**Vers une chimie sélective en liaison et en mode : Dissociation de méthane sur métaux**

**Toward mode- or/and bond-selective chemistry: Methane dissociation on metals**

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The study of mode- or/and bond selective reactivity is one forefront in the current researches of chemistry. Recently, the fully selective cleavage of a C-H bond in a partially deuterated isotopologues of methane (i.e., $CH_{4\_x}H_x$, x=1,2,3) has been realized by two groups, A.L. Utz (Tufts University, USA) et R. Beck (Ecole Polytechnique Fédérale de Lausanne, Suisse), with cutting edge molecular beam techniques [1_9]. Achieving a high selectivity is one of the major goals in catalysis because this allows for producing preferentially the desired products. Currently, the theoretical study in this new domain legs behinds the experimental one. The state-of-the-art theoretical approach is based essentially on the combination of density functional theory (DFT) and molecular dynamics (MD) simulation, which allows for determining the reaction probability of simple surface reactions (mainly the dissociative adsorption of diatomic molecules). The simulation involving poly-atomic molecules, even as small as the methane, represents a computational challenge. For a rigid surface model, the potential energy surface (PES) of $CH_4$ on a metal is of 15 dimensions. The simulation of such a system is currently out of the reach of a quantum dynamics method, e.g., wave-packet propagation. Within the framework of classical dynamics, ab initio molecular dynamics (AIMD) method is the most accurate one but very time-consuming. So, it is not possible to apply it to study surface reactions with a very low probability, e.g., $CH_4$ dissociation on Ni or Pt. Recently, we developed a method which allows for increasing significantly computational efficiency. Our approach combines reactive force fields with a quasi-classical molecular dynamics (QCMD) method [10-13]. The validity of such an approach for studying methane dissociation on Ni(111) and Pt(111) surfaces has been established recently [12]. Our method is $10^5$ times faster than AIMD so that it is currently the only method allowing for describing the degrees of freedom of the adsorbate and those of the substrate on the same footing. Now, we are examining in details a series of fundamental questions in order to elucidate the microscopic mechanism of mode- or/and bond selective reactivity. Experiments indicate that the dissociation of $CH_4$ on Ir takes place through a precursor. To our best knowledge, no theoretical investigation has been made for studying the dynamics of such a process. The trapping of methane in the precursor state before dissociation can increase significantly its interaction time with the substrate. To account for this, very long simulations are needed and makes such an investigation even more challenging. Due to some technical limitation, it is difficult to obtain experimentally high rotational excitations of methane. Therefore, theoretical investigations can be particularly useful for studying the effect of molecular rotation on its reactivity. We hope that some new insights can be gained into mode- or/and bond-selective chemistry from the results to be obtained with this project. We have established contacts with the leading experimental groups in this domain (Utz in Boston, USA and Beck in Lausanne, Suisse) and close collaborations with them will be undertaken so that our theoretical predictions can be tested experimentally. We will collaborate also with the theoretical groups lead by Prof. H.F. Busnengo at Universidad Nacional de Rosario in Argentine and Prof. X.J. Shen at Zhengzhou University in China.

**Required background for the candidate:**

Good knowledge in physical chemistry or chemical physics, skills in methods of numerical calculation and programming are highly desirable.

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