Ab-initio simulations of metallic clusters

P. Koval, F. Marchesin, M. Barbry, J. Aizpurua and D. Sánchez-Portal

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People involved

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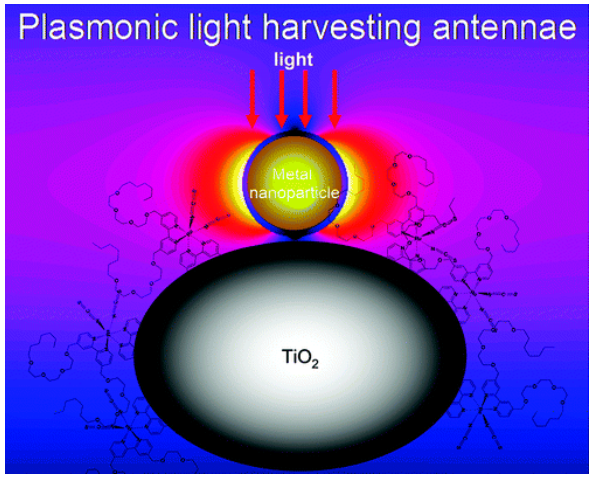
Nerea Zabala

Javier Aizpurua

Plasmonics: applications of local field enhancement

Enhancement of efficiency in photo voltaics



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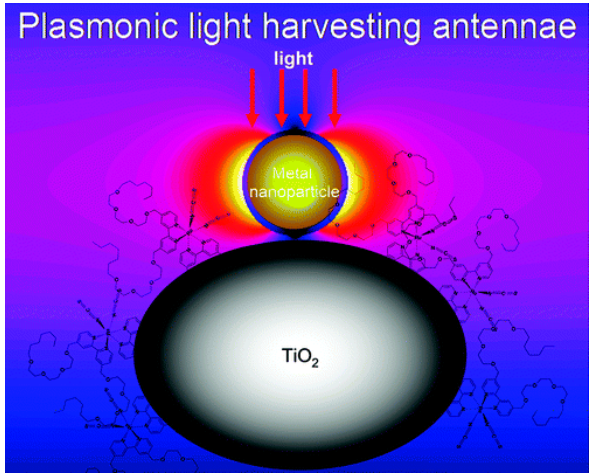
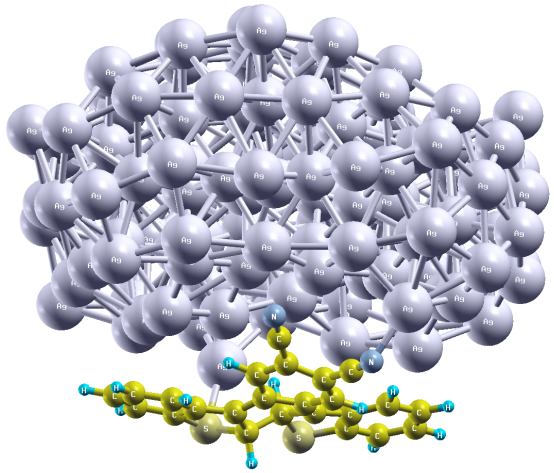
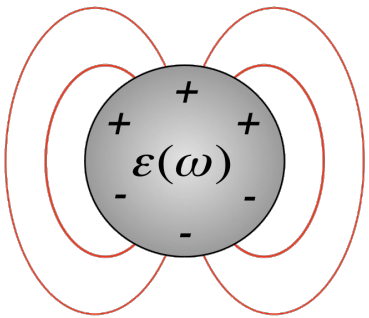


Surface-enhanced Raman Spectroscopy SERS/TERS



Classical electrodynamics of continuum media

- Formalism of dielectric functions $\varepsilon(\omega, \boldsymbol{r})$



Continuity of $\phi(\boldsymbol{r})$ and $\boldsymbol{D}(\boldsymbol{r}) = \varepsilon \boldsymbol{E}(\boldsymbol{r}) \Rightarrow$

Static resonance condition $\varepsilon_{\text{sphere}} = -2$;

Drude model function $\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \Rightarrow$

$\omega_{\text{surface}} = \frac{\omega_p}{\sqrt{1+2}}$

- Works best for macroscopic sizes
- With some care the range of validity can be extended[1]
  - Boundary-element method (BEM) for arbitrary shapes
  - Atoms — spheres of Wigner-Seitz radius r_s — material dependent

[1] M. Urbieta, M. Barbry, Y. Zhao, et al., ACS Nano 12, 585-595 (2018)

Classical electrodynamics: out of range

Dielectric function formalism ceases to work at microscale

- To understand the dielectric functions we need ab-initio theory
  4d-electrons in silver: $\varepsilon(\omega) = \varepsilon_{4d} - \frac{\omega_p^2}{\omega^2} \Rightarrow \omega_{\text{surface}} = \frac{\omega_p}{\sqrt{\varepsilon_{4d}+2}}$
  Size-dependent resonance frequency $\omega_{\text{surface}}(R) \Rightarrow \varepsilon(R, \omega)$???

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- . . . the Raman spectroscopy we need atomistic theory
- . . . the effects of temperature we need ab-initio atomistic theory
- . . . TEM experiments we need ab-initio theory

Ab-initio theory

- Quantum mechanics $\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$
- Density-functional theory (DFT) $E = E[n]$

$$n(\boldsymbol{r}) = \int \Psi^*(\boldsymbol{r}, \boldsymbol{r}_2 \ldots, \boldsymbol{r}_N)\Psi(\boldsymbol{r}, \boldsymbol{r}_2 \ldots, \boldsymbol{r}_N) dr_2 \ldots dr_N$$

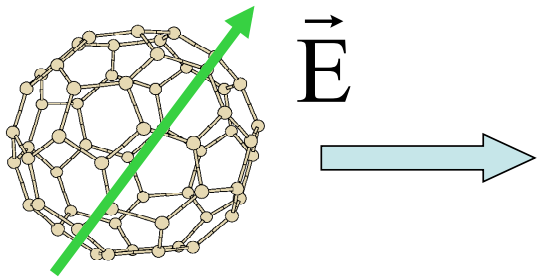
- Kohn-Sham (KS) picture $\left(\hat{T} + V_{\text{ext}} + V_{\text{Hxc}}\right)\Psi_n(\boldsymbol{r}) = E\Psi_n(\boldsymbol{r})$

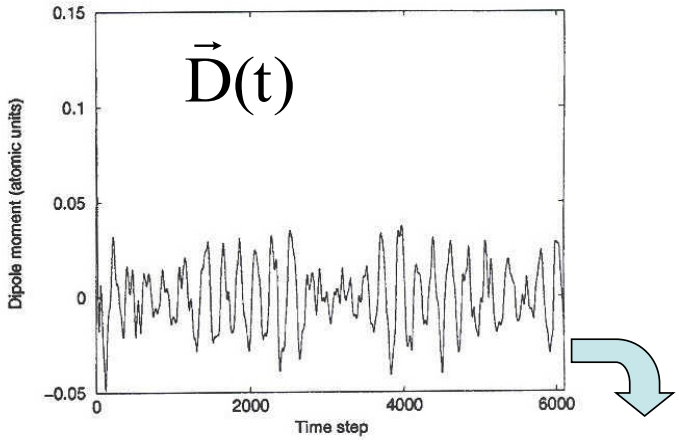
$$n(\boldsymbol{r}) = \sum_{n \in \text{occ}} \Psi_n^*(\boldsymbol{r})\Psi_n(\boldsymbol{r})$$

- Time-dependent DFT (TDDFT) in KS $\hat{H}_{\text{KS}}\Psi_n(\boldsymbol{r}) = \mathrm{i}\frac{\partial}{\partial t}\Psi_n(\boldsymbol{r})$
- Kinetic-energy density functionals $T = T[n]$ would be great, but too inaccurate so far

Ab-initio theory: real-time propagation of wave-packets

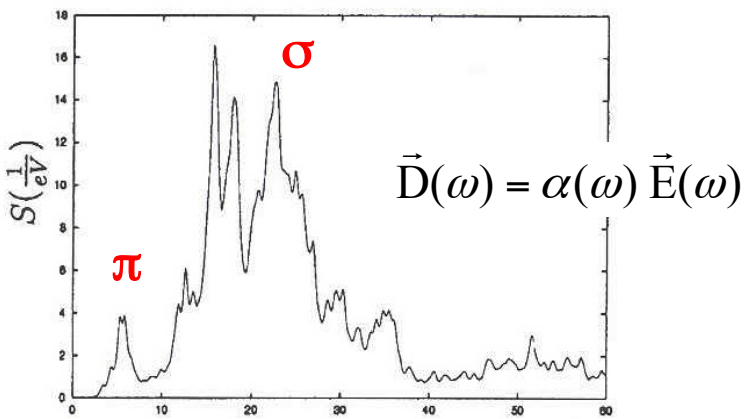
A. Tsolakidis, D. Sánchez-Portal, R. M. Martin, PRB(2002), adapting a recipe by Kazuhiro Yabana and George Bertsch, PRB (1996)





Low energy peaks with TDLDA

SIESTA	Yabana	Exp.
3.5	3.4	3.8
4.4	4.3	
5.4	5.3	4.8
5.8	6.0	5.8



RT TDDFT is capable to model a broad range of scenarious, but this is superfluous for spectroscopy

Ab-initio theory: linear response

- Casida equation: exchange/hybrid functionals ☺

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- Formalism of linear response functions $\chi(\omega)$: comput. cheap ☺

$$\delta n(\boldsymbol{r},\omega) \equiv \int \chi(\boldsymbol{r},\boldsymbol{r}',\omega)\delta V_{\text{ext}}(\boldsymbol{r}',\omega)d\boldsymbol{r}', \text{ or } \Rightarrow \chi(\omega) = \frac{\delta n}{\delta V_{\text{ext}}}$$

$$V_{\text{eff}} = V_{\text{ext}} + V_{\text{Hxc}}[n] \Rightarrow \qquad \frac{\delta V_{\text{eff}}}{\delta n} = \frac{\delta V_{\text{ext}}}{\delta n} + \frac{\delta V_{\text{Hxc}}[n]}{\delta n}$$

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)K\chi(\omega),$$

$$\chi_0(\omega) = (f_n - f_m)\frac{\Psi_n(\boldsymbol{r})\Psi_m(\boldsymbol{r})\Psi_m(\boldsymbol{r}')\Psi_n(\boldsymbol{r}')}{\omega - (E_m - E_n)}$$

Products of wave-functions appear in $\chi_0(\omega)$

and interaction kernel K is known for semi-local functionals.

