

Nicolas Brosseau-Habert^{1,2}, Sylvain Picaud¹, Michel Devel²

¹UTINAM Institute, UMR CNRS 6213, UFC – SPACE Team – 16, route de Gray, 25000 Besançon

²FEMTO-ST Institute, UMR CNRS 6174, UBFC – MN2S Department – 15B, Avenue des Montboucons, 25000 Besançon

Among the methods used to estimate the absorption cross-section of dust particles in Earth's atmosphere, the Atomic Dynamic Point Dipole Interaction (ADPDI) model 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 coordinates and polarizabilities of all atoms in the particle. Using LAMMPS, We computed the relaxed atomic coordinates for 2 onion-like carbon spherules more or less interpenetrated. As a result of the interpenetration distance, a decrease of aromatic over aliphatic C ratio is obtained. Then, We show that this causes possibly measurable shifts of the maxima of the absorption peaks of the absorption cross-section spectra, computed with ADPDI model, that increase with the degree of interpenetration.

Computational method:

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

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

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

$$\vec{T}(\vec{r}_i, \vec{r}_j, \omega) = -\frac{1}{\epsilon_0} \left(\nabla_{\vec{r}_i} \otimes \nabla_{\vec{r}_j} + \frac{\omega^2}{c^2} \vec{I} \right) \left(-\frac{e^{i\frac{\omega}{c}|\vec{r}_i - \vec{r}_j|}}{4\pi|\vec{r}_i - \vec{r}_j|} \right)$$

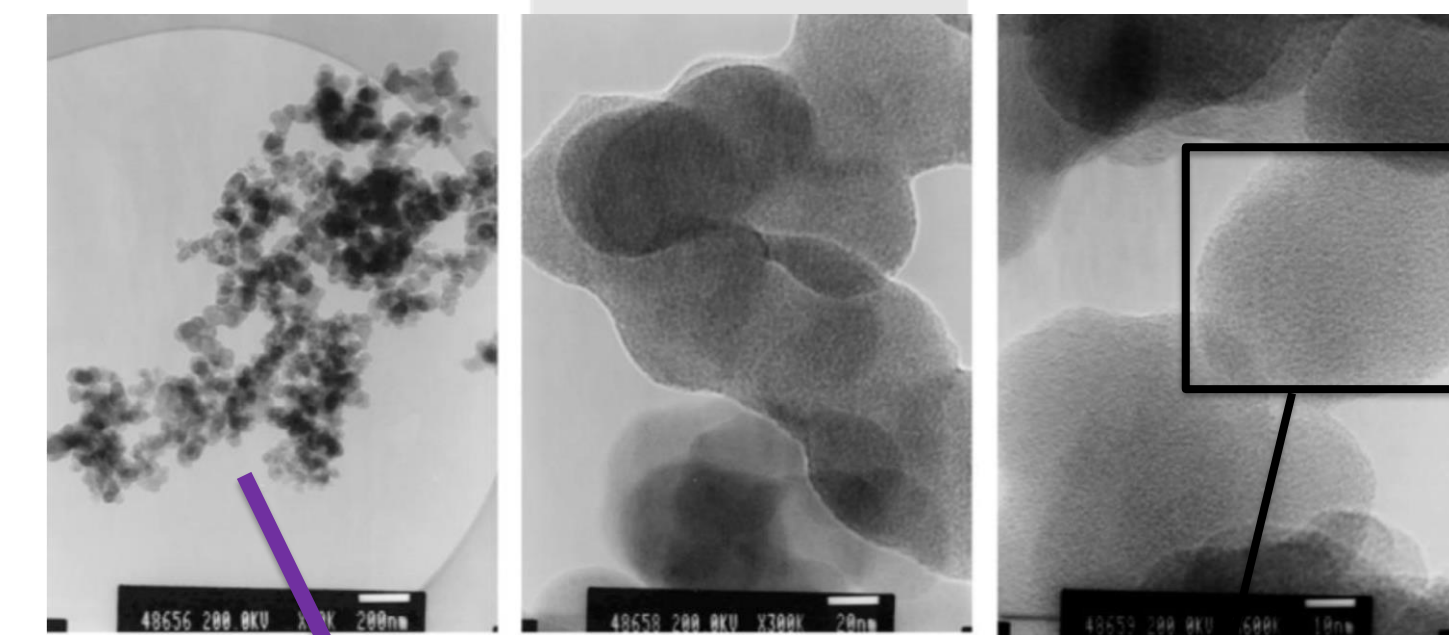
With c the speed of light, ϵ_0 the vacuum permittivity and \vec{I} the identity tensor.

