral molecule**
- Chiral arrangement of achiral plasmonic NPs




**Only electronic circular dichroism (ECD) is considered here**

A. O. Govorov, Z. Fan, P. Hernandez, J. M. Slocik and R. R. Naik, *Nano Lett.*, **10**, 1374 (2010)
M. Hentschel, M. Schaferling, X. Duan, H. Giessen and N. Liu, *Sci. Adv.*, **3**, e1602735 (2017)
N. S. Shahana Nizar, M. Sujith, K. Swathi, C. Sissa, A. Painelli and K. G. Thomas, *Chem. Soc. Rev.*, **50**, 11208 (2021)

# RT-PCM-NP for ECD

- Same multiscale method as for photocatalysis (RT-PCM-NP)
- Electric (external + induced) perturbation to the time-dependent induced magnetic dipole moment

$$
\begin{aligned}
\Delta\vec{m}(t) &= \vec{m}(t) - \vec{m}(0) \\
\vec{m}(t) &= \sum_{\lambda,\lambda'} C_{\lambda}^{*}(t) C_{\lambda'}(t) \langle\lambda|\hat{\vec{m}}|\lambda'\rangle
\end{aligned}
$$

# RT-PCM-NP for ECD

- Same multiscale method as for photocatalysis (RT-PCM-NP)
- Electric (external + induced) perturbation to the time-dependent induced magnetic dipole moment

$$\begin{aligned} \Delta\vec{m}(t) &= \vec{m}(t) - \vec{m}(0) \\ \vec{m}(t) &= \sum_{\lambda,\lambda'} C^*_\lambda(t) C_{\lambda'}(t) \langle\lambda|\hat{\vec{m}}|\lambda'\rangle \end{aligned}$$

- ECD spectrum as Fourier transform of $\Delta\vec{m}(t)$

$$P_{nl}^{ECD}(\omega) = -\frac{i}{2\pi\omega E^0_{ext,n}(\omega)} \int_0^{+\infty} -\Delta m_l(t) e^{i(\omega+i\Gamma)t} dt$$

M. Monti, M. Stener and EC, *J. Chem. Phys.*, 158, 084102 (2023)
L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and EC, submitted

# RT-PCM-NP for ECD

- Same multiscale method as for photocatalysis (RT-PCM-NP)
- Electric (external + induced) perturbation to the time-dependent induced magnetic dipole moment

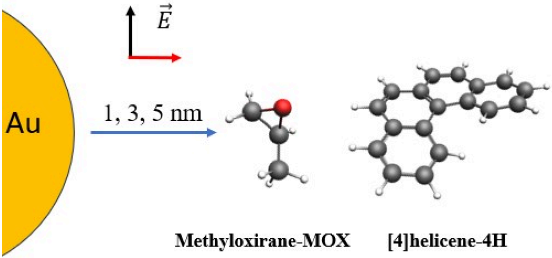
$$
\begin{aligned}
\Delta\vec{m}(t) &= \vec{m}(t) - \vec{m}(0) \\
\vec{m}(t) &= \sum_{\lambda,\lambda'} C^*_\lambda(t) C_{\lambda'}(t) \langle\lambda|\hat{\vec{m}}|\lambda'\rangle
\end{aligned}
$$

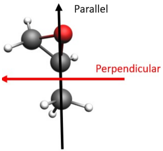
- ECD spectrum as Fourier transform of $\Delta\vec{m}(t)$

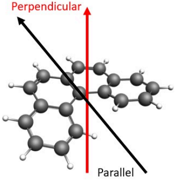
$$
P^{ECD}_{nl}(\omega) = -\frac{i}{2\pi\omega E^0_{ext,n}(\omega)} \int_0^{+\infty} -\Delta m_l(t) e^{i(\omega+i\Gamma)t} dt
$$

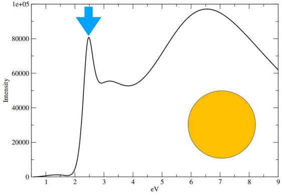
M. Monti, M. Stener and **EC**, *J. Chem. Phys.*, **158**, 084102 (2023)
L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and **EC**, submitted

