Activation and fixation of CO_2 molecule and carboxylate moiety by a single metal atom center. Experimental, theoretical, and statistical investigation of reaction mechanisms and molecular properties.

The capture, activation and fixation of the CO_2 molecule and carboxylate moiety by metal atom is currently a very attractive and challenging research topic across the scientific fields, especially for chemistry and applied physics. The increasing atmospheric level of CO_2 poses one of the most serious challenges to mankind, and is of worldwide concern. Besides reducing the total combustion of hydrocarbons, there exist two potentially viable strategies for counteracting the increasing CO_2 levels. One is to capture CO_2 from effluent gases from fossil-fuel power plants and deposit the catchment into geological formations (CO_2 catchment). The other is to incorporate CO_2 into chemical production as a feedstock for synthetic fuels, commodity chemicals or polymers like polycarbonates (CO_2 fixation). In the latter strategy, either a carbon-carbon bond or a carbon-hydrogen bond between CO_2 and a second substrate molecule has to be established in the reaction, and normally energy input is required, typically by transfer of electrons, either to activate CO_2 or the other substrate (reductive coupling). When CO_2 in used in the synthetic laboratory (scientific purposes or pharmaceutical industry) as a basic chemical reagent (e.g. in the form of *dry ice*) its practical value comes from scientific publications where the particular reactivity is well recognized.

In recent years, the metal-mediated CO_2 activation, reduction or decarboxylative new C-C bond formation reactions become one of the most important topics in metalorganic chemistry, due to its high practical value and easy accessibility of the substrates (gaseous CO_2 and carboxylic acids). Progress in the utilization of carbon dioxide as a reactant in synthetic laboratory or even in chemical industry, and better insight into biological and artificial photosynthetic fixation of CO_2, requires detailed knowledge of the mechanism in terms of each of the elementary transformation and the molecular factors that govern reactivity in each of these steps. In this respect, understanding the reaction mechanisms is central to all research in this fast growing field. There is an articulated understanding that the fundamental knowledge in this field is insufficient.

Current knowledge on the chemical reactivity of metal-based compounds widely used in organic chemistry and electrochemistry is mostly based on diffuse knowledge relaying on the structurally diverse molecules and laboratory protocols. Besides a few attempts, there is a clear lack of systematic recognition of single-metal catalytic strength and bonding abilities in its pristine form. Considering this, one of the main goals of the current proposal is fill this gap by providing a systematic study on metal activities in the form of molecular trends across the alkali and transition metal atoms (Fig. 1.).

Our extensive efforts will concentrate on three chemical processes of much current interest, namely: **(I)** the capture of CO_2 by metal atoms and its conversion into CO, **(II)** the formation and reactivity of metal-organic (M-R) compounds – a Grignard perspective, and **(III)** decarboxylative C-C bond formation catalyzed by metal atoms (Fig. 1.).

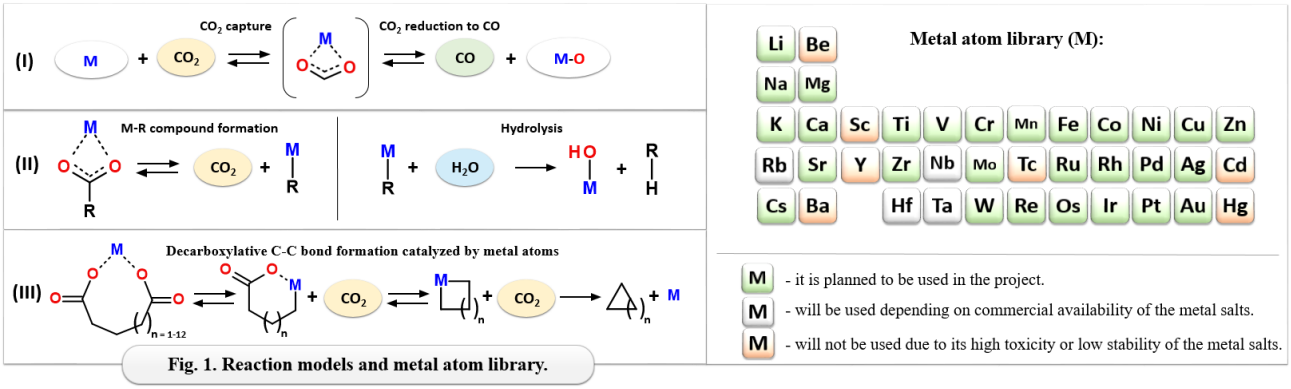

Fig. 1. Reaction models and metal atom library.

The proposed project addresses the comprehensive research on reaction mechanisms of metal atoms with CO_2 molecule (CO_2 catchment and reduction) and metal-carboxylate compounds already posing $-CO_2^-$ moiety within its structures (R-M or C-C bond formation) through mass spectrometry measurements, quantum chemical computations and statistical investigations. The novel aspect of the project will encompass efforts to screen the significance of systematic studies in molecular and structural recognition and to bring a comprehensive physicochemical knowledge of the metal atoms by incorporating *state-of-art* statistical methods. It is believed that laboratory findings will set the basis for the implementation of novel synthetic, industry useful strategies and developing a new metal-based catalyst dedicated to CO_2 transformation processes.