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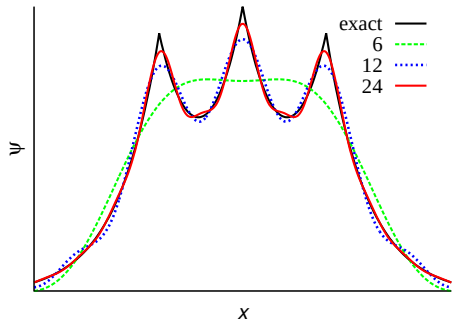
Basis sets

$$\Psi_n(\boldsymbol{r}) = \sum_a X_a^n f^a(\boldsymbol{r})$$

Plane-wave (PW) basis sets: $\exp(\mathrm{i}\boldsymbol{G}\boldsymbol{r})$



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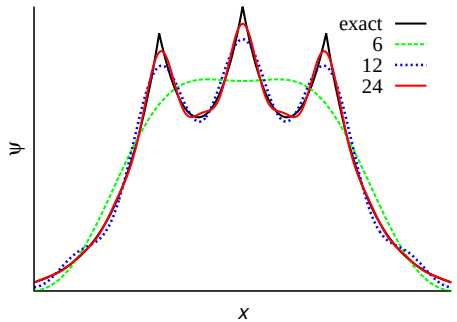
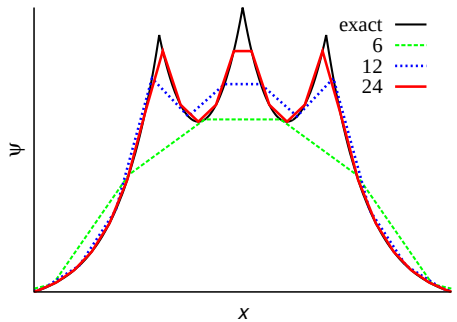


Real-space grids (RSG): $\{\boldsymbol{r}_i\}, i = 1 \ldots N$



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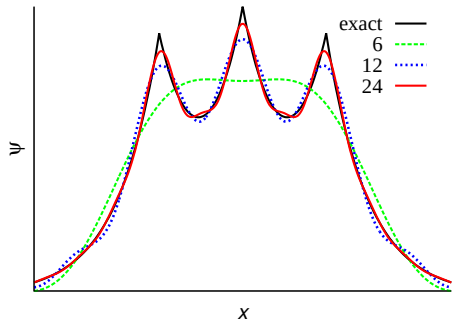

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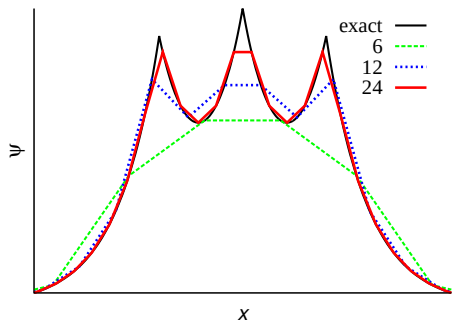

- Numerical atomic orbitals (NAO): $f^a(r)\mathrm{Y}_{lm}(\boldsymbol{r})$
  - Parsimonious for atomic systems
  - Need density-fitting basis

Product basis: PW vs RSG

For NAO $f^a(\boldsymbol{r})$ we need an auxiliary basis $f^a(\boldsymbol{r})f^b(\boldsymbol{r}) = V_\mu^{ab} F^\mu(\boldsymbol{r})$

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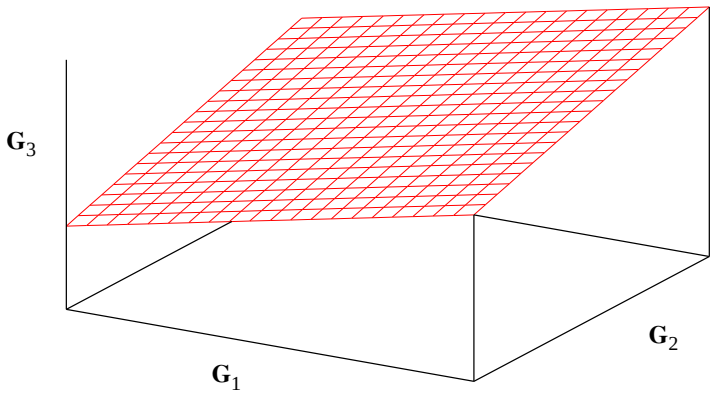
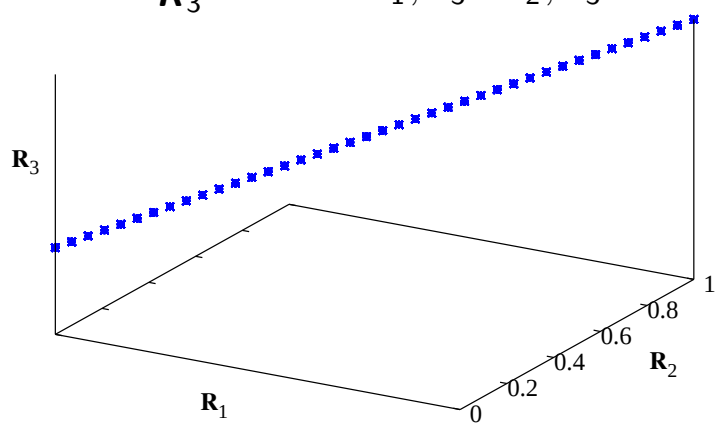
$$V_{\boldsymbol{G}_3}^{\boldsymbol{G}_1\boldsymbol{G}_2} = \delta_{\boldsymbol{G}_1+\boldsymbol{G}_2,\boldsymbol{G}_3}$$



$O(N^2)$

Sparse

$$V_{\boldsymbol{R}_3}^{\boldsymbol{R}_1\boldsymbol{R}_2} = \delta_{\boldsymbol{R}_1,\boldsymbol{R}_3}\delta_{\boldsymbol{R}_2,\boldsymbol{R}_3}$$

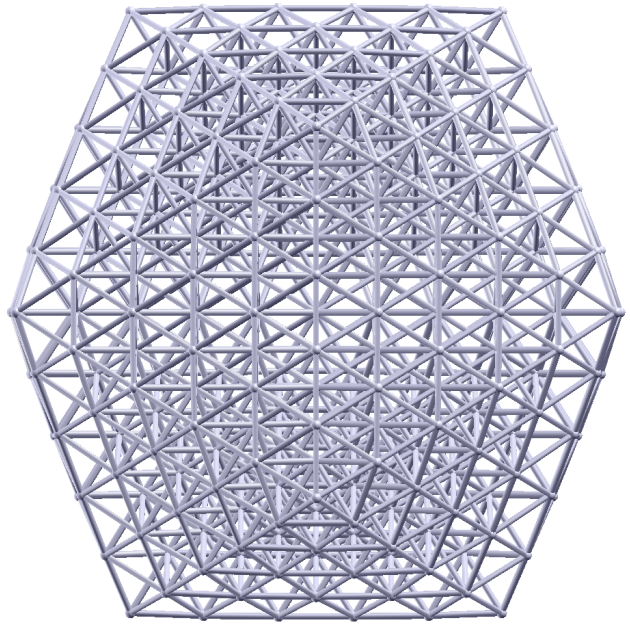


$O(N)$

Double sparse

$\Rightarrow$ Potential advantage of localized basis sets

DFT with SIESTA: NAO in action



Open-source[2]

- DFT with NAO
- Energies & Forces $\Rightarrow$ Molec. dyn.

[2] https://launchpad.net/siesta

[3] http://www.simune.eu

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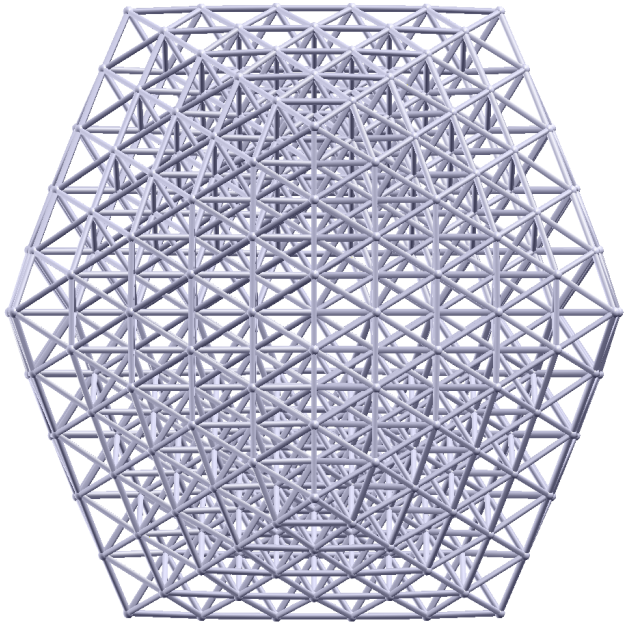

Open-source[2]

- DFT with NAO
- Energies & Forces $\Rightarrow$ Molec. dyn.
- Commercial support for industry partners[3]