# Modelling the systems



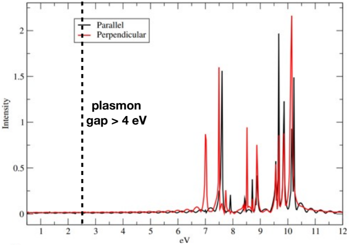



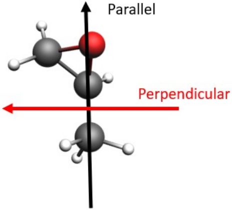




Ground-state geometry of MOX and 4H from literature. TDDFT/B3LYP/TZP: 20 electronic states for MOX, 40 for 4H.
150-fs dynamics, time step of 0.7 as, $\delta$ pulse with FWHM of 94 as.
NP radius equal to 2.5 nm, 2700 tesserae, exp Au dielectric function

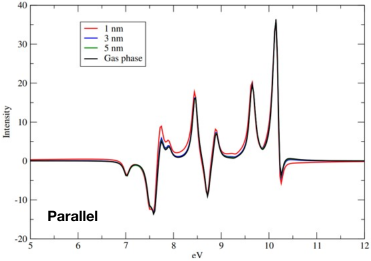
L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and **EC**, submitted

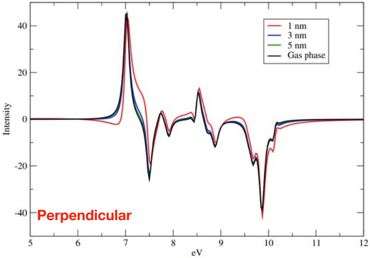



Linear absorption



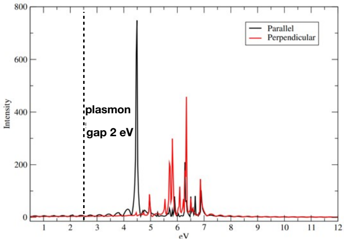

ECD



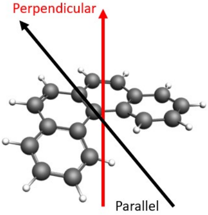




No plasmonic effect for MOX

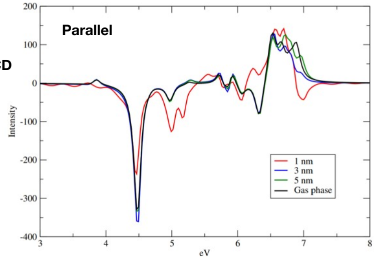
L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and **EC**, submitted

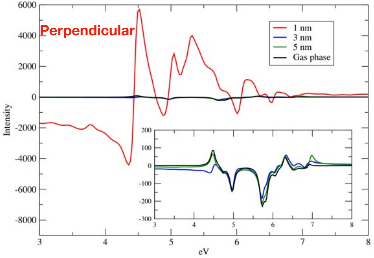



linear absorption




ECD




Enhancement by a factor 60 for perpendicular configuration

L. Biancorosso, P. D'Antoni, S. Corni, M. Stener and **EC**, submitted

# Conclusions

- General model for hot-carrier dynamics
- Microscopic understanding of plasmon-assisted reaction selectivity in $CO_2$ hydrogenation
- Massively parallel computational scheme (SSE)
- (De)coherence as a further design element in nanoplasmonics and plasmon-mediated photocatalysis

# Conclusions

- General model for hot-carrier dynamics
- Microscopic understanding of plasmon-assisted reaction selectivity in $CO_2$ hydrogenation
- Massively parallel computational scheme (SSE)
- (De)coherence as a further design element in nanoplasmonics and plasmon-mediated photocatalysis
- Plasmon-enhanced electronic circular dichroism

# Conclusions

- General model for hot-carrier dynamics
- Microscopic understanding of plasmon-assisted reaction selectivity in $CO_2$ hydrogenation
- Massively parallel computational scheme (SSE)
- (De)coherence as a further design element in nanoplasmonics and plasmon-mediated photocatalysis
- Plasmon-enhanced electronic circular dichroism

# Acknowledgements

- Stefano Corni (Univ. Padova & CNR)
- Giulia Dall'Osto (Univ. Padova)
- Mirko Vanzan (Univ. Milano)
- Margherita Marsili (Univ. Bologna)
- Leonardo Biancorosso (Univ. Trieste)
- Mauro Stener (Univ. Trieste)

