Reverse-DADI method: a tool for computing dynamic atomic polarizabilities

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Among the methods used to estimate the absorption cross sections of dust particles in Earth's atmosphere and in Interstellar Medium (ISM), the Dynamic Atomic Dipole Interaction (DADI) model developed in Besançon has the advantage of being sensitive to the atomistic geometry of the particles and to the chemical functions it contains [1]. However, it requires the knowledge of the atomic polarizabilities of all atoms in the particle. We present here an adequate parametrization of the atomic polarizabilities for certain atomic species over the UV-visible spectrum. In particular, we fitted atomic polarizabilities for carbon and hydrogen, depending on the chemical function they were involved in, thanks to UV-visible absorption cross sections of PAHs that were computed with an *ab initio* code, Octopus. These parameters were then used to compute Mass Absorption Cross sections (MAC) of primary soot nanoparticles.

DADI model:

Similarly to DDA [2], we can compute dipoles on each atom i with DADI model by solving the following equation system, for all i from 1 to N :

$$\vec{p}_i(\omega) = \bar{\bar{\alpha}}_i(\omega)\vec{E}_0(\vec{r_i},\omega) + \sum_{j=1}^{N} \bar{\bar{\alpha}}_i(\omega)\,\bar{\bar{T}}(\vec{r}_i,\vec{r}_j,\omega)\vec{p}_j(\omega)$$

Where $\bar{\bar{\alpha}}_i(\omega)$ is the atomic polarizabilities tensor, $\vec{E}_0(\vec{r_i},\omega)$ the incident electric field applied to the particle and $\bar{\bar{T}}(\vec{r}_i,\vec{r}_{j\neq i},\omega)$ that can be computed with the double gradient of the generalized Green's function for the Helmholtz equation :

$$\bar{\bar{T}}(\vec{r}_i,\vec{r}_{j\neq i},\omega) = -\frac{1}{\varepsilon_0}\left(\nabla_{\vec{r}_i}\otimes\nabla_{\vec{r}_j} + \frac{\omega^2}{c^2}\,\bar{\bar{I}}\right)\left(-\frac{e^{i\frac{\omega}{c}|\vec{r}_i-\vec{r}_j|}}{4\pi|\vec{r}_i-\vec{r}_j|}\right)$$

With c the speed of light, ε_0 the vacuum permittivity and $\bar{\bar{I}}$ the identity tensor.

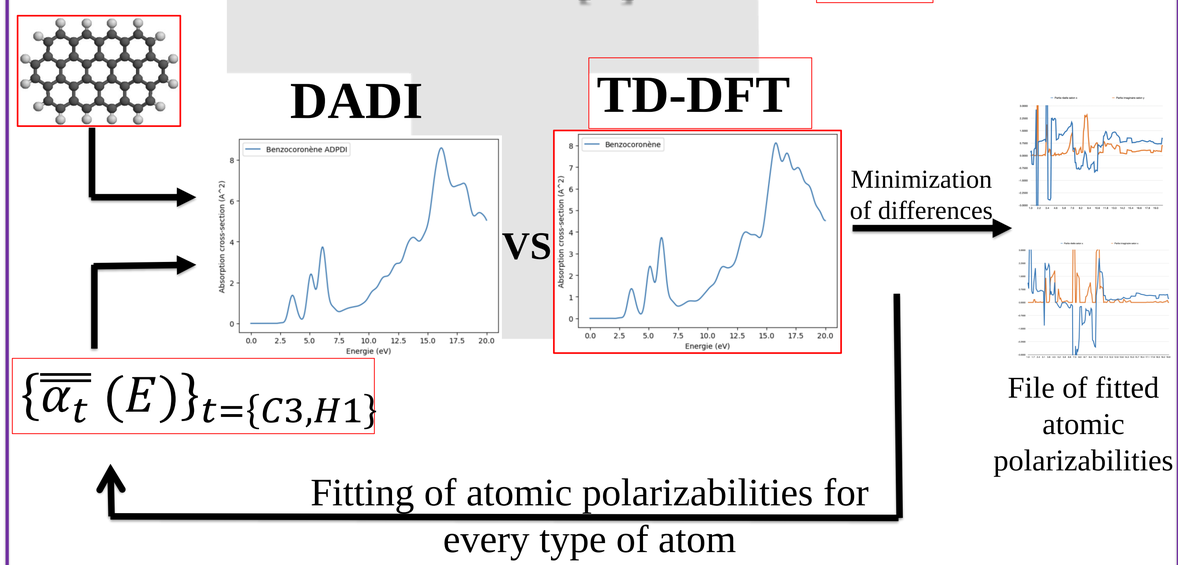
Because in DADI the point dipoles are supposed to represent atoms much smaller than the discretization volumes used in the DDA [2], the $i = j$ terms of the interaction tensor $\bar{\bar{T}}$ are assumed to simplify to :

$$\bar{\bar{T}}(\vec{r}_i,\vec{r}_i,\omega) = i\frac{2}{3}\frac{\omega^3}{c^3}\frac{1}{4\pi\varepsilon_0}\,\bar{\bar{I}}$$

Once the values of the dipoles are self-consistently computed, they can be used to compute various optical quantities of interest (such as Müller matrix or the extinction, diffusion and absorption cross sections) as in DDA [2].