SIMUNE ATOMISTIC SIMULATIONS

Industrial Forum

Imaginenano2018

Thu, 11:30-13:30

[2] https://launchpad.net/siesta

[3] http://www.simune.eu

Iterative computation of induced density

- Induced density $\delta n(\omega)$ due to an external perturbation $\delta V^{\mathrm{ext}}(\omega)$

$$\delta n(\omega) = \chi_0(\omega)\delta V^{\mathrm{eff}}(\omega)$$

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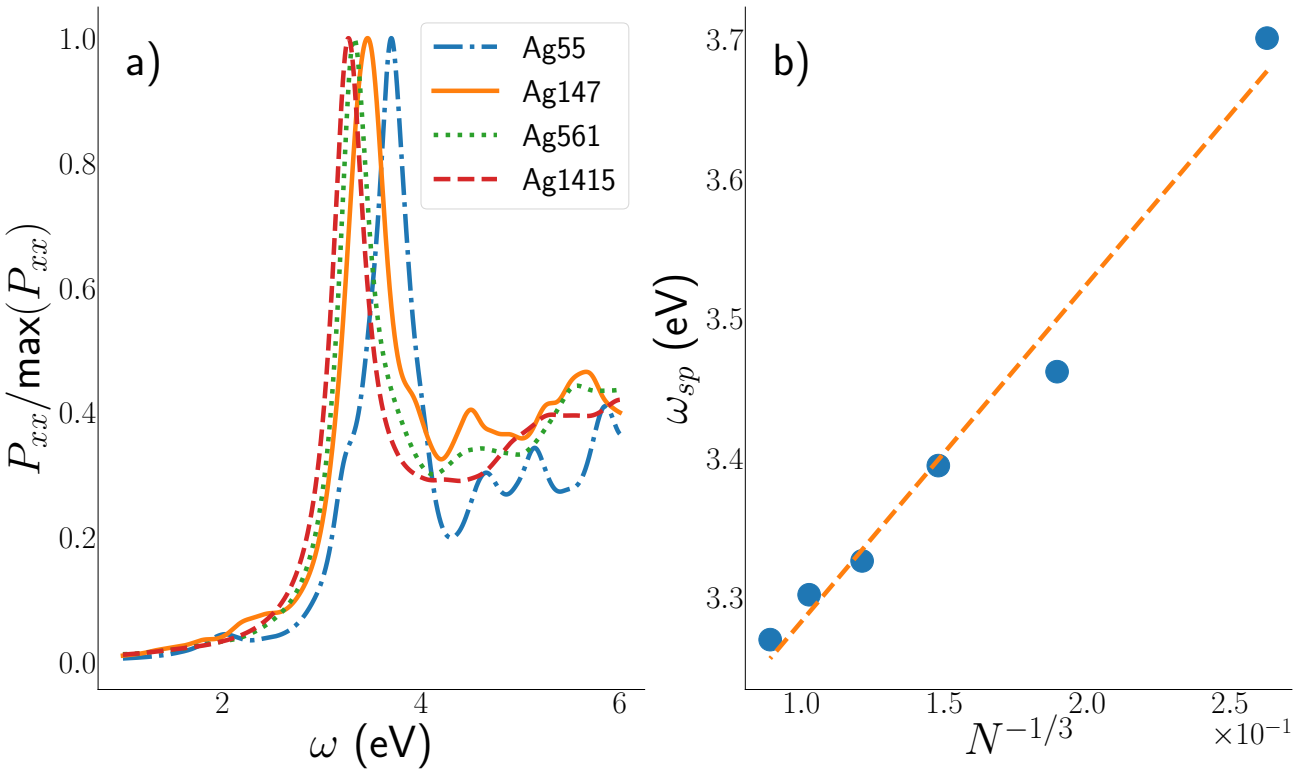
- We solve the SLE above with Krylov subspace methods

$$\chi^0_{\mu\nu} z^\nu = V^{ab}_\mu \, X^n_a \, X^m_b \, X^m_c \, V^{cd}_\nu z^\nu \, X^n_d$$

- $O(N^3)$ operations or less, where N is number of atoms

Silver clusters with PySCF-NAO

- Open-source, Python-based implementation
  https://github.com/cfm-mpc/pyscf



- The plasmonic resonance of silver clusters blue-shifts for smaller sizes

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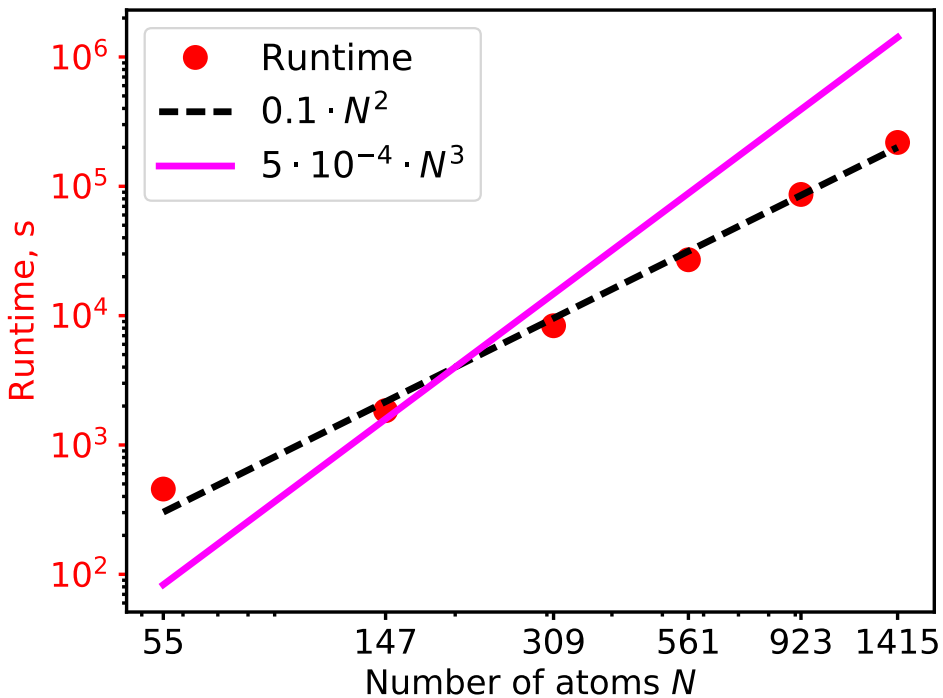
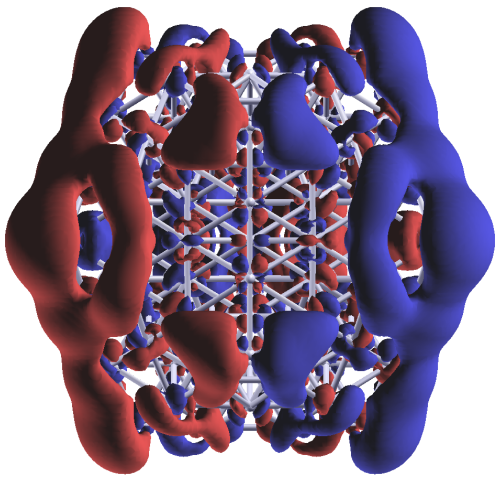


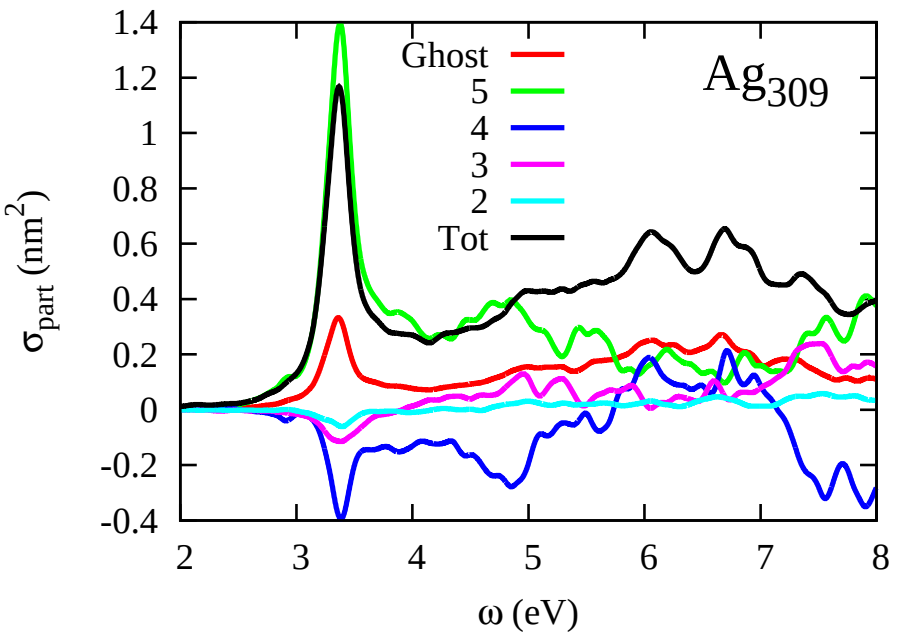
- The runtime on 12 cores of Intel® Xeon® Processor E5-2680 v3

Silver clusters analysis

We can split response in multiple ways: including atomic layer's contributions[4]

$\delta n(\boldsymbol{r},\omega) = \delta n_\mu(\omega) F^\mu(\boldsymbol{r})$ and $F^\mu(\boldsymbol{r})$ is the atom-centered product basis





