Université de Lille

CaPPA Labex

## Master 2: Research Training 2023-2024

Laboratory: PhLAM, PC2A

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Collaborator: Eventually CaPPA Work Package: WP-1 From gas phase to aerosols

### Study of Atmospheric Radicals Reactivity: Coupling of a Fast Flow Tube Reactor with Chirped Pulse Fourier Transform Millimeter-wave Spectroscopy

Radicals play an important role in the atmosphere, controlling its oxidative capacity. Characterizing the reactions of radicals in the atmosphere is an ever present challenge. Spectroscopic methods have proven successful in measuring radicals in different reactors through their UV-visible or infrared spectra. However, rotational spectroscopy would allow absolute specificity in determining the identity of radicals as well as molecules from experiment. The distinguishing factor of rotational spectroscopy over other techniques is in its absolute determination of structural isomers, such as $CH_3O$ and $CH_2OH$, which have the same mass but entirely different rotational spectra.

The Fast Flow Tube apparatus in PC2A/CERLA will be combined with the Chirped Pulse Fourier Transform Millimeter-wave Spectrometer in PhLAM (Figure 1) to address two scientific goals: **1) Measure the spectra of Radicals with Large Amplitude Motion (RLAMs)** and **2) Measure product branching ratios of chemical reactions.** RLAMs are represented in most organic radicals, as many contain a -$CH_3$ moiety that can rotate, causing tunneling splitting from the large amplitude motion. This large amplitude motion challenges theoretical descriptions, including the prediction of chemical reactions rates from *ab initio* calculations. RLAMs are prominent as reactants and products in the atmosphere, with the methyl peroxy ($CH_3O_2$) serving as a prime example. Most RLAMs rotational spectra are unknown though, so the collaboration between PC2A and the SPECTRO team in PhLAM will search for these spectra relating it to their structure and then search for them as products of reactions of atmospheric relevance.

The radicals will be generated in the flow tube reactor using microwave discharges of fluorine (or chlorine) and reactions with precursors, they will then be reacted with oxygen to make peroxy radicals or new reaction products. The laminar flow of this reactor and radicals generation possibilities give ideal conditions to control reactions before expansion into a differentially pumped chamber, where the radicals would be probed at lower pressures more conducive to rotational spectroscopy experiments. The chirped pulse Fourier transform Millimeter-wave spectrometer from PhLAM ranging from 50-500 GHz will be used to probe a variety of molecules and radicals, and determine relative branching ratios. Spectroscopy will first be proven on ideal systems and then applied to reactions of atmospheric interest.

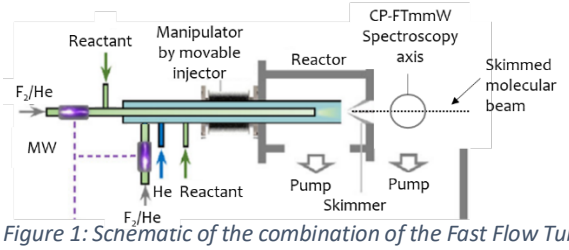


*Figure 1: Schematic of the combination of the Fast Flow Tube and Chirped pulse Fourier transform Millimeter-wave spectrometer*

This project is addressed to candidates interested in the experimental aspects of the research and having knowledge in atmospheric chemistry and/or spectroscopy.

Keywords: Atmospheric Chemistry, Spectroscopy, Oxidation, Radicals