Because in ADPDI 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 \vec{T} are assumed to simplify to:

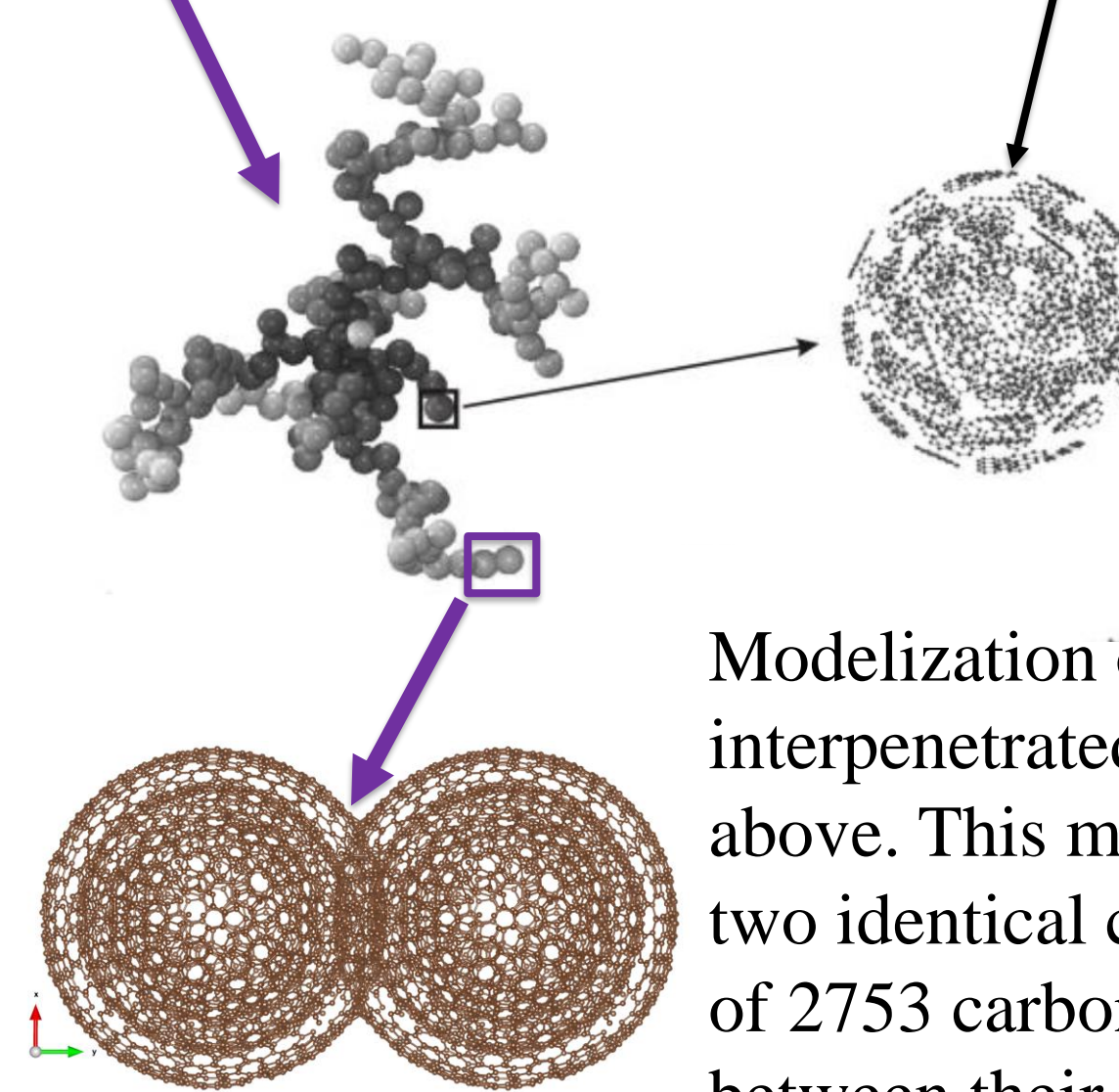
$$\vec{T}(\vec{r}_i, \vec{r}_i, \omega) = i \frac{2}{3} \frac{\omega^3}{c^3} \frac{1}{4\pi\epsilon_0} \vec{I}$$

