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Variation of the Radiative Properties during Black Carbon Aging: Theoretical and Experimental Intercomparison

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1. Motivations

- Black carbon (BC) atmospheric aging: freshly emitted BC aggregates coated by soluble materials through condensation, coagulation, and chemical oxidation.
- Laboratory experiments found substantial variations of radiative properties during BC aging, depending on coating material, thickness, and structures [e.g., *Zhang et al.*, 2008; *Shiraiwa et al.*, 2010; *Qiu et al.*, 2012].
- Atmospheric observations showed complex structures for BC coated by other aerosol components [*Adachi and Buseck*, 2013; *China et al.*, 2015], significantly affecting BC radiative properties [*Cappa et al.*, 2012; *Lack et al.*, 2012].
- This study develops a theoretical BC aging model to quantitatively understand the evolution of BC optical properties during aging and compares it with experiments.

2. Methods

Theoretical BC Aging Model

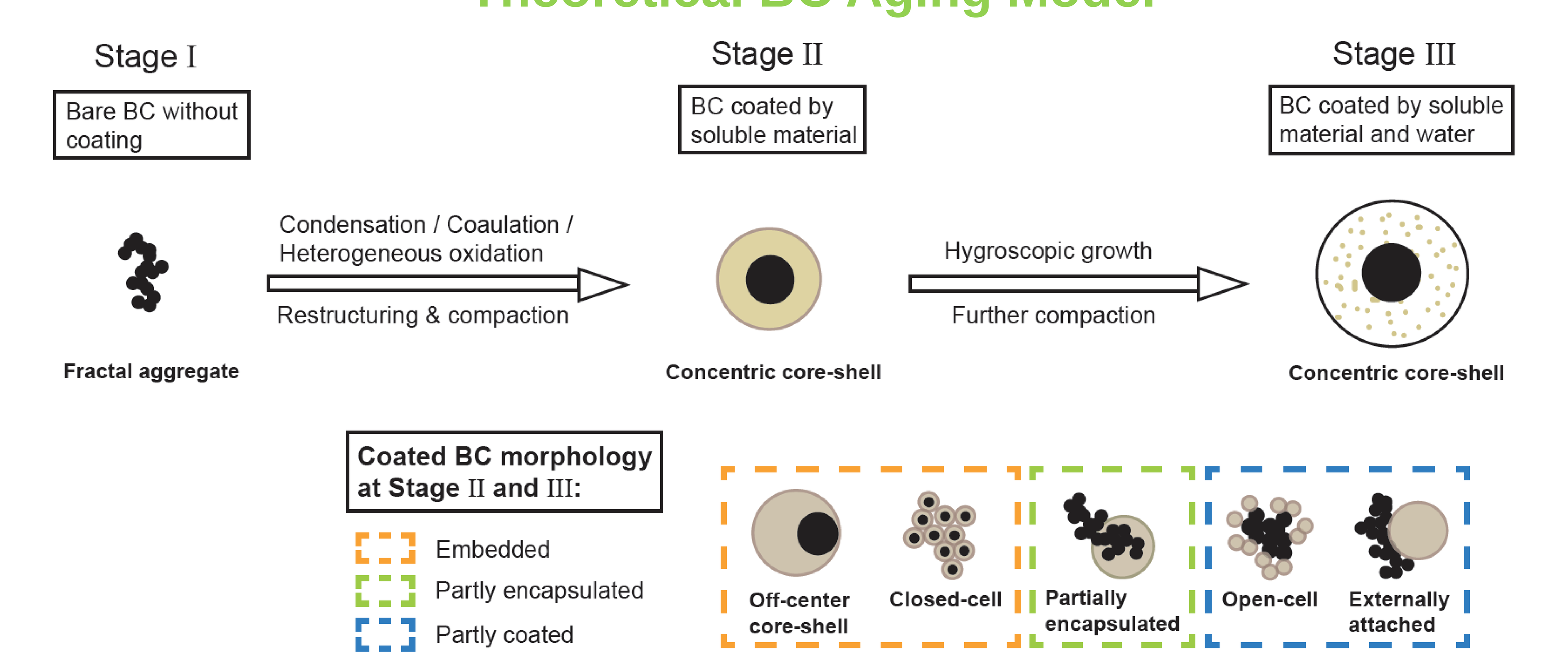

Fig. 1. A theoretical BC aging model that accounts for three evolution stages. Six typical structures for coated BC are considered based on observations.