$\delta n(\boldsymbol{r},\omega_{sp})$

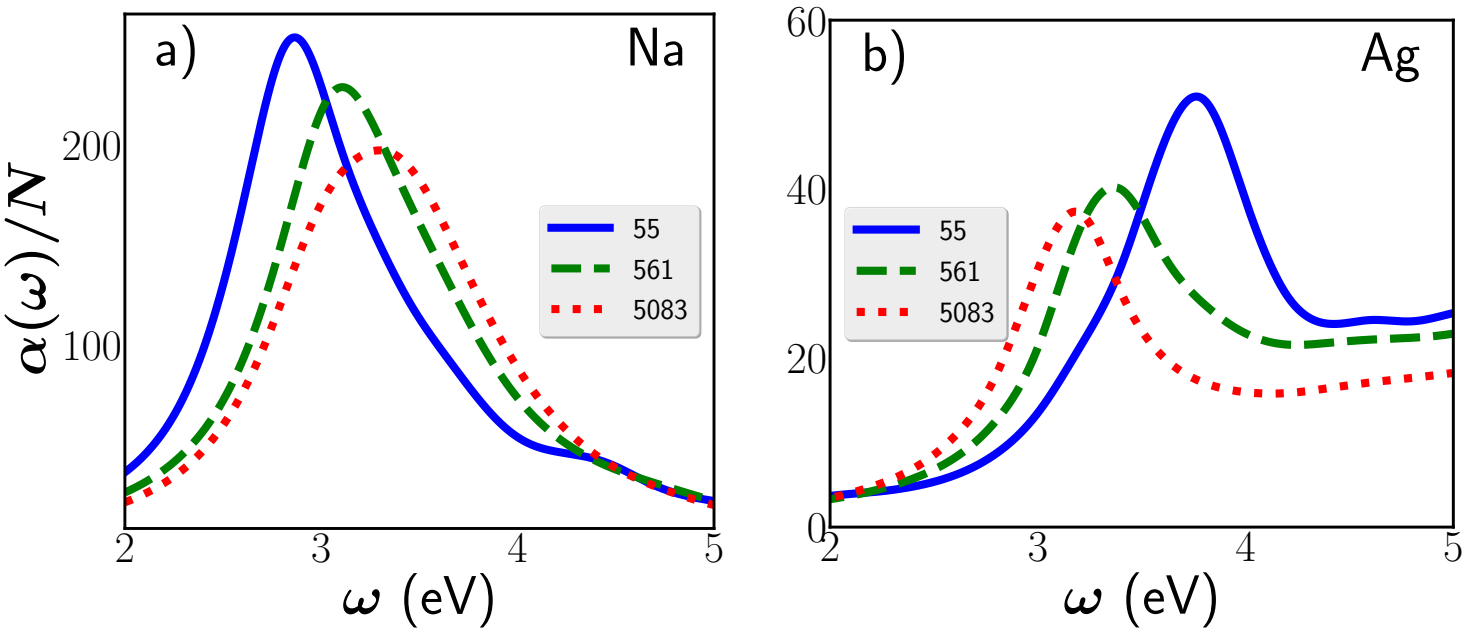
$\alpha(\omega) = \int \boldsymbol{r}\delta n(\boldsymbol{r},\omega) dr$

[4] J. Phys.: Condens. Matter 28 (2016) 214001

Size/material dependence: Na vs Ag

Being ab-initio theory TDDFT allows to see straight away

- dependence on the size N — number of atoms
- . . . material: Na 3s; Ag $4d^{10}$ 5s

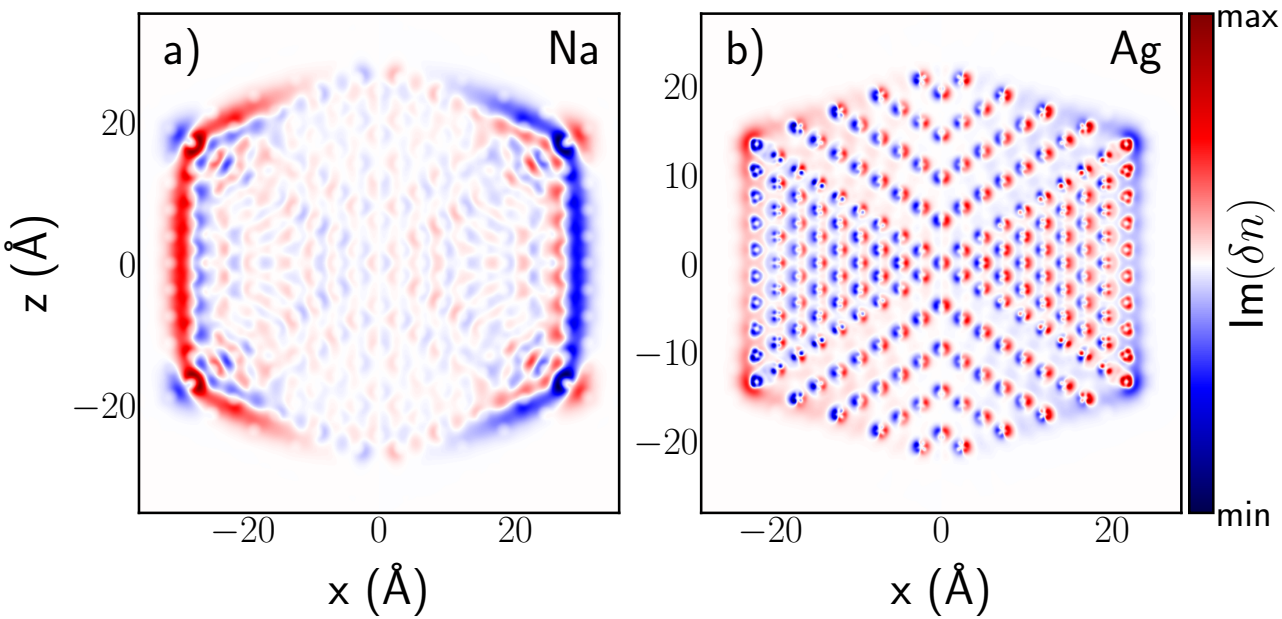


- Why that?

Size/material dependence: reason

Reason for the opposite size dispersion

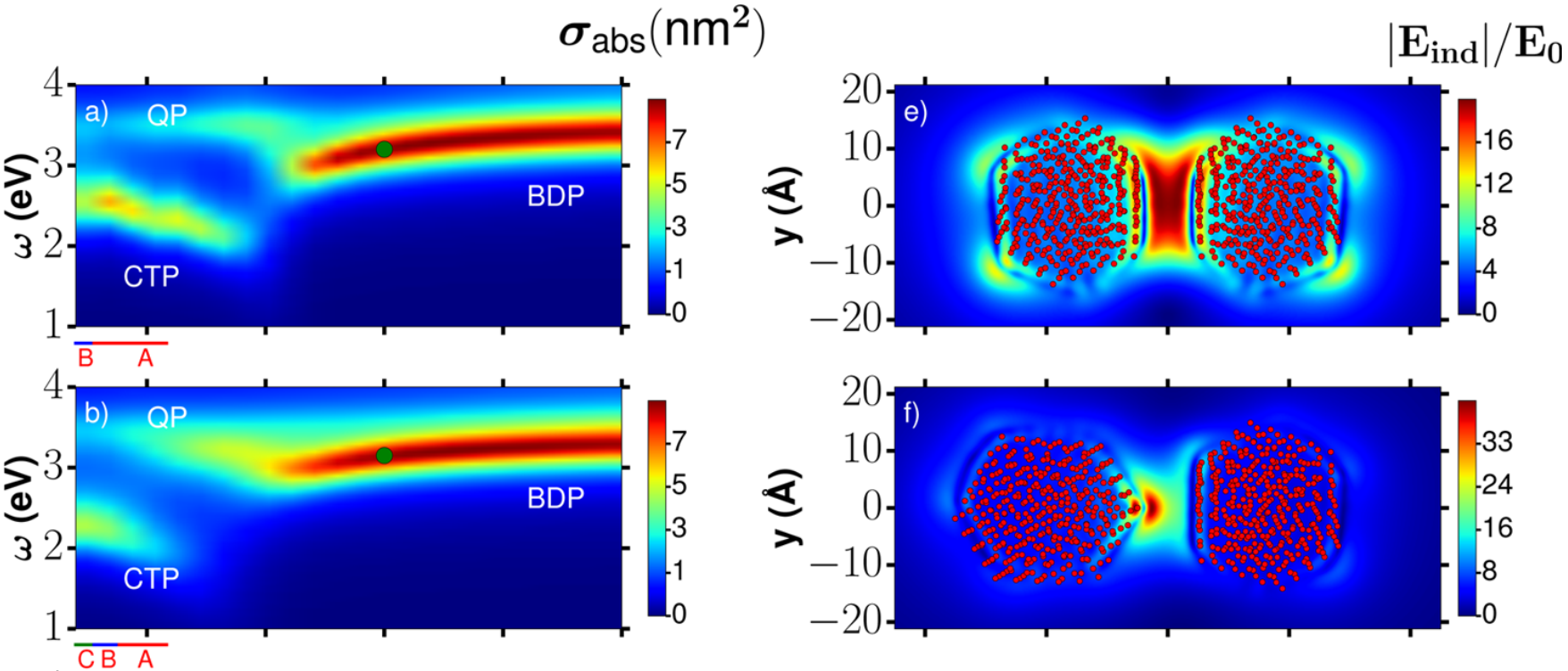
- Without the Coulomb interaction Na and Ag clusters blue shift — quantum confinement
- Without d-electrons Ag dispersion flattens: screening



- Dependence on the shape

Shape dependence for a plasmonic cavity

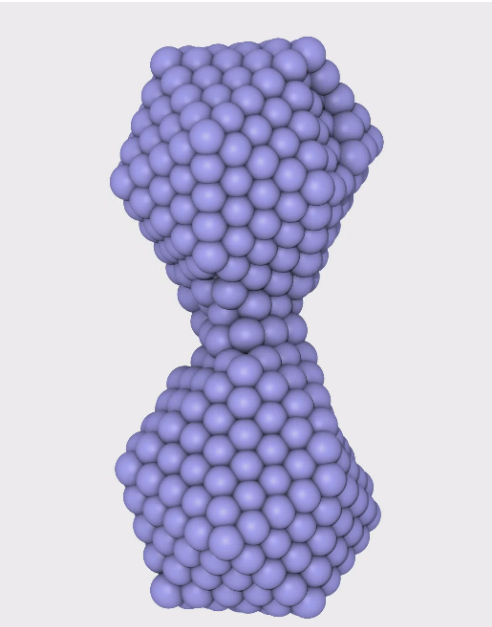
Na_{380} dimer is a model of plasmonic cavity (EM antenna)[5]



