



Université Claude Bernard



Etude des processus photosensibilisés troposphériques

Tropospheric Multiphase Chemistry: Going Beyond OH Radicals

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Understanding the processing chain of tropospheric aerosols and radicals from sources to sinks is key for our ability to understand climate change. Numerous indicators, however, show that our knowledge is far from complete. As an example, secondary organic aerosols (SOA) can well be quantified, but their sources are subject to intense scientific discussion as the tropospheric budget of SOA is far from being closed. Photosensitized reactions have been suggested to be an important oxidation pathway in atmosphere, but their quantitative contribution was beyond reach (1, 2). However recently, Kaur et al. (3) suggested that this oxidative pathway might be even more important than the one induced by the main radical oxidant, the hydroxyl radical (OH). Therefore, this Ph.D. project aims at quantifying the tropospheric importance of photosensitized reactions in the liquid phase (*i.e.*, cloud droplet and aerosols).

Indeed, understanding atmospheric chemical processes is important in a threefold way as they: (i) contribute to atmospheric composition change (ii) are involved in the coupling of atmospheric chemistry and climate and (iii) lead to products affecting air quality (4-6), visibility (7), and climate (8).

Volatile organic compounds (VOCs) and SOA have to be considered as a system evolving in the atmosphere through physico-chemical and dynamical processing involving chemical feedbacks with oxidants. As a result, the ambient organic aerosol is typically highly oxidized (9). However, the total SOA mass measured at several sampling sites cannot be explained by the simple presence of such VOCs (10). Therefore, a current issue in the physical-chemistry of atmospheric organic particulate matter is that the models based on available parameterizations from laboratory studies (such as the Volatility Based Set approach – VBS) underestimate SOA, and do not fully capture aerosol particle growth observed in the atmosphere. Hence, the difference of SOA concentrations between observations and models suggests the possibility of other significant sources that may have not been yet identified and characterized.

Important efforts were consequently made to explain and close the gap between observations and modeling. It has been pointed out for instance that small dicarbonyl or carboxylic acid species which are formed in large amount during oxidation of VOC, can significantly contribute to SOA mass through cloud multiphase chemistry. Such multiphase processes have also been shown to produce light absorbing compounds in the particle phase. However, certain types of OA absorb radiation efficiently in the UVA-UVB (300–400 nm) and visible ranges. Very recently the terminology “brown carbon” (BrC), has emerged to describe this type of aerosol, characterized by an absorption spectrum that smoothly increases from the vis to UV wavelengths. Such absorbing molecules may also induce new photochemical processes within the aerosol particles (3). A significant body of literature exists on photo-induced charge or energy transfer in organic molecules (mainly in surface waters) (11).

These are photosensitized processes where the absorbing species (photosensitiser) is excited into a triplet state, and depending on the redox properties of the medium and reaction partners, charge or energy transfer can occur. While aquatic photochemistry has recognised several of such processes that accelerate degradation of organic molecules, only little is known thus far about such processes in/on atmospheric particles.

The potential existence of such photosensitized processes is overall affecting the oxidation potential of the tropospheric condensed phases... if the triplet state steady-state concentration is large enough to induce significant chemical transformations. This Ph.D. project is therefore designed to follow an investigation chain from basic photochemical studies and initial screening of compounds into quantified information on the importance of photosensitized reactions as a key driver of tropospheric multiphase oxidation and impactful for the description of haze.

Profile of the candidate:

The Ph.D. work will combine various tools arising from the field of chemistry and physics, such as laser photolysis, time resolved UV-visible and fluorescence spectroscopy, high resolution mass spectrometry, etc..., and it will aim at characterizing the chemistry of the triplet state of various chromophores found in atmospheric aerosols. The outcome of this work is a better description of aerosols photochemistry, and will improve our capability of description their impact on air quality and climate change.

Candidates with a background in chemistry, physical or analytical chemistry, or physics are therefore encouraged to send their CV.

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