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].

Modelization:



TEM images at different scales of a soot nanoparticle.



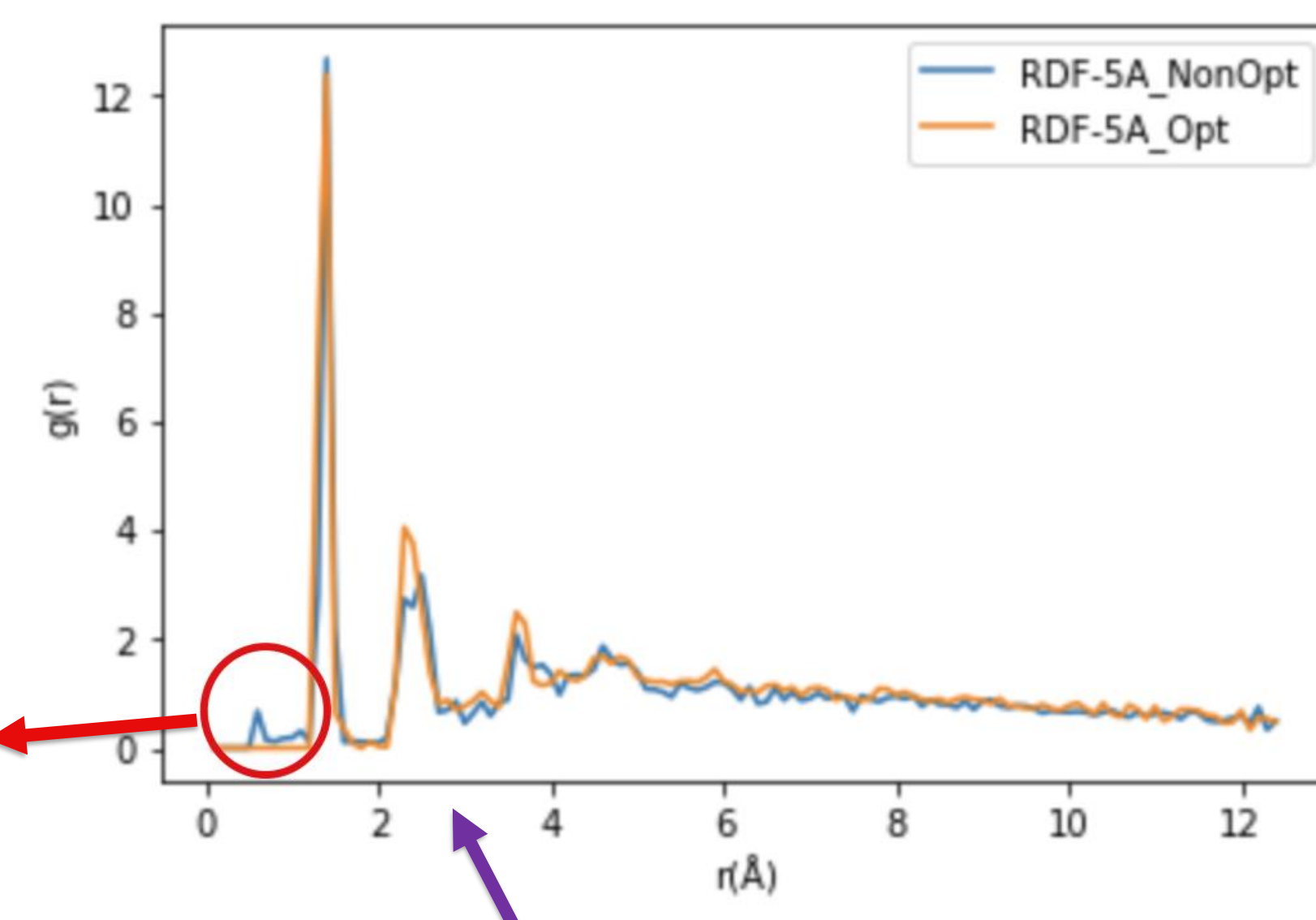
Modelization of 1 spherule from the soot nanoparticle above [3].