[5] Barbry *etal* Nano Lett. 15 (2015) 3410

Relaxations in the Na_{380} cavity

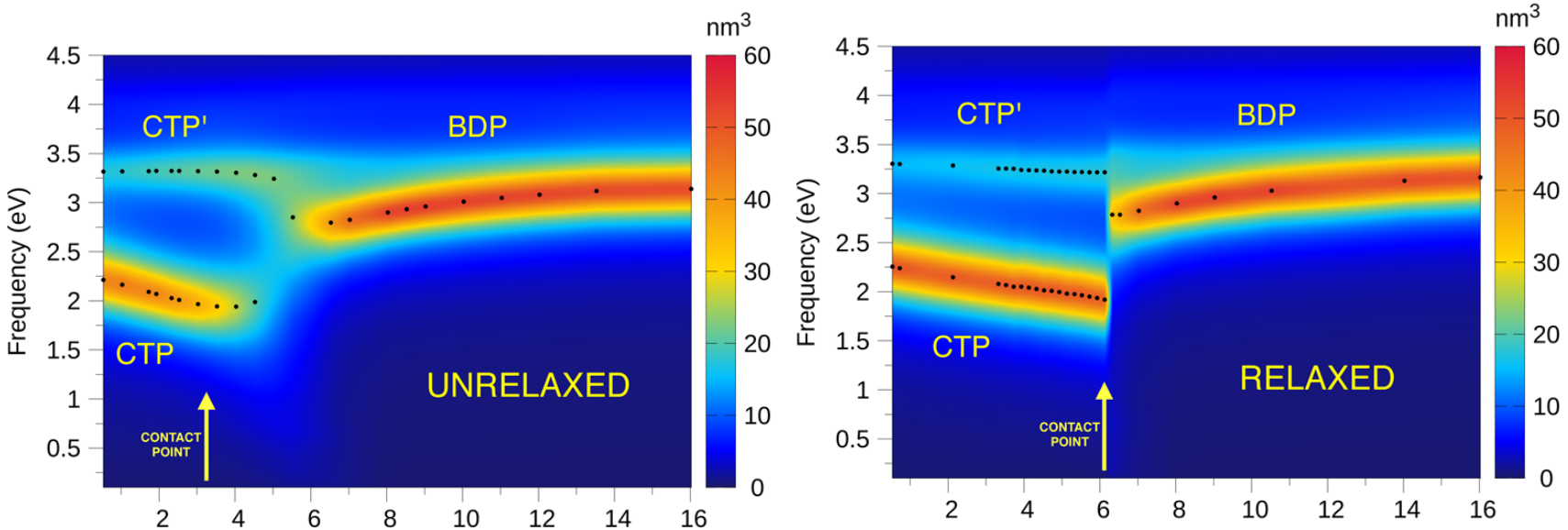
What happens if we allow the atoms to move?



Play movie

Effect of relaxations on polarizability

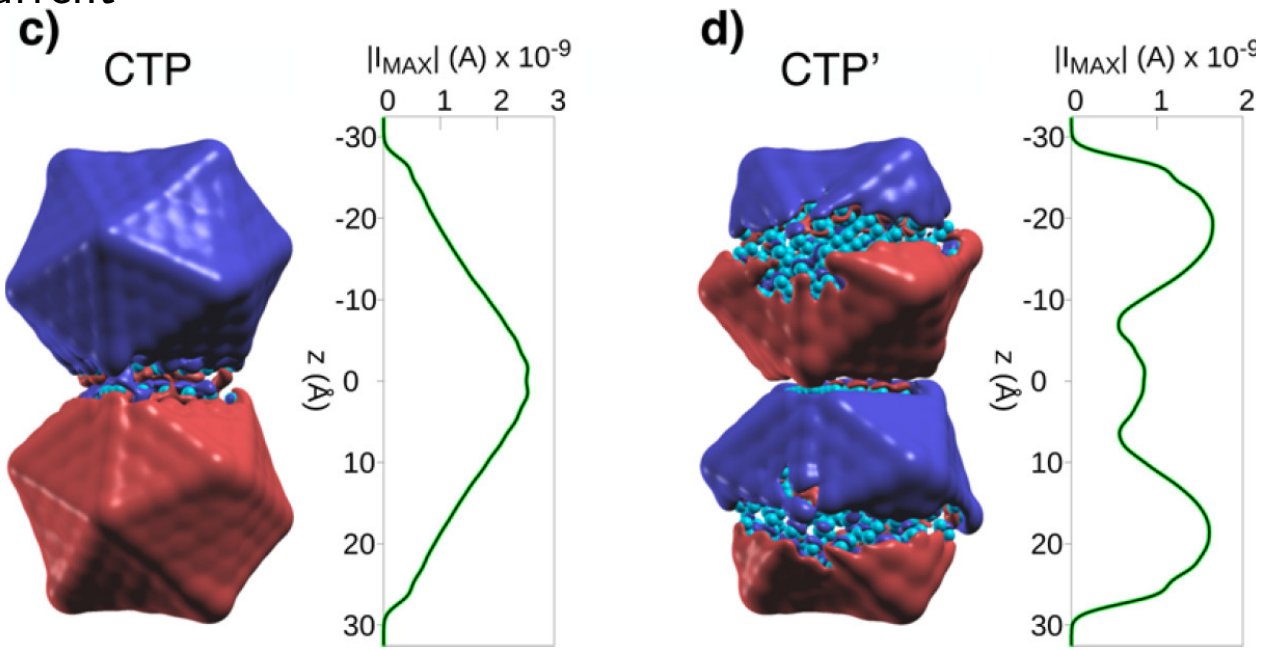
Since we use atomistic theory, we can model inelastic microscopic rearrangements [6]



[6] FM, PK, MB, JA, DSP, *ACS Photonics* **3** (2016) 269

Induced density and current at different frequencies

Because we have the induced density in real space, it is also possible to find the induced current

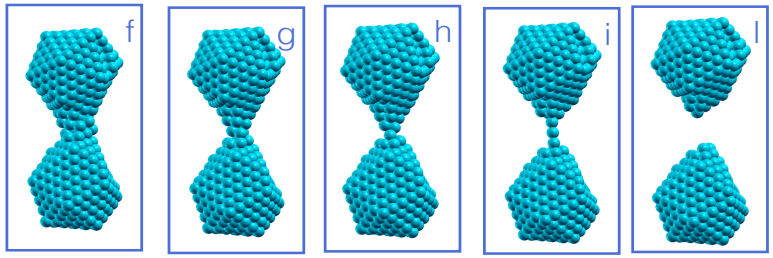


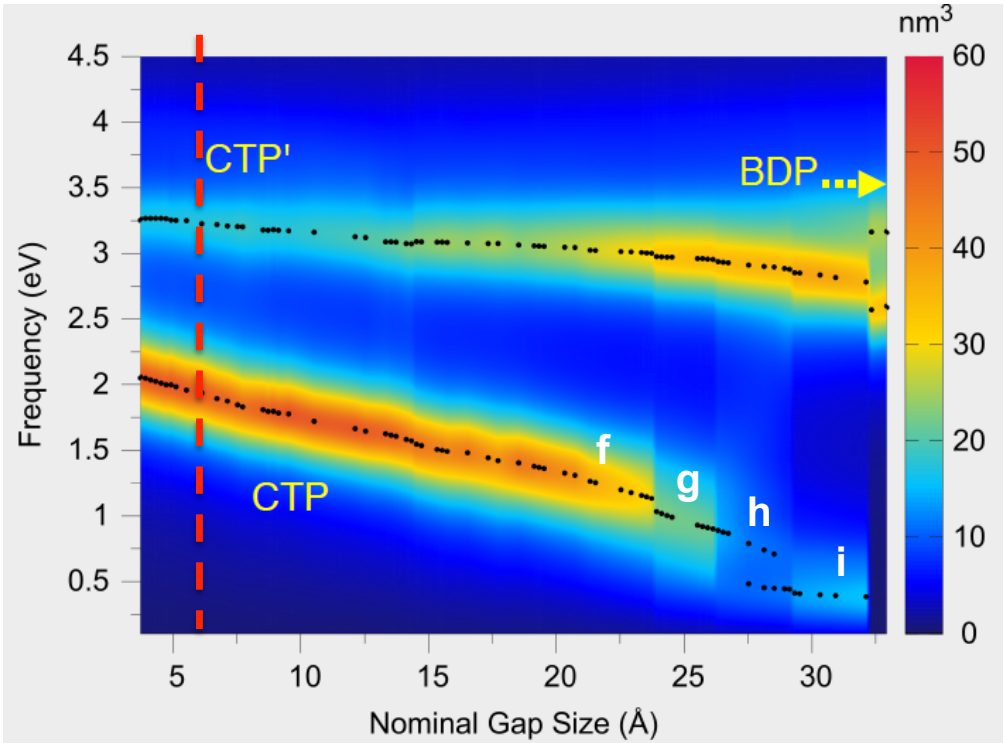
Imaginary part of the induced density and the corresponding modulus of the electron current flowing through the middle of the dimer 2 x Na_{380}[7]

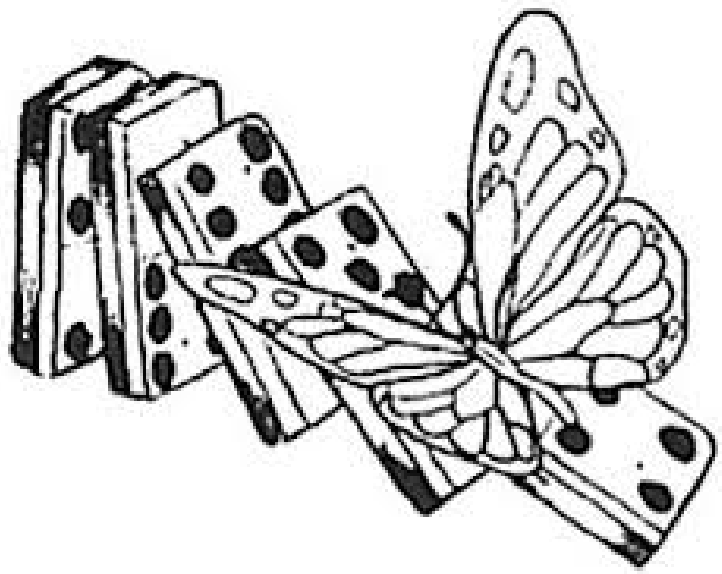
[7] FM, PK, MB, JA, DSP, *ACS Photonics* **3** (2016) 269

