Characterization of aerosols precursors and their hydrated complexes from microwave and infrared spectroscopy supported by quantum chemistry calculations.

Subject:

Volatile organic compounds (VOCs) play a significant role in the mechanisms of formation of ozone and greenhouse gases. Their presence in the gas phase in the atmosphere is due to many anthropogenic sources (combustion of fuels, paintings, adhesives, solvents, pesticides, etc) and also biogenic sources (defense or pollination mechanisms of plants, fermentation products, etc). In addition to their impact on the radiative budget of the Earth, they have effects on health going from simple respiratory problems to carcinogenic effects. VOCs and their degradation products are also known as sources of secondary organic aerosols (SOA), themselves influencing the terrestrial climate by absorption/diffusion of the radiation and formation/modification of the lifetime of the clouds. In this realm, the characterization of the molecular properties of VOCs and their degradation products as well as their nucleation processes is a major issue in physical chemistry of the atmosphere.

Preliminary to the atmospheric studies, the spectroscopy in laboratory at the molecular scale is an invaluable tool. Indeed, the comprehension of the physico-chemical properties of carbonaceous molecules in aqueous medium comes from the analysis of their pure rotation and/or rovibrational spectrum with the support of quantum chemistry calculations. The recording and the modeling of the spectrum of the free molecule lead for example to the experimental identification of the energetically most stable conformations. In a next step, the same study applied to the molecule in the presence of water gives access to the micro-solvation processes and the structural modifications upon hydration. These data are then extremely useful for the quantification of molecules observed at a given site and for the simulations of phenomena such as nucleation process.

The target systems will be among the families of acids, aldehydes, polycyclic aromatic hydrocarbons, monoterpenes and their hydrated complexes. This project will be centered mainly on the Fourier transform microwave (FTMW) spectrometers (pure rotation spectroscopy in the 2-20 GHz range) managed by the supervisors. The samples will be observed in the gas phase within a supersonic jet supplied with an injection line entirely controlled in temperature and pressure. The spectra will be analyzed thanks to available spectral simulation programs taking into account the spectroscopic properties of the studied system. Analysis tools (homemade programs) could be developed/improved in order to interpret the spectroscopic constants in terms of physico-chemical properties (structure and dynamics of the hydrogen bonds, constant of dimerization/hydration, free energy of formation, etc). Quantum chemistry calculations will be carried out thanks to the calculations facilities available at the laboratory (cluster of 400 CPU) and the university. In addition, the infrared signatures (rovibrational spectroscopy in the 50-4000 cm^{-1} range) could be recorded, via deposits of proposals to the synchrotron facility SOLEIL, using the Jet-AILES apparatus (managed in collaboration with researchers from IPR/Rennes 1, LADIR/Paris VI and the AILES beamline) and the long absorption pass cell (in collaboration with O. Pirali, ISMO/Paris XI). Other internal collaborations (PhLAM, PC2A) could be considered, linking the present project of the *Work Package 1* to the *Work Package 2* of the Labex CaPPA, as well as external collaborations with the IPR and the LADIR (usual partners for the infrared region).

References:

- *Secondary organic aerosols from anthropogenic and biogenic precursors,* U. Baltensperger et al., Faraday Discuss., 130 (2005), pp. 265-278
- *Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols,* M. O. Andreae, D. Rosenfeld, earth-science reviews, 89 (2008), pp. 13-41
- *Research on aerosol sources and chemical composition: Past, current and emerging issues,* A. I. Calvo et al., Atmos. Res. 120 (2013), pp. 1-28
- *Conformational flexibility in hydrated sugars: The glycolaldehyde-water complex*, J.-R. Aviles Moreno, J. Demaison, T. R. Huet, J. Am. Chem. Soc. 128 (2006), pp. 10467-10473
- *The $(CH_2)_2O{-}H_2O$ Hydrogen Bonded Complex. Ab Initio Calculations and Fourier Transform Infrared Spectroscopy from Neon Matrix and a New Supersonic Jet Experiment Coupled to the Infrared AILES Beamline of Synchrotron SOLEIL.*, M. Cirtog et al., J. Phys. Chem. A 115 (2011), pp. 2523-2532.
- *Hydrated Complexes of Atmospheric Interest: Rotational Spectrum of Diacetyl-Water*, L. B. Favero, W. Caminati, J. Phys. Chem. A 113 (2009), pp. 14308-14311
- *Water clusters adsorbed on polycyclic aromatic hydrocarbons: Energetics and conformational dynamics*, A. Simon, F. Spiegelman, J. Chem. Phys. 138 (2013), 194309

Requirements:

The candidate should have a master degree in physics or physical chemistry. This project needs mainly experimental skills. Spectral and data analyses and quantum chemistry calculations will also be performed.

Funding:
Co-funding Labex CaPPA – région Nord Pas de Calais
Start: October 2014; deadline to apply: 15 june 2014
The monthly salary will be 1685 Euros including social, medical insurance and retirement contributions.

Recruiting laboratory:
The Physique des Lasers, Atomes et Molécules (PhLAM) laboratory is a world recognized institute in physics, specialized in the fields of molecular spectroscopy, theoretical molecular chemical physics, cold atoms, nonlinear optics and photonics. The molecular spectroscopy group possesses state of the art spectrometers used to study molecular systems of astrophysical and atmospheric relevance. The present project is supported by the laboratoire d'excellence Chemical and Physical Properties of the Atmosphere (labex CaPPA).

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