PhD Proposal

ICB Université de Bourgogne

Heterogeneous catalysis: description at the elementary level including quantum effects

Heterogenous catalysis is a very important field for many applications in chemistry. Just one example: the main route for producing hydrogen for industrial chemical synthesis is steam reforming, in which water and methane react at high temperatures on nickel catalysts to produce hydrogen and carbon dioxide [1]. In this PhD, we will focus on solid phase catalysts and gas phase reactants involving the breaking and the formation of a C-H bond. Different substrates will be investigated. Understanding all the different aspects of these fundamental processes may bring an invaluable information to chemists to improve the conditions of these elementary steps. Many questions are still open: how does the process change with the substrate? What is the role of the motion of the atoms of the substrates, what is the precise role of all the degrees of freedom of the reactant (vibrations, rotations, etc.)? Do non-adiabatic aspects (i.e. coupling between different electronic states) play a role or not?

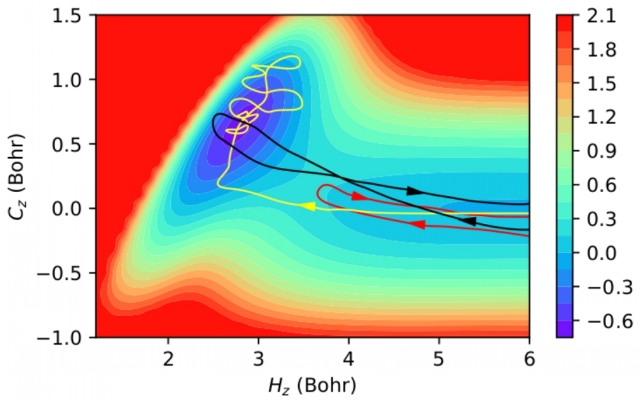

Figure 1: The colliding atom with the graphene surface can (i) come back with the same energy (elastic process, red curve), (ii) come back and exchange energy with the surface (inelastic process, black curve) or (iii) create a C-H bond. Cz describes the motion of the C atom perpendicular to the surface, Hz the motion of the colliding H atom perpendicular to the substrate.

First, quantum chemistry simulations must be performed that allow one to determine the presence of physisorption, chemisorption wells, the height of the chemical barriers, the possible role of excited electronic states. All strongly depend on the substrate of course. After these essential steps, we aim at going further and, for specific systems: having the potential energy surfaces, we will adopt a full

quantum approach to simulate the dynamics of the molecule interaction with the substrate. We shall use the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) method that allows one to simulate the quantum dynamics with dozens of atoms [2]. We will simulate the cross sections of the breaking of CH-chemical bond of CH4 on metals such as Nickel or Gold after excitation of different modes of vibration and rotation to explain or predict experiments where the different degrees of freedom have been excited by a laser pulse in experiments [1]. We will also investigate the formation of C-H bond on substrates like graphene that can serve for hydrogen storage. Experimental recent breakthrough has indeed permitted to measure very precisely *the formation of the C-H bond* and the exchange of energy from the H –atom to the graphene [3]. The number of degrees of freedom exerts a profound influence on quantum molecular dynamics computations. It has already been proven that MCTDH can treat the quantum dynamics of this kind of systems in full dimensionality [4]: many investigations and now possible in direct collaboration with experimentalists.

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References:

[1] Beck R. D., Maroni P., Papageorgopoulos D. C., Dang T. T., Schmid M. P., Rizzo T. R., Vibrational mode-specific reaction of methane on a nickel surface. *Science **302***, 98–100 (2003).

[2] Multidimensional quantum dynamics: MCTDH theory and applications, HD Meyer, F Gatti, GA Worth

John Wiley & Sons (2009).

[3] Imaging covalent bond formation by H atom scattering from graphene, H Jiang, M Kammler, F Ding, Y Dorenkamp, FR Manby, AM Wodtke,

Science 364 (6438), 379-382 (2019).

[4] Lei Shi, PhD thesis, Université Paris-Saclay, 2023.