Modelization of 2 spherules, more or less interpenetrated, from the soot nanoparticle above. This model is obtained by considering two identical carbonaceous spherules made of 2753 carbon atoms, varying the distance between their centers.

Results of the relaxation:

Parameters:

Interatomic potential : AIREBO [5]
Minimisation algorithm : Conjugate Gradient
Temperature : 5 K
Ensemble : NVT
Timestep for equilibration : 1 fs
Equilibration time : 10 ps



The first peak in the RDF of the non-optimized structure is probably due to the random position of atoms in the coalescence zone, it disappears during the minimization, when atoms are rearranging

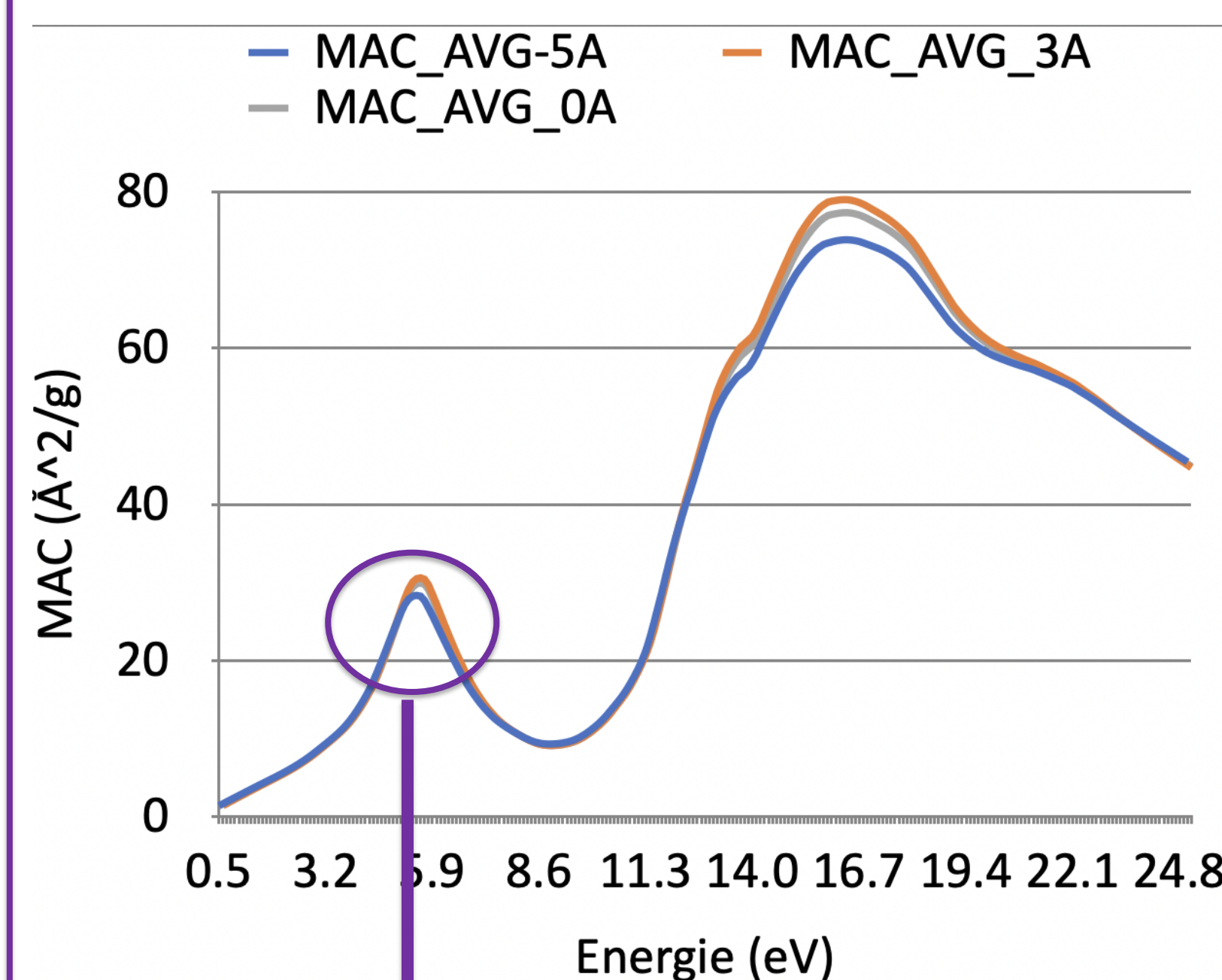
Plot of RDF for the maximum interpenetration