Geometric-optics Surface-wave (GOS) Approach

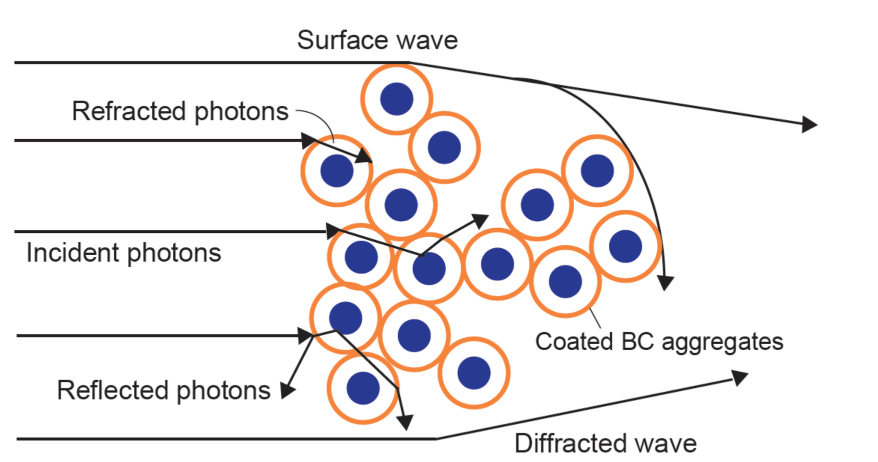

Fig. 2. A graphical representation of the geometric-optics surface-waves approach (GOS) for the calculation of light absorption and scattering of coated BC aggregates.

- Particle structures are constructed/simulated by a stochastic procedure [*Liou et al.*, 2011]. Light absorption and scattering are computed by the GOS approach [*Liou et al.*, 2011, 2014; *He et al.*, 2014].
- The GOS approach compares reasonably well with other methods, including Lorenz-Mie, FDTD, DDA, and T-Matrix. See *Liou et al.* [2010, 2011, 2014] and *Takano et al.* [2013] for details.
- GOS advantages: apply to a wide range of particle size and structure with a high computational efficiency.

Laboratory Experiment

- BC aging after exposure to sulfuric acid vapors at different relative humidity [*Zhang et al.*, 2008*; Khalizov et al.*, 2009].
- (1) BC mass: aerosol particle mass (APM) analyzer; (2) BC size: tandem differential mobility analyzer (TDMA); (3) BC extinction (532 nm): cavity ring-down spectrometer (CRDS) (4) BC scattering (532 nm): integrating nephelometer

Model Simulations

Aging Stage	Pure BC Mobility diameter (nm)	Pure BC Mass (10^{-16}g)	Coating material Species	Coating material Mass (10^{-16}g)	Standard calculation	Sensitivity calculation
I	155 245 320	5.13 13.0 20.3	–	–	BC aggregates with a fractal dimension of 2.1, BC refractive index of 1.95–0.79*i*, and 164/416/651 primary spherules with diameters of 15 nm for three experimental cases, respectively	(1) BC refractive index of 1.75–0.63*i*; (2) Fractal dimension of 2.5; (3) Primary spherule diameter of 20 nm; (4) Single volume-equivalent BC sphere
II	155 245 320	5.13 13.0 20.3	Sulfuric acid (H_2SO_4)	3.67 11.0 17.9	Concentric core-shell coating structures with BC refractive index of 1.95–0.79*i*	(1) BC refractive index of 1.75–0.63*i*; (2) Off-center core-shell structure; (3) Closed-cell structure; (4) Open-cell structure; (5) Partially encapsulated structure; (6) Externally attached structure
III	155 245 320	5.13 13.0 20.3	Sulfuric acid and water (H_2SO_4-H_2O)	7.59 20.7 33.6	Concentric core-shell coating structures with BC refractive index of 1.95–0.79*i*	(1) BC refractive index of 1.75–0.63*i*; (2) Off-center core-shell structure; (3) Closed-cell structure; (4) Open-cell structure; (5) Partially encapsulated structure; (6) Externally attached structure

• The mass and size of BC and coating material at each stage are derived from laboratory measurements.