ICSC
Centro Nazionale di Ricerca in HPC,
Big Data and Quantum Computing

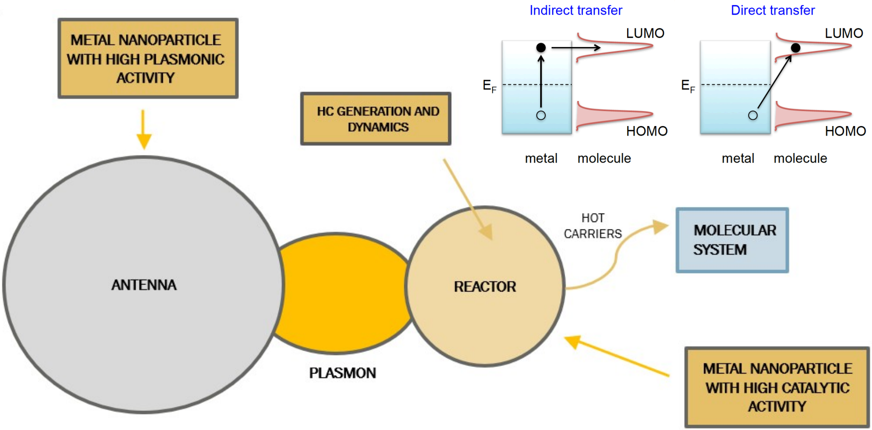
PRACE

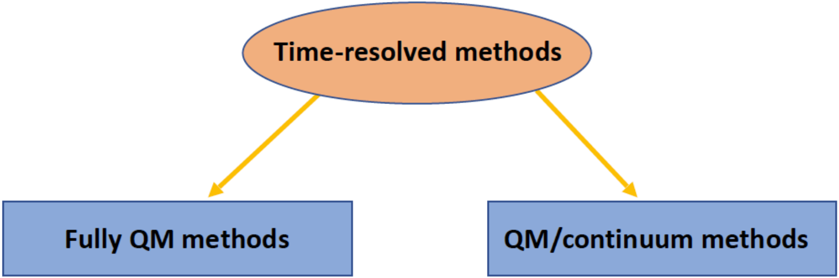
lrz Leibniz-Rechenzentrum
der Bayerischen Akademie der Wissenschaften

erc

TAME Plasmons
A THEORETICAL CHEMISTRY APPROACH TO TIME-RESOLVED MOLECULAR PLASMONICS

# Plasmon-assisted photocatalysis






**Fully QM methods**

- High computational cost
- Approximations to study the plasmonic system
- Small sizes

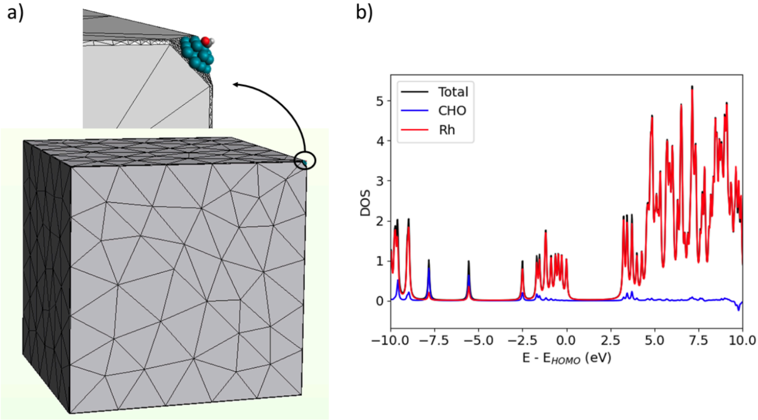
- Atomistic description of the nanostructure
- Description of the quantum effects at the interface

**QM/continuum methods**

- Non atomistic description of the nanoparticle
- No quantum effects at the interface

- Low computational cost
- No limitations on the size
- Accurate description of the molecular system

## Ground-state PDOS (after equilibration)




Anti-bonding orbitals populated

G. Dall'Osto, M. Marsili, M. Vanzan, D. Toffoli, M. Stener, S. Corni and **EC**, submitted

# Competitive reactions

Methanation

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

Carbon monoxide formation

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Rate-determining step (rds)

$$CO^* + H^* \rightarrow CHO^*$$
$$CHO^* \rightarrow CH^* + O^*$$

# Competitive reactions

Methanation

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

Carbon monoxide formation

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Rate-determining step (rds)

$$CO^* + H^* \rightarrow CHO^*$$
$$CHO^* \rightarrow CH^* + O^*$$

# Competitive reactions

- Desorption of CO from Rh has the rds of CO production
- Dissociation of CH-O as the rds for $CH_4$ production
- Competition between CO desorption and C-O bond cleavage in CHO dictates the product selectivity