Molecule after equilibration phase		
Total No. of atoms	5506	5506
Distance between the surface layer of the two particles	+3 Å	-5 Å
Aromatic/Aliphatic C ratio	8.27	6.78
5-members rings	594	474
6-members rings	223	178
7-members rings	204	139

Before coalescing, the soot grains have defects on their surface layer i.e. a random distribution of holes created by removing 10% of carbon atoms from the outer fullerene.

The Aromatic/Aliphatic C ratio decreases by 18 % as the surface layer of one particle reaches the secondary layer of the other.

Computation of the absorption cross sections:



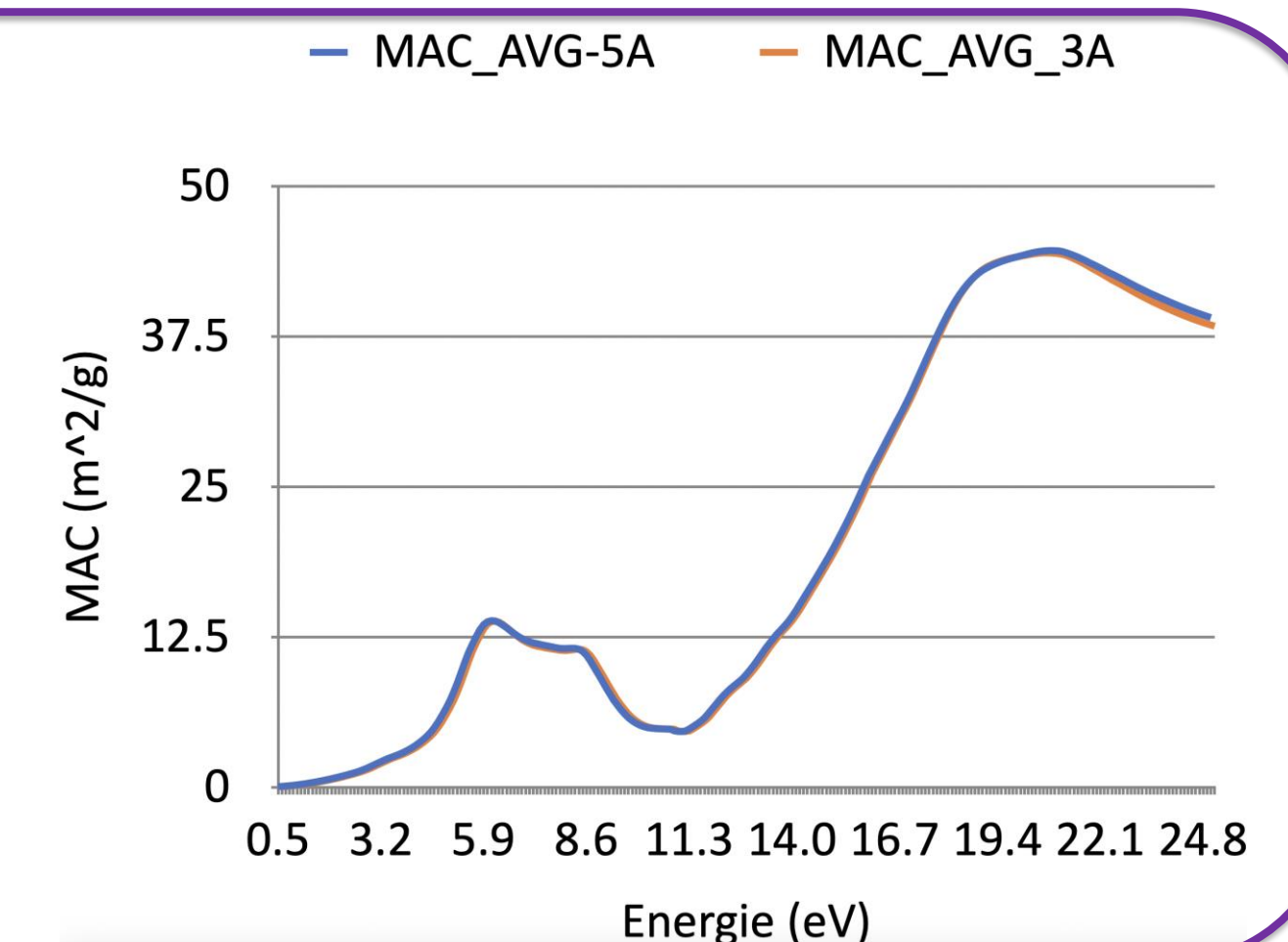
The first peak correspond to free-electron peak, the one that is usually measured experimentally. There is no shift visible when the surface layer of the particle are in contact but we have a shift in position and amplitude, that could be experimentally measured [7], when particles are coalescing.

The anisotropic atomic polarizabilities used for these computations were taken from the parameters given by Draine [6] for graphite

Energy (eV)	Wavelength (nm)	MAC (m²/g) at + 3 Å	MAC (m²/g) at - 5 Å
4.99	248.46	30.358	28.178
5.03	246.48	30.436	28.277
5.05	245.50	30.455	28.293
5.07	244.54	30.456	28.277
5.15	240.74	30.553	28.143
5.17	239.81	30.537	28.078
5.23	237.06	30.355	27.743

Verification of the influence of the change of geometry:

Computation of the MAC with the same isotropic atomic polarizabilities for every type of atoms, thus fixing the parameters of chemical composition. No effect caused by the modification of the geometry due to the coalescence is visible.



Conclusion: The aim of this work was to link the morphological variations generated by the interpenetration of two soot grains to the optical response of those particles. As expected, the necking of spherules leads to an evolution in the type of carbon atom bonds, particularly in the coalescence zone. This results in a shift in the position and amplitude of the absorption peaks, which could be measured experimentally. It would therefore be possible to relate differences in structure on an atomic scale to variations in optical properties using the model developed at Besançon, which would open up the possibility of using a classification of experimental spectra to make an inverse identification.

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Contacts

Brosseau-Habert Nicolas

Tél. – E-mail : +33 6.14.03.07.54 – nicolas.bh@femto-st.fr

Besançon, Belfort, Montbéliard, Sévenans
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