3. Results

Theoretical and Experimental Comparison

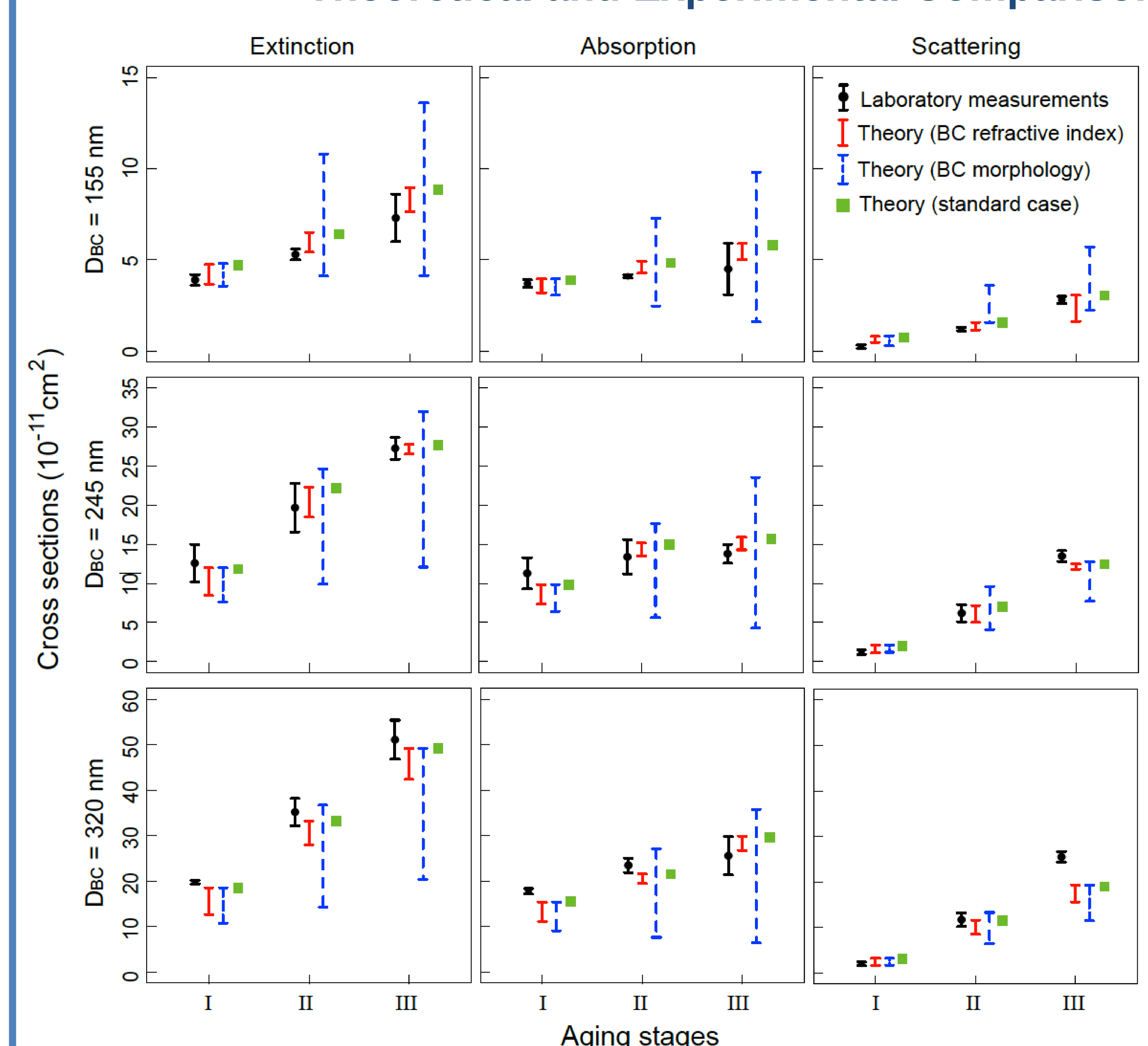

Fig. 3. Laboratory measurements and theoretical calculations of BC extinction, absorption, and scattering cross sections (532 nm) for three aging stages with different initial BC mobility diameters.

