PhD Proposal 2017

School: École Centrale de Paris (CentraleSupélec)/ University of Central Florida	
Laboratory: SPMS /LGPM	**Web site: www.spms.ecp.fr**
Team: Electronic structure, modelling and simulations	**Head of the team: P. CORTONA**
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Collaboration with other partner during this PhD: **In USA : Prof V. Kokoouline at University of Central Florida**	**In China: to be considered with the candidate**

Title: Data productions: cross sections for excitation and ionization of NO_x molecules by electron impact for control and reduction of atmospheric pollution by NO_2.
Scientific field: Chemical physics, quantum physics, basis on mathematical modelling and simulation, applied physics, engineering sciences
Key words: electron molecule collisions, cross sections, R-matrix approach, pollution

Details for the subject:

Ionization of the nitrogen dioxide NO_2 plays an important role in a number of plasma applications [R.K. Janev (1995) and X. Guo, *et al.* (2001)]. The molecule is also a common pollutant in combustion engines exhausts and contributes significantly to chemistry in the stratosphere and the troposphere. In stratosphere, NO_2 reaction cycles are important mechanisms in the formation and maintenance of ozone. In troposphere, NO_2 is formed due to the high temperatures of combustion of airplane fuel that dissociate oxygen and nitrogen molecules into their atomic constituents, which subsequently recombine. Although NO_2 is an essential contributor to the chemistry of upper atmosphere, it is an undesirable pollutant in the troposphere [J.H. Seinfeld and S.N. Pandis (1998)].

In addition, during last years, in large cities such as Paris or London, the NO_2 fraction in the NO_x exhaust of diesel cars has been continuously increasing due to the introduction of oxidative after-treatment technologies (see Fig. 1 as an example of the impact of NOx emission on average NO_2 concentrations in Paris). As a direct effect, NO_2 ambient concentrations close to the emission source increase.

Many previous works have been done to elucidate nitrogen-dioxide molecule properties and their interaction with photons and electrons. However, only a few works on the electron ionization of NO_2 have been reported so far. Hence accurate ionization cross sections for NO_2 are important for monitoring of this species in the atmosphere and plasma modelling. The experimental determination of ionization cross sections includes those of Rapp and Englander-Golden (1965) and Lopez *et al.* (2003). For more details see P. Bhatt, S. Pal (2006) and references therein. As for the theoretical point of view, calculations for open shell molecule such as NO_2 are particularly challenging. The rigorous quantum mechanical approach for the calculations for molecules is limited to the application of simple molecules. Contrary to it, there now exists binary encounter Bethe formalism by Kim *et al.* (1997), semi-empirical formalism by Khare *et al*. (1989), and DM-formalism by Probst *et al.* (2001).

Research subject, work plan:

The aim of this project is to contribute to enrich the cross sections database for excitation of NO and NO_2 molecules by electron impact. The cross sections will be evaluated using the electron-molecule scattering codes. In particular, the UK R-matrix code [J. Tennyson *et al*. (2007)] will be employed. The obtained cross sections of collision processes will be introduced into databases used for modeling the dynamics of destruction of NO_x particles.

The PhD work consists of two main tasks:

Task 1 – Following our recent work in the calculation of the rate constants for vibrational excitation of HeH^+ molecule by electron impact [Ayouz2016], we propose here to use the Quantemol software and the implemented the UK R-matrix formalism (Fig. 2) to determine rovibrational and electronic excitations and ionization cross sections of NO, N_2O and NO_2 molecules. Cross sections for these processes are needed for modelling atmospheric plasma. For this purpose, the UK R-matrix formalism [J. Tennyson (1996)] is an efficient method for calculating low-energy electron-molecule scattering cross sections. The basic idea relies on the partitioning of configuration space into an inner and outer region. The boundary is a sphere, with a radius noted “a”, centered at the center of mass of the molecule. This radius is chosen such as the electronic charge cloud of the target is negligible at the boundary. Usually in the inner part of configuration space, exchange and polarization interactions are dominant between *N*-electrons target and the scattering one. As a result, the collision problem within finite volume can be treated as a molecular bound state problem by constructing and diagonalizing an Hamiltonian matrix leading to solve a *N*+1 eigenvalue problem. In the outer region asymptotic expansion such as long range multipolar interactions between the

scattering electron and the target is used. Once the wave functions are generated in the inner region, the R-matrix is constructed at the boundary between the both regions for a given incident energy and it is propagated to the outer region where the radial scattering electron wave function can be matched to an analytical expression. In consequence, the scattering matrix elements are determined as well as the cross sections.

Take 2- The above-mentioned calculations will be compared and validated with experiments performed in laboratory. These data will be also included in the atomic and molecular databases for plasma modelling such as ADAS (http://open.adas.ac.uk/) and KIDA (http://kida.obs.u-bordeaux1.fr/).

This work will be carried out with a strong collaboration with Prof V. Kokoouline at the University of Central Florida (UCF). An exchange and long term stay at UCF is planned during the PhD.

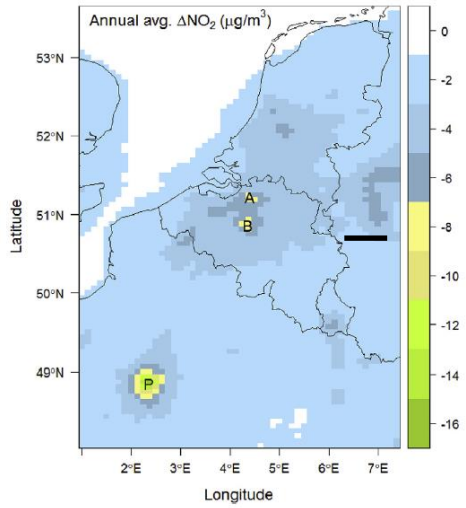

Fig. 1: Impact of NO_x emission levels on annual NO_2 concentrations in the Benelux zoom area. City locations are A: Anwerp, B: Brussels and P: Paris. (Bart Degraeuwe, et al. 2016).

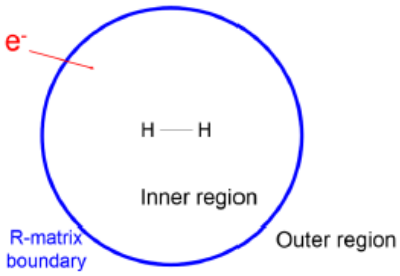

Fig. 2: Schematic representation of the R-matrix formalism for electron H_2 collision. The inner region, inside the blue circle, where Schrödinger equation is solved and the outer region using the asymptotic expansion such as a long range multipolar interactions.

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