# Carrier injection

Electron injection

$$\frac{1}{2}\int_{-\infty}^{\infty}\left[\Delta\text{PDOS}(t,\epsilon)+|\Delta\text{PDOS}(t,\epsilon)|\right]d\epsilon$$

Hole injection

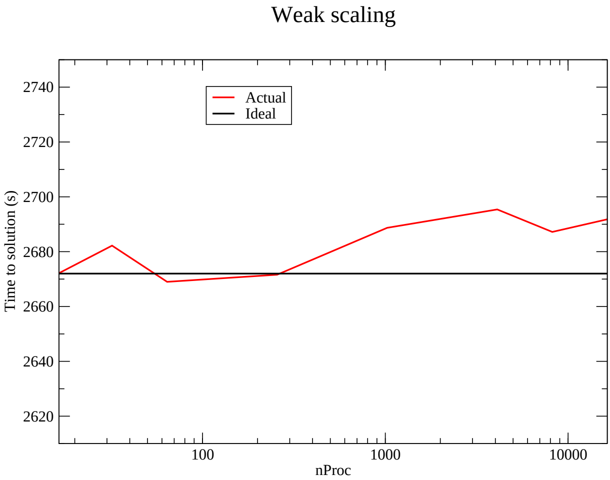
$$\frac{1}{2}\int_{-\infty}^{\infty}\left[\Delta\text{PDOS}(t,\epsilon)-\Delta\text{PDOS}(t,\epsilon)\right]d\epsilon$$

# Equilibration step

- Starting from a GW-BSE calculation in vacuum
- A finite set of $|\lambda\rangle_{vac}$ states is chosen as the "active space"
- The total energy of the NP/molecule system is self-consistently minimized from the molecule in its vacuum ground-state $|0\rangle_{vac}$ close to NP
- NP is provided of a set of starting polarization charges
- The molecule is in a novel ground-state $|0\rangle_{eq} = \sum_\lambda a_\lambda^{GS} |\lambda\rangle_{vac}$
- The NP polarization, frozen at the ground-state, provides a modified molecular Hamiltonian that is diagonalized in the molecular active space, obtaining a new set of excited states $|\lambda\rangle_{eq} = \sum_{\lambda'} a_{\lambda'}^{\lambda} |\lambda'\rangle_{vac}$

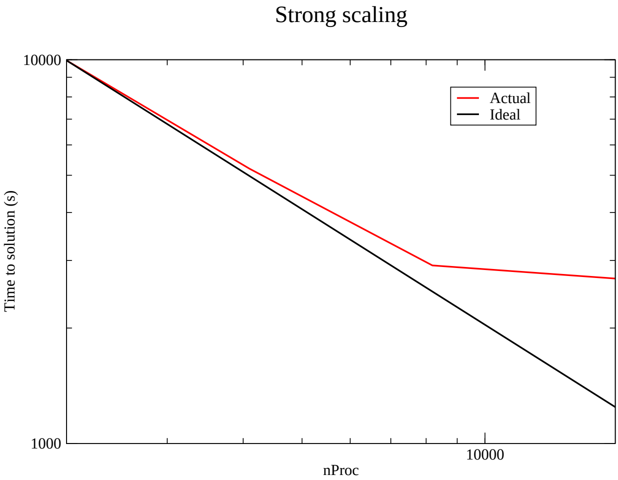
# OpenMP+MPI parallelization for SSE

- PRACE Preparatory Project 2010PA4253 on Curie (2/2/2018 - 2/8/2018)
- Molecule+NS system

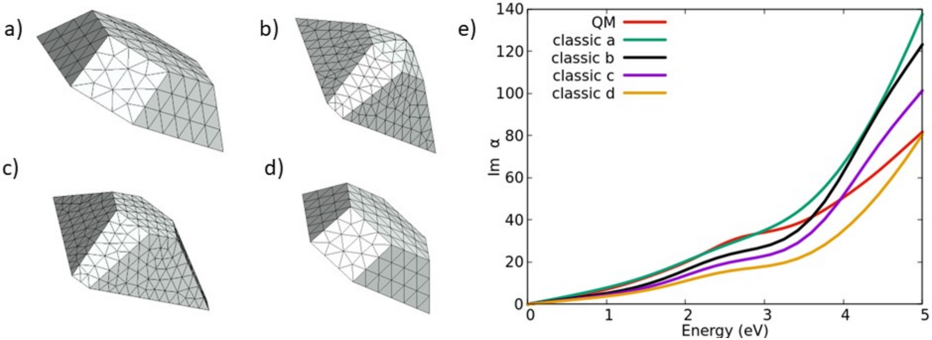


# OpenMP+MPI parallelization for SSE

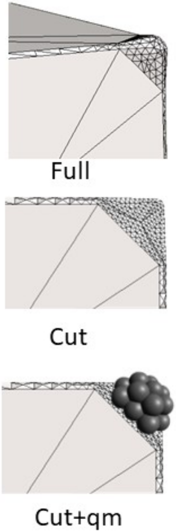
- PRACE Preparatory Project 2010PA4253 on Curie (2/2/2018 - 2/8/2018)
- Molecule+NS system

