

INTERNSHIP OFFER: Electrochemical reaction kinetics under vibrational coupling with infrared plasmons

Chemistry under ultraviolet or visible irradiation increases reaction rates by exciting reagent species into higher energy electronic states which facilitates access to final product states. The energy of infrared photons is typically too small to accomplish this. Recently however [1], a series of tantalizing works have suggested that chemical reaction rates can be modified by performing reactions in Fabry-Perot cavities tuned to the (infrared) vibrational energy of molecule(s) along the reaction path. Since all molecules have vibrational modes in the infrared, this has given birth to a new field of research known as *cavity chemistry* [2]. This exciting field offers not only the possibility to modify the energetic cost of chemical reactions, but may also help to shed light on their fundamental, rate-limiting mechanisms.

In this internship we propose to apply these concepts to *electrochemical* reactions.

Since electrochemical reactions take place at conducting electrode surfaces, the mirrors of Fabry-Perot cavities (where electric fields are zero) are not well adapted to cavity electrochemistry. For this reason, we propose to confine infrared photons at electrode surfaces by structuring them into plasmonic cavities. The cavities will be based on ultrathin Au films (< 10 nm) formed of either densely packed monolayers of nanoparticles or arrays of antennas. The films may be grown electrochemically or by evaporation in vacuum using microfabrication techniques. They will be deposited on Si prisms and hemispheres for backside illumination of the electrode by tunable, infrared quantum cascade lasers. In both electrode configurations the electrochemical cell design allows for normal electrochemical operation with no limitation due to ionic diffusion or electrolyte conductivity. The ultrathin Gold films may also be electrochemically covered by an ultrathin layer of catalyst (e.g. Ir, Pt, Cu) which will be chosen as a function of the electrochemical reaction under study (Ir for the oxygen evolution reaction, Pt and Cu for CO₂ reduction). These two electrochemical reactions are important for energy and CO₂ conversion. For the oxygen evolution reaction, we will focus on coupling to the OH and H₂O vibrational modes. For the CO₂ reduction, we will be interested in the reaction products and focus on the CO vibration modes.

This interdisciplinary work will allow the candidate to develop experimental competencies in electrochemistry (sample preparation & electrochemical characterizations), analytical chemistry (infrared spectroscopy), optics (plasmonics), and device engineering (design & microfabrication of antenna arrays). The project is funded by the ANR jointly between physics and chemistry groups of the multidisciplinary PMC laboratory.

[1] W. Ahn et al., *Modification of ground-state chemical reactivity via light-matter coherence in infrared cavities* Science **380**, 1165 (2023)

[2] K. Hirai et al., *Molecular chemistry in cavity strong coupling* Chemical Reviews **123**, 8099 (2023).