- The measured optical cross sections are generally captured (differences <30%) by theoretical calculations for fresh BC aggregates and coated BC (Stages II and III).
- Theoretical calculations still miss some observed features. For example, it tends to overestimate extinction and absorption for coated BC with smaller sizes and to underestimate scattering for larger BC sizes at Stage III.
- BC extinction and absorption cross sections at Stage I (Stages II and III) vary by 20-40% (5-20%) due to the use of upper and lower bounds of BC refractive indices (RI), while the variation of scattering reaches 50-65% (40-50%).

Effects of BC structures on Optical Properties

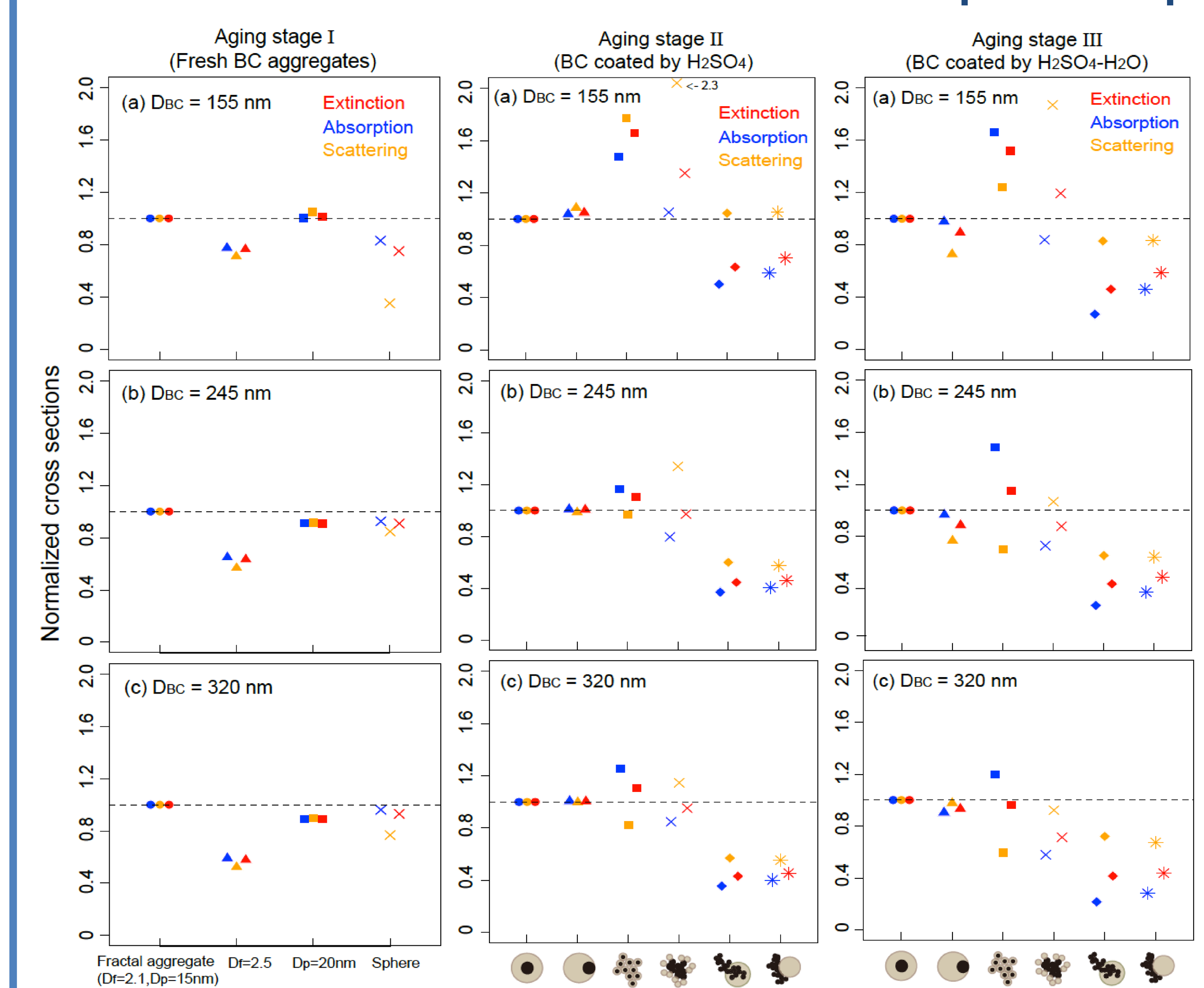

Fig. 4. Sensitivities of BC optical cross sections to BC structures at Stages I, II, and III with different initial sizes based on theoretical calculation.