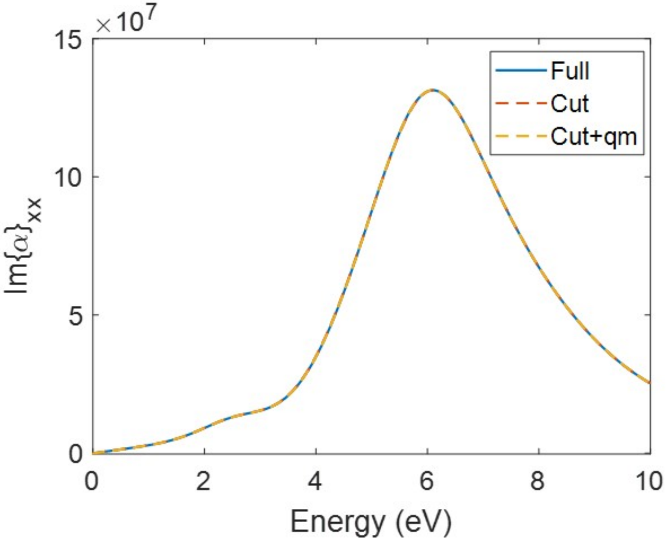


# Modeling the Rh nanocube

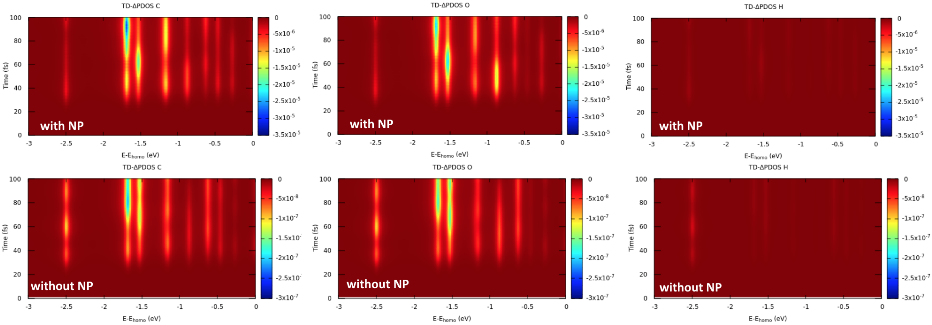


# Modeling the Rh nanocube

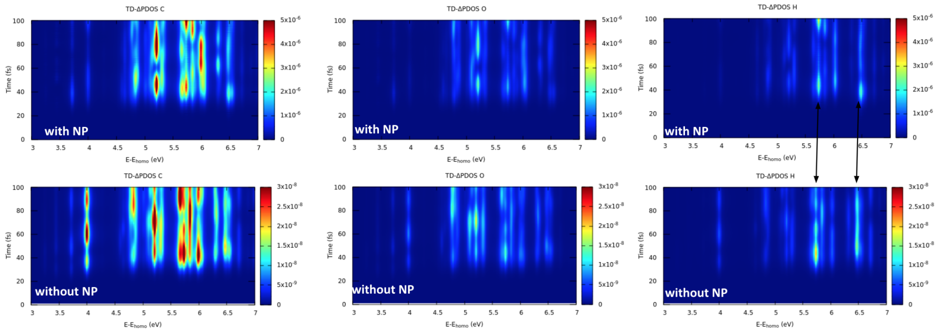


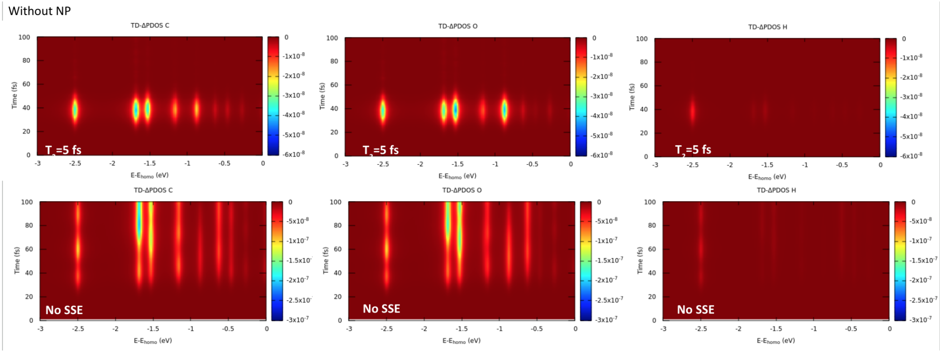
# Valence band



# Conduction band

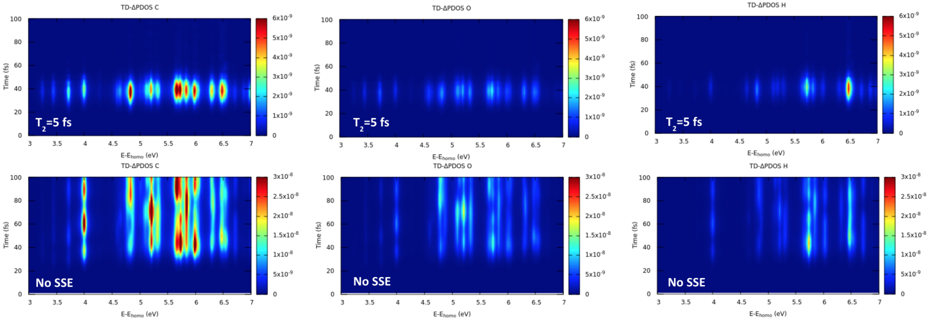