Butterfly effect at large strain

Small action leads to large changes when rectracting[8]







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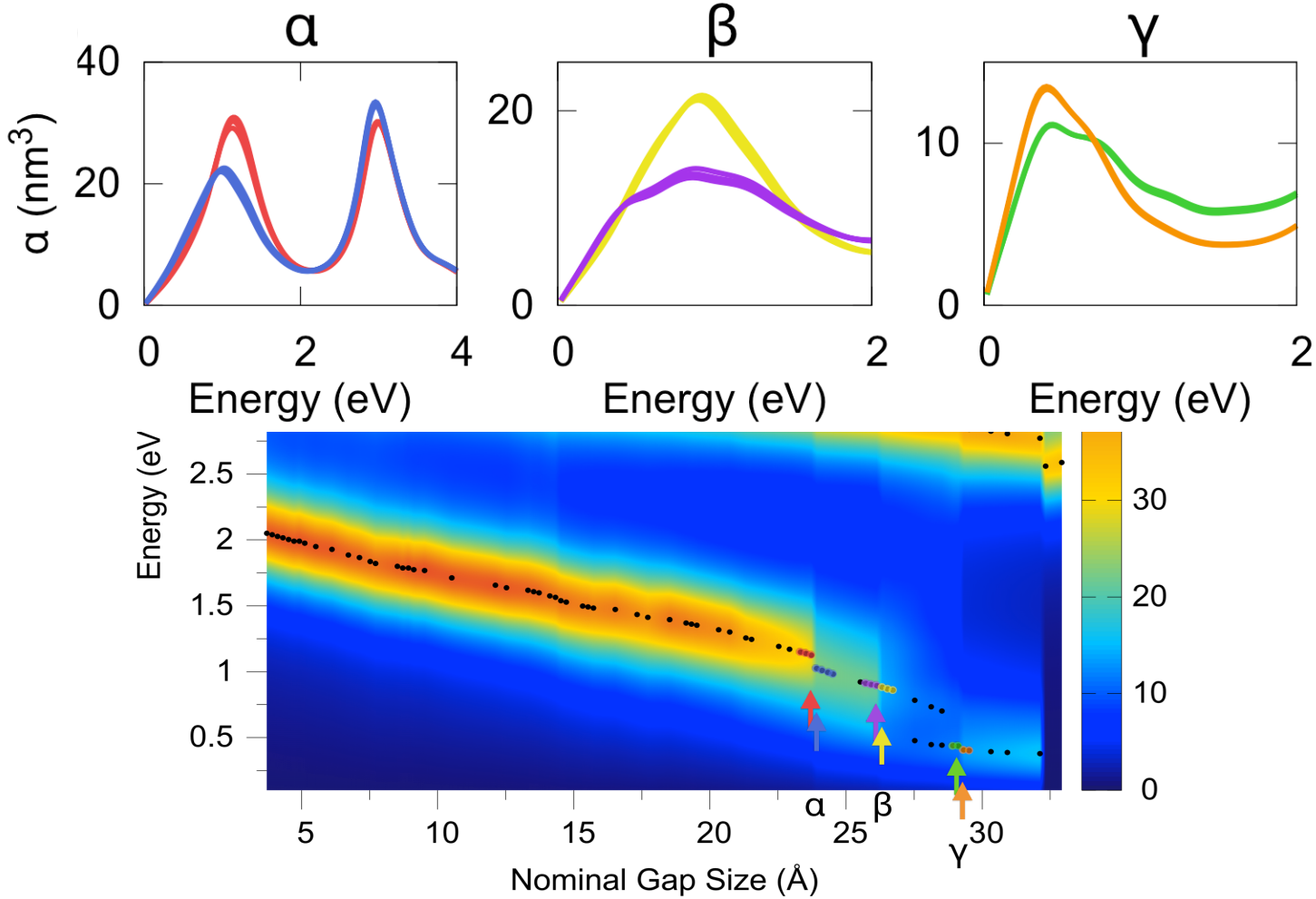
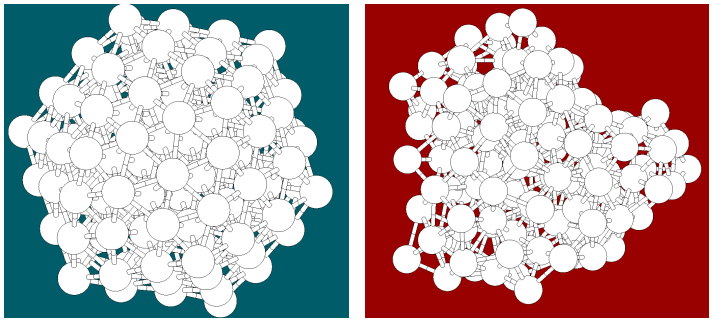
Butterfly effect at large strain

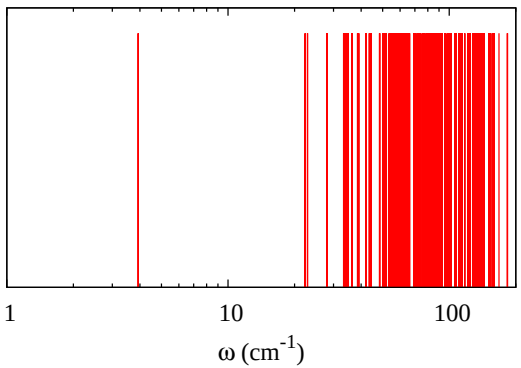
Polarizability $\alpha(\omega)$ as common graphs



Semi-empirical molecular dynamics (MD) for Ag_{147}



- Atomistic Simulation Environment (ASE) to organize SEMD
- Langevin dynamics for $T_{\text{ion}} = 300$, 600 and 900 K
- Atomistic effective potentials used[9]

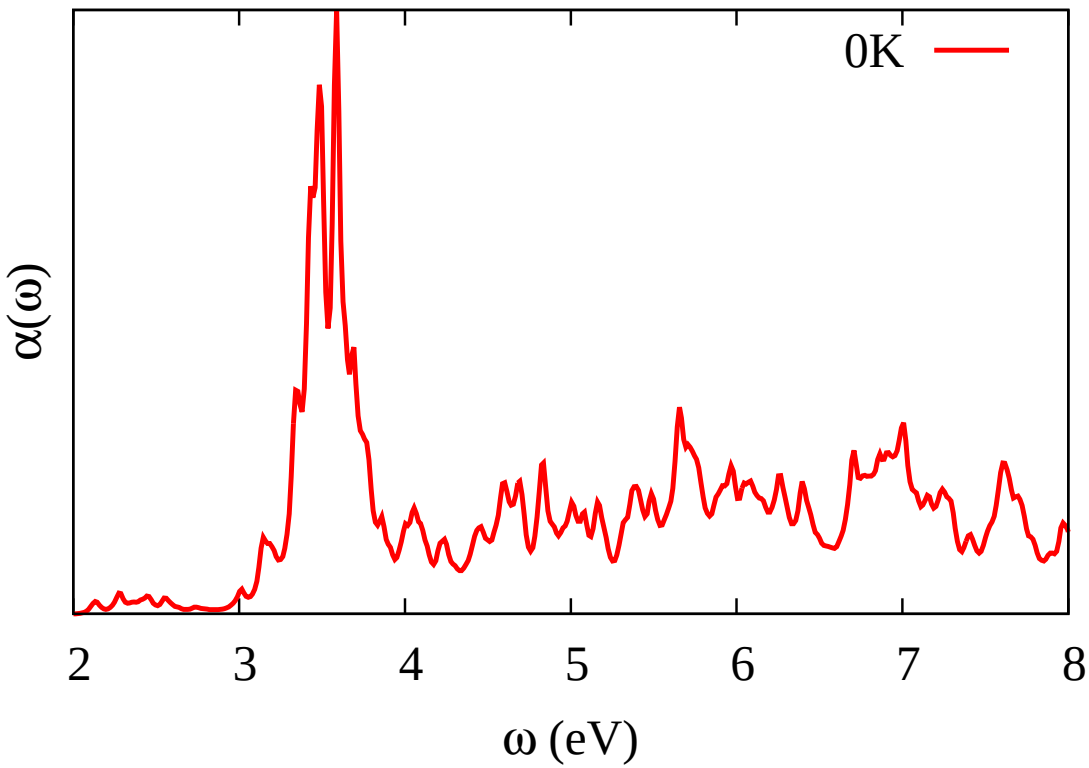


Vibration spectrum of Ag_{147}

- Vibration spectrum was computed with VIBRA utility
- Vibration spectrum was used to justify the MD parameters Δt and T_{total}
- 800 snapshots in TDDFT