- Optical cross sections of fresh BC aggregates are much more sensitive to fractal dimension than the size of primary spherules. Aggregate structure enhances BC absorption and scattering compared with mass-equivalent sphere.
- The off-center core-shell structure shows up to 30% less absorption and scattering than the concentric core-shell structure for thick coating.
- The open-cell structure tends to have weaker absorption and stronger scattering, while the reverse is true for the closed-cell structure.
- The partially encapsulated and externally attached structures have substantially smaller absorption and scattering.

Evolution of BC Absorption and Scattering

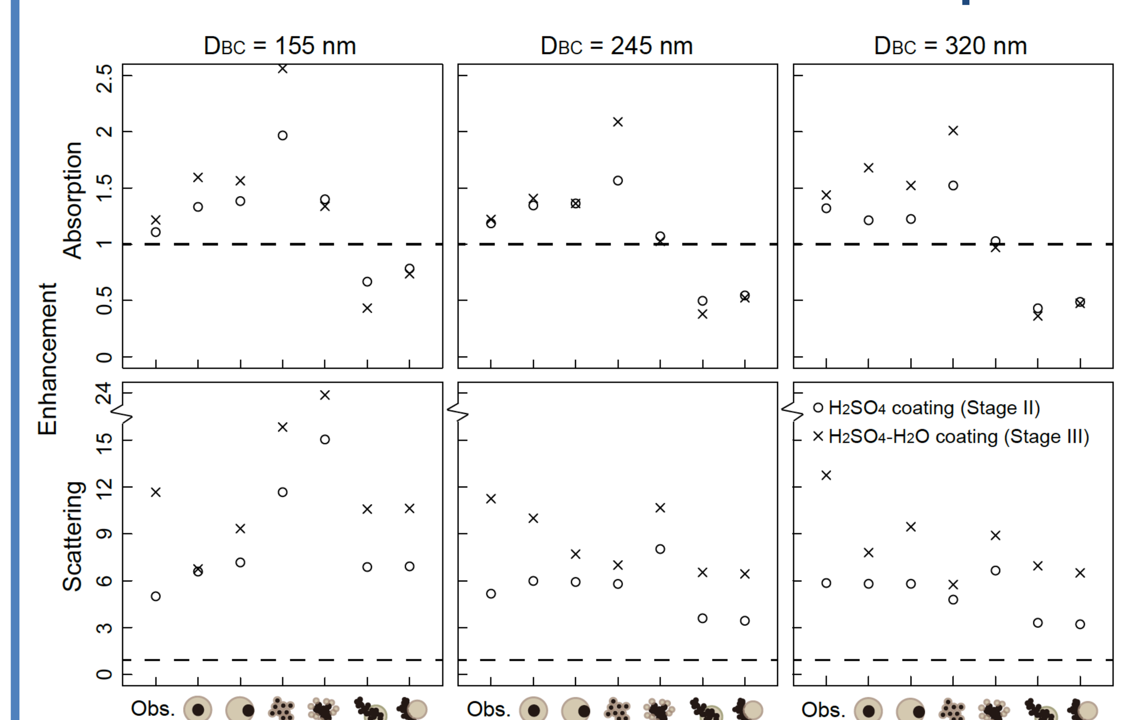

Fig. 5. Enhancement in BC absorption and scattering cross sections during aging from Stage I to II and III.

- The absorption enhancement during aging varies by a factor of >2, depending on BC size, coating structure, and aging stage.
- The increase in scattering is much stronger than absorption, ranging from a factor of 3 to 24.

Atmospheric Implications

- This study shows that BC absorption and scattering are highly sensitive to coating states (e.g., coating thickness, morphology, and composition), suggesting the evolution of BC coating states during aging in the real atmosphere could exert significant impacts on BC radiative properties and thus its climatic effects.
- Thus, a reliable estimate of BC radiative effects requires the incorporation of a dynamic BC aging process accounting for realistic coating amount, structure, and composition in climate models.