Reverse-DADI method [3]:

: Input files



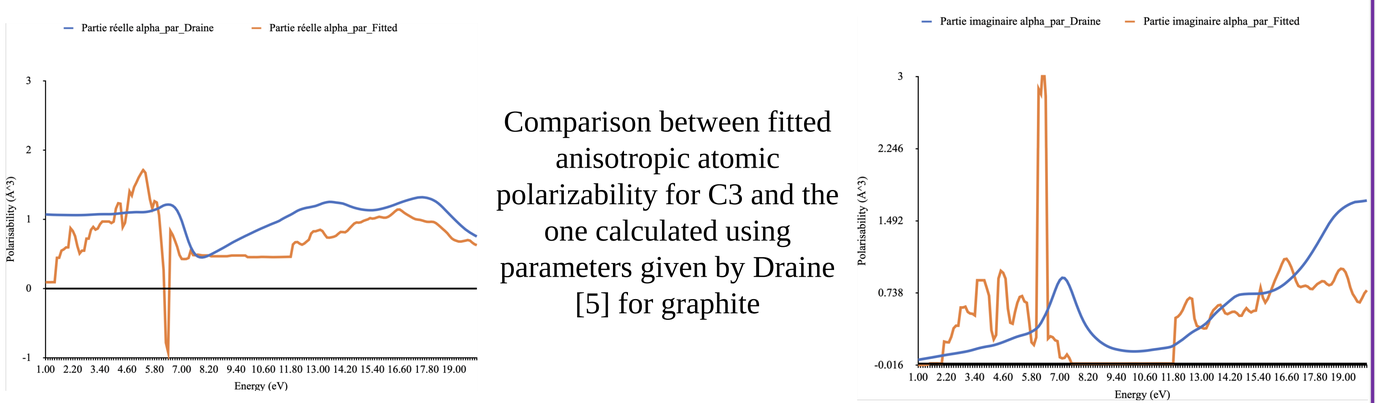
With DADI, absorption cross sections are computed from atomic polarizabilities

With reverse-DADI, atomic polarizabilities are computed from a database of absorption cross sections of small molecules, computed by TD-DFT.

Fit of atomic polarizabilities: preliminary results

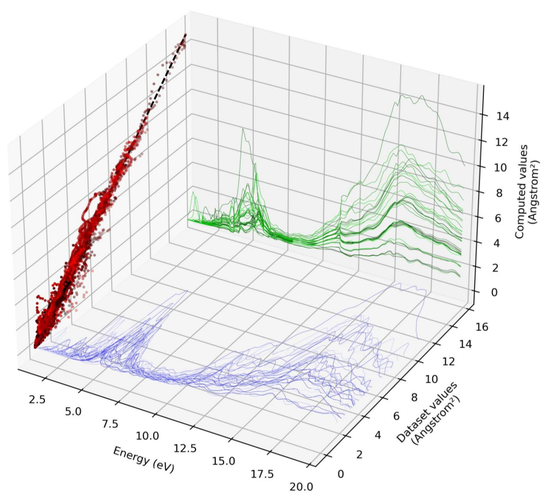
Database: Malloci et al. [4]

We have considered absorption cross sections of 36 polycyclic aromatic hydrocarbons (PAHs) computed with TD-DFT. These molecules go from Naphthalene ($C_{10}H_8$) to Circumcoronene ($C_{54}H_{18}$) and contain only C3 and H1 atom types.

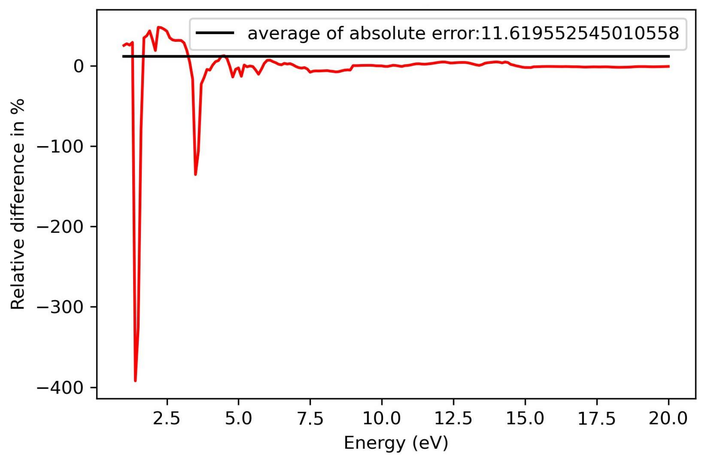


Comparison between fitted anisotropic atomic polarizability for C3 and the one calculated using parameters given by Draine [5] for graphite