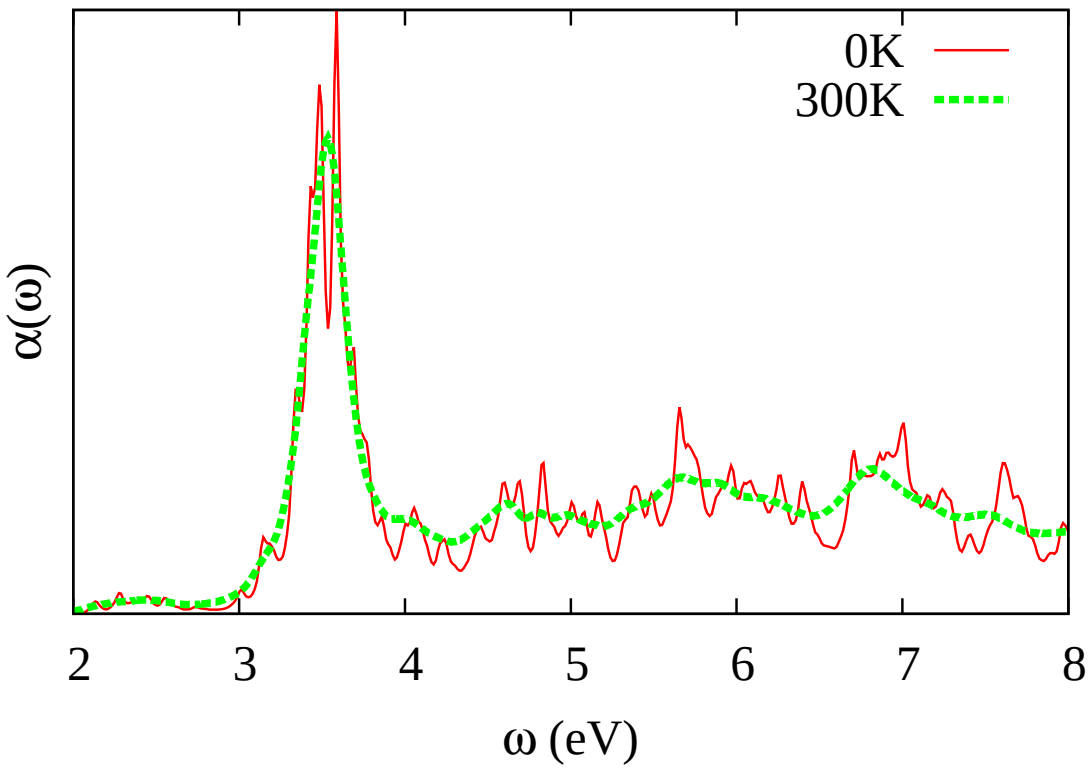
[9] Hale, Wong, Zimmerman and Zhou, *Modelling Simul. Mater. Sci. Eng.* 21 (2013) 045005

SEMD for Ag_{147}



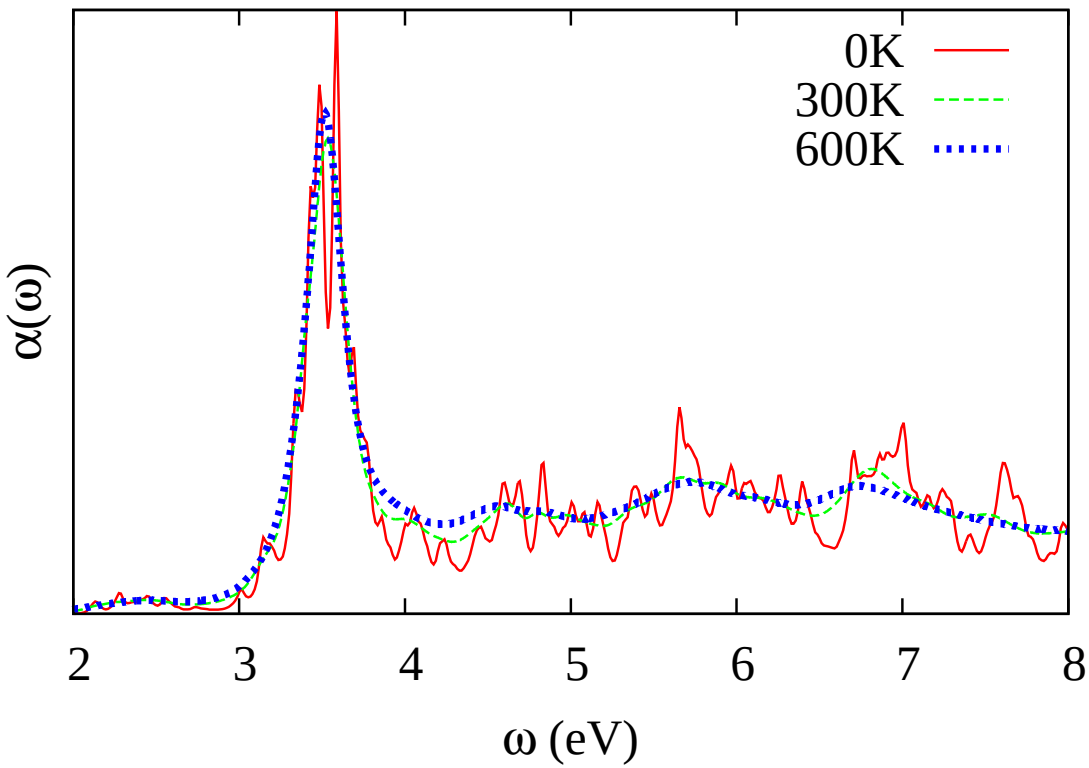
- Icosahedral modes at 0K

SEMD for Ag_{147}



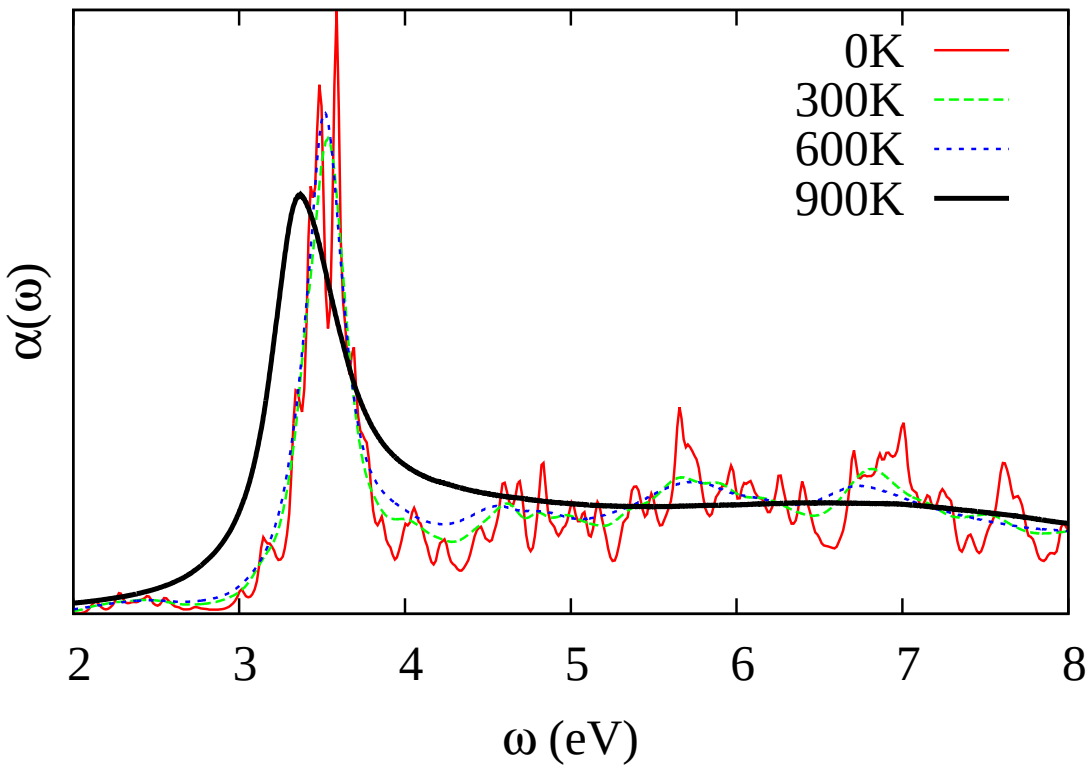
- Icosahedral modes at 0K
- merge at room temp 300K

SEMD for Ag_{147}



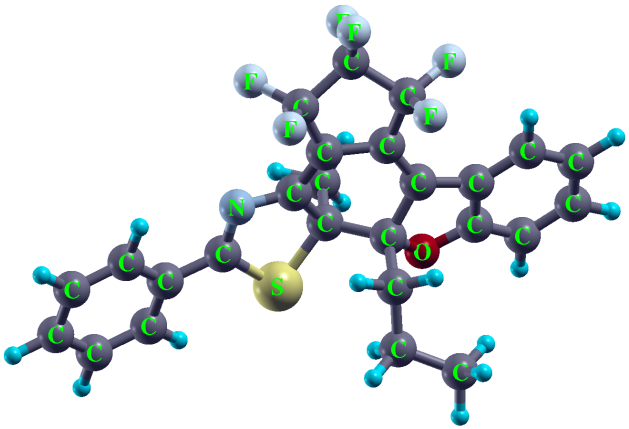
- Icosahedral modes at 0K
- merge at room temp 300K
- and stay unaltered between 300 and 600K

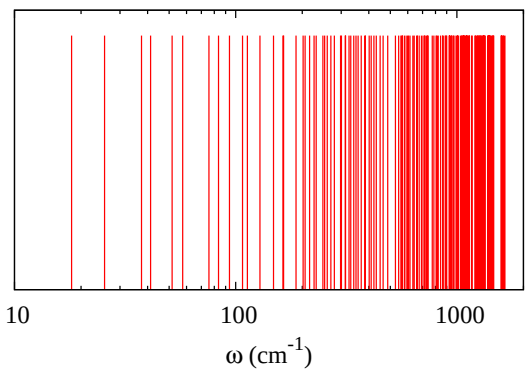
SEMD for Ag_{147}



- Icosahedral modes at 0K
- merge at room temp 300K
- and stay unaltered between 300 and 600K
- Melting affects the optical polarizability

AIMD for a diarylethene as a comparison





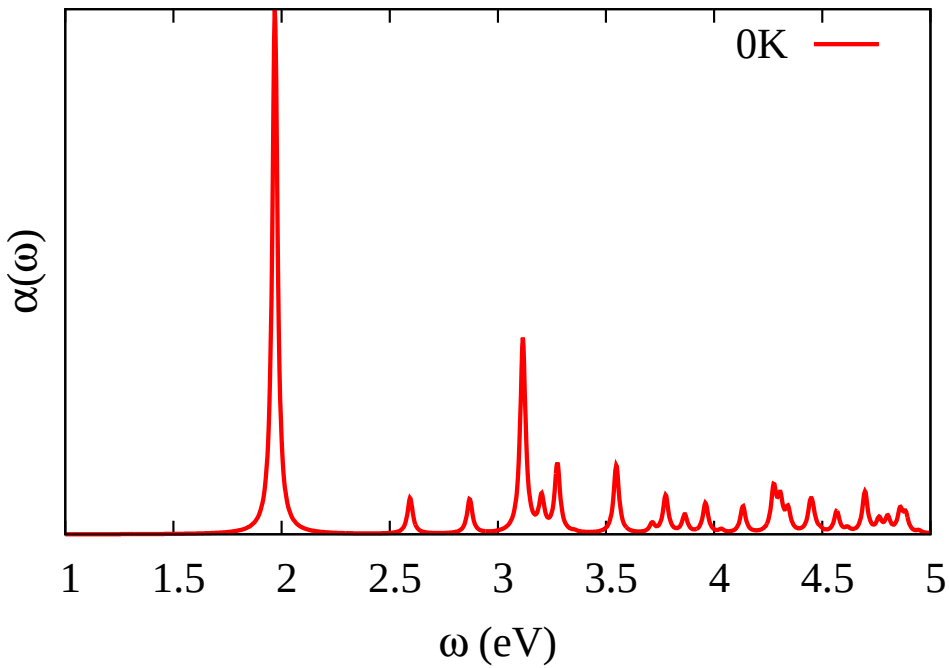
Vibration spectrum

- DFT+MD package SIESTA[10]
- Nosé thermostat $T_{\text{ion}} = 100$, 300 K
- PBE GGA