# $T_2$ = 5 fs, valence band

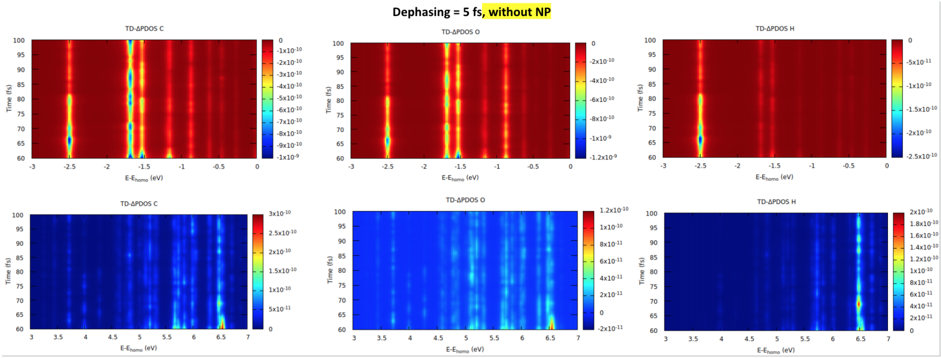


# $T_2$ = 5 fs, conduction band

Without NP

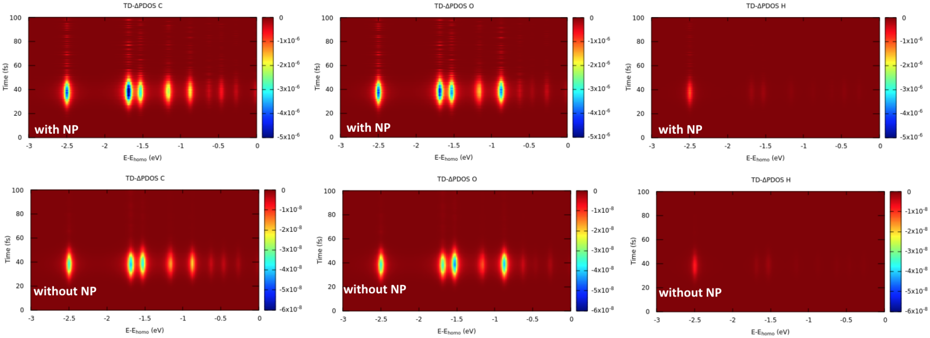


# $T_2 = 5$ fs



Dephasing = 5 fs, without NP
TD-ΔPDOS C
TD-ΔPDOS O
TD-ΔPDOS H
Time (fs)
E-E$_{homo}$ (eV)

# $T_2$ = 5 fs, valence band



# $T_2$ = 5 fs, conduction band

**Dephasing = 5 fs**