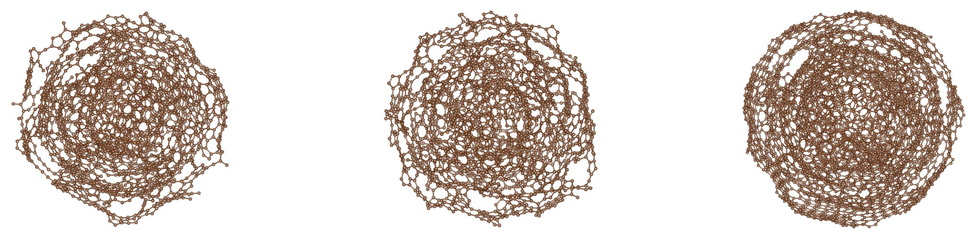
Computation of the absorption cross sections with DADI for 36 PAHs used for the fit of dynamic atomic polarizabilities with least-squares method



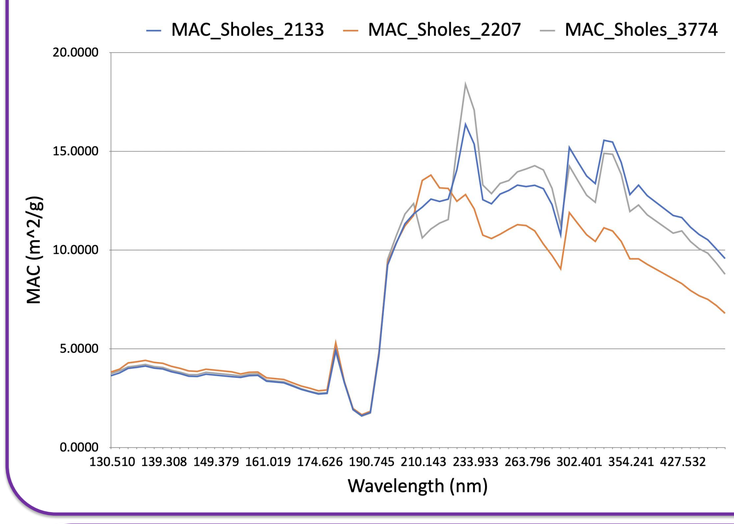
Relative difference between cross sections computed with DADI and with TD-DFT



Absorption cross sections of primary soot nanoparticles made of x C atoms with holes [6]:

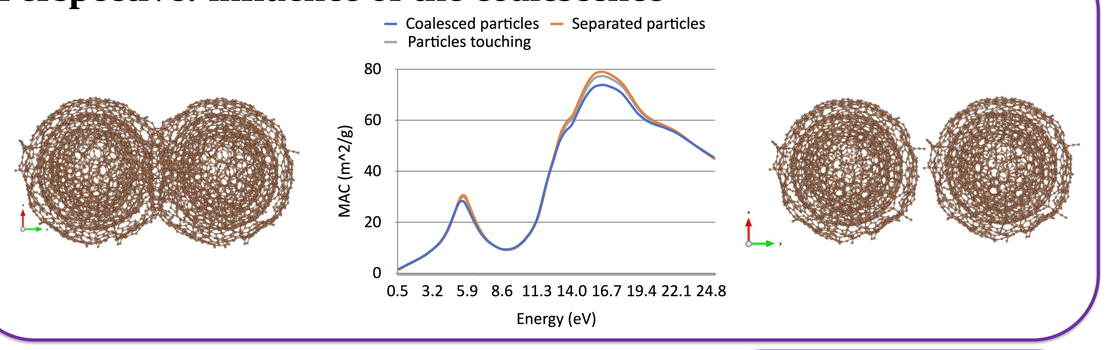


X = 2133 X = 2207 X = 3774



Absorption peak shift in position and amplitude as a function of atomic characteristics of the particle

Perspective: influence of the coalescence



Conclusion: In this contribution, we have shown the advantage of using the reverse-DADI method to get values of dynamic atomic polarizabilities for C and H atoms involved in different chemical functions. These parameters have then been used to calculate, using the DADI model, the optical properties of model soot nanoparticles which contain too many atoms for computation with quantum chemical methods in a reasonable time. This has allowed to evidence a noticeable effect of the coalescence process of two soot particles on their optical properties, due to the change in the coordination of certain atoms in the coalescence zone

References:
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