- PySCF-NAO: optical gap 1.97 eV
- PySCF-GTO: optical gap PBE 2.03 eV, B3LYP 2.33 eV
- VIBRAtion spectrum was used to justify the MD parameters Δt and T_{total}
- 800 snapshots in TDDFT

[10] José M Soler *et al* 2002 J. Phys.: Condens. Matter 14 2745

AIMD+TDDFT for a diarylethene compound



- HOMO-LUMO well-separated

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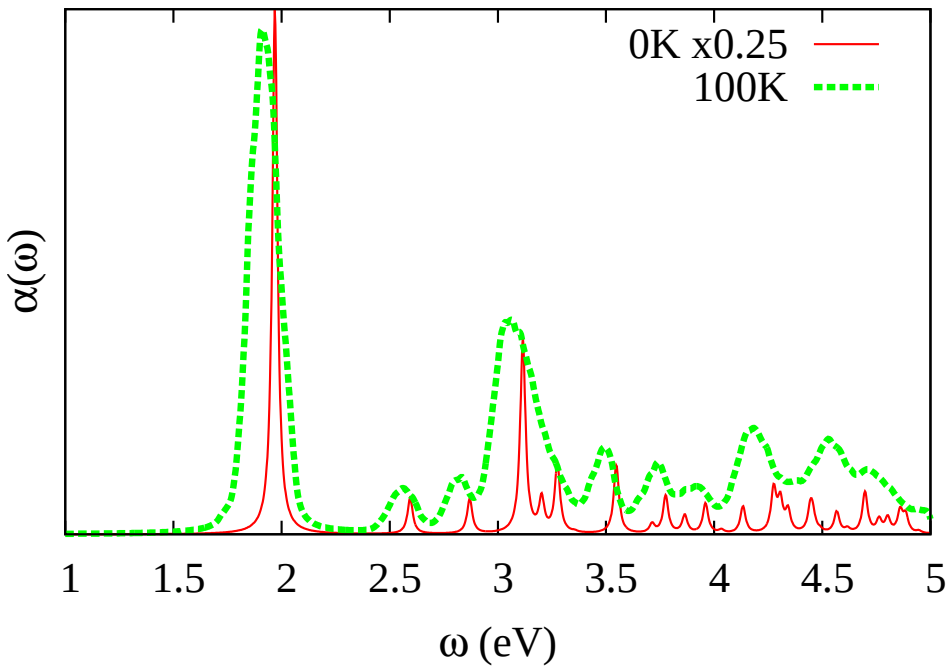

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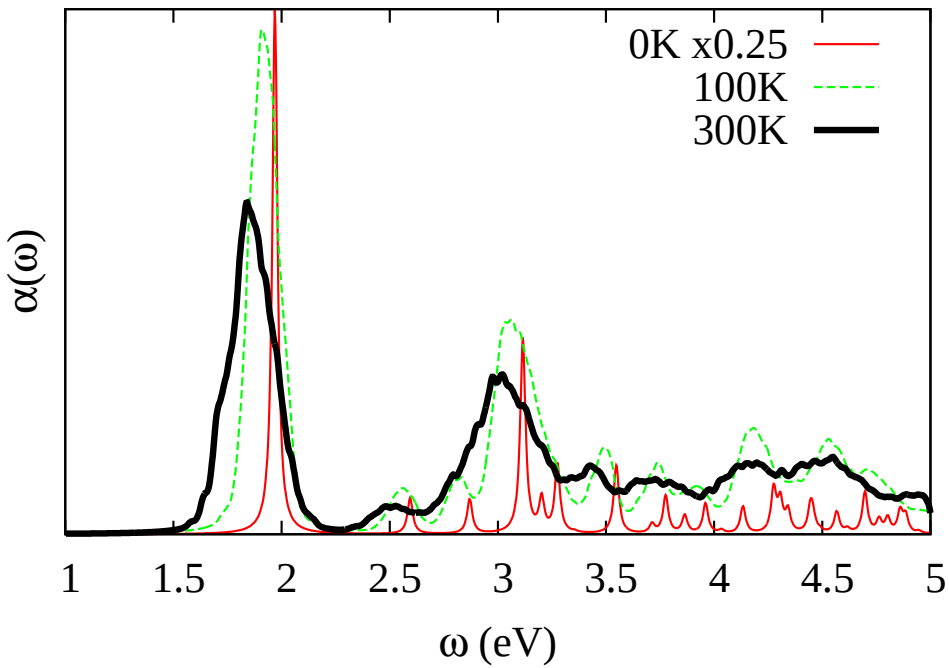

- HOMO-LUMO well-separated
- In contrast to Ag_{147}, the resonance frequencies are affected at low $T_{\text{ion}} = 100K$
- Similarly to Ag_{147}, the resonance frequencies $\omega_i \searrow$ are red-shifted while $T_{\text{ion}} \nearrow$

Valence electron energy loss spectra

Other stimuli is well possible[11]

$$\delta V_{\text{ext}}(\boldsymbol{r},\omega) = \int \mathrm{e}^{\mathrm{i}\omega t}|\boldsymbol{r} - \boldsymbol{r}_{\text{probe}}(t)|^{-1} dt$$

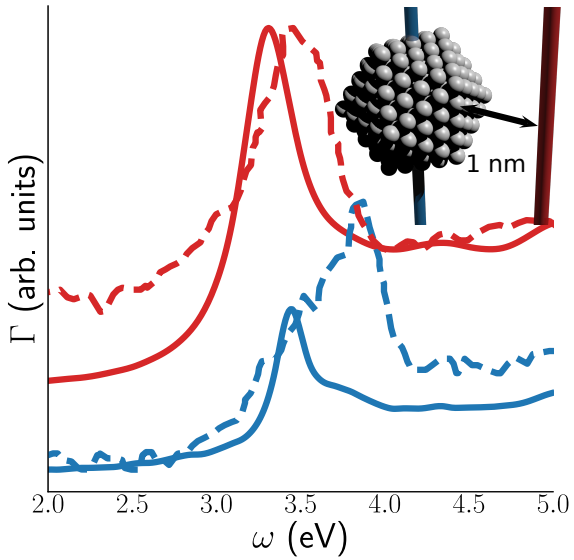

FIG. 4. Experimental [23] (dashed lines) and *ab initio* (full lines) EELS for silver icosahedral cluster. Two distincts trajectories of the electron beam are represented, one crossing the cluster at its center (blue lines) and the other near the surface of the cluster (red lines). The cluster geometry used for the calculations together with the beam trajectories are represented in the figure. The colors of the beams are corresponding to the colors of the lines.

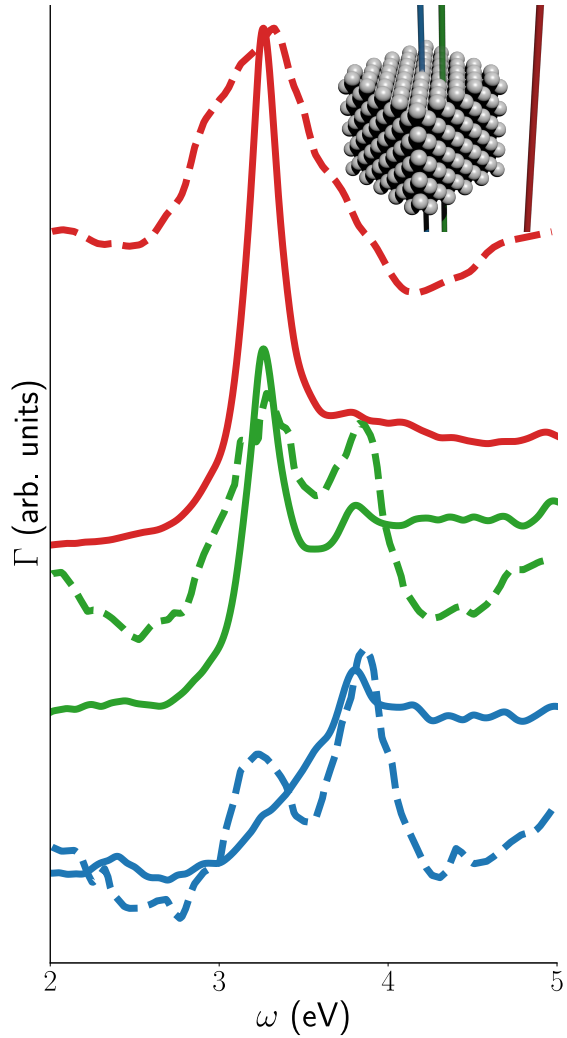

FIG. 5. Experimental [22] (dashed lines) and *ab initio* (full lines) EELS for a silver cube composed of 500 atoms and presenting a fcc lattice. Three distincts trajectories of the electron beam are represented, one crossing the cluster at its cen-

[11] MB, PK, DSP, Ab-initio theory of EELS, in preparation (2018)

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- PySCF-NAO – available online already
- Atomistic approach allows to address a wealth of phenomena

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Thank you for your kind attention!