

## Photochemical formation of large molecular weight oligomers from low-molecular weight keto-carbonyls in haze aerosol

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The optical properties of the atmospheric aerosol play a fundamental role in the Earth's radiative balance. Since ~60% of the aerosol mass consists of complex natural and anthropogenic organic matter that absorbs in the ultraviolet and, particularly, in the visible regions of the solar spectrum, it is important to establish the chemical identity of the organic chromophores and the mechanism by which they contribute to aerosol color. Here we report studies on the chemical composition versus chromism of photolyzed ( $\lambda > 305$  nm) solutions of PA, under a variety of experimental conditions that include substrate concentration, temperature and the presence of relevant spectator solutes, such as ammonium sulfate. We use high resolution mass and  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectrometries to track chemical speciation in photolyzed solutions as they go through thermochromic and photobleaching cycles. The chemical identity of the components of these mixtures does not change in these cycles, in which photobleached solutions gradually recover their yellow color in the dark with non-conventional kinetics typical of aggregation processes, we infer that visible absorptions involve the intermolecular coupling of carbonyl chromophores in supramolecular assemblies.

## Advanced analytical methods for understanding the chemistry of iodine in the marine boundary layer

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Measurements of trace compounds in the gas and particle phase are essential for understanding the chemistry of the troposphere. Within the last few years the impact of iodine on the chemistry of the marine boundary layer (MBL) received increasing attention. One reason is that gaseous iodine precursors have been proposed to be involved in the enrichment of iodine in marine aerosols, the formation of new particles in the MBL and their evolution to form cloud condensation nuclei [1,2]. Although progress has been made, a number of uncertainties about the sources, sinks, kinetic parameters and the recycling of iodine remain and the identification and quantification of reactive key species are still challenging analytical problems [3].

Interest in iodine atmospheric chemistry has been greatly stimulated in the last few years by the suggestion that molecular iodine ( $\text{I}_2$ ) rather than biogenic iodocarbons (e.g.,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ) is the most important precursor for new particle formation and also the dominant source of coastal reactive iodine in the MBL. Other key iodine compounds can also be formed within tropospheric reaction cycles, such as hypoiodous acid (HOI). Uptake of HOI on sea-salt aerosol has been proposed to enhance chlorine and bromine activation by the reaction of HOI with  $\text{Cl}^-$  and  $\text{Br}^-$ . The subsequent products,  $\text{ICl}$  and  $\text{IBr}$ , can again be released from the sea salt particles. However, the exact underlying chemical mechanisms leading to the different iodine species are still not understood, mostly due to the lack of analytical techniques to accurately measure certain key species, such as  $\text{I}_2$ , HOI or  $\text{ICl}$  [4]. This contribution focusses on advanced analytical methods used for iodine speciation in the gas and particle phase, including some recent developments using an Aerodyne TOF aerosol mass spectrometer.

[1] O'Dowd *et al.* (2002) *Nature* **417**, 632–636. [2] O'Dowd & Hoffmann (2005) *Environ. Chem.* **2**, 245–255. [3] von Glasow & Crutzen (2007) *Treatise on Geochemistry Update* **1**, 1 – 67. [4] Huang & Hoffmann (2009) *Anal. Chem.*, in press.