PhD Proposal 2025

School - Location: CentraleSupélec, Gif-sur-Yvette (10 miles from Paris)	
Laboratory: SPMS	Web site: https://spms.centralesupelec.fr/
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Title: Theoretical modelling of electronic collisions of nitrogen molecules for plasma-assisted ammonia synthesis

Scientific field (one among the list- remove other choices):

Physics

Engineering & Technology: Chemical engineering

Free Key words: *ab initio* calculations, cross section, rate coefficient, R-matrix code, polyatomic molecules, normal mode approximation, ammonia synthesis, plasma-assisted catalysis, chemical reaction catalysis

Remarks: Possible joint PhD (cotutelle) with the University of Central Florida

Period: from now (for 3 years)

Details for the subject:

General context:

Ammonia (NH_3) is the primary ingredient in fertilizers and is also widely used for the production of base chemicals (urea, ammonium salts, etc.) [1]. More recently, NH_3 was proposed as an H_2 carrier thanks to its high energy density of 5.2 kWh kg-1 and high hydrogen gravimetric content of 17.6 wt.% [2], not to mention the thermodynamically favorable cracking reaction. To date, 2.4% of global fossil fuel feedstock is consumed for NH_3 synthesis and H_2 production, reflecting its current CO_2 footprint (1.2 % of the global annually produced CO_2). NH_3 today is almost exclusively (>96%) produced by thermal catalysis, the Haber-Bosch (H-B) process [3], which is a high energy consuming due to severe operating conditions, i.e. T>500°C and P>150 bars [4]. From a thermodynamic point of view, NH_3 synthesis is favored at high P and low T [5]. However, commercialized catalysts are not able to work at T as low as 300°C, a temperature affording a significant decrease in operating pressures (P<50 bars). Therefore, the reaction temperature must be relatively high to activate and break the nitrogen triple bond. The breakage of the N triple bond is the rate-determining step in the H-B process [6].

Recently, plasma was demonstrated to facilitate the cleavage of the strong N≡N bond, thus achieving NH_3 synthesis under mild conditions. While several plasma types exist, non-thermal plasma is characterized by an electron temperature (T_e) that is much higher than the temperature of heavier species (ions and neutrals). Therefore, the radicals and excited species within the plasma discharge are formed at T close to the ambient. This non-thermal distribution of energy allows overcoming the kinetic and thermodynamic limitations of thermal catalysis (H-B process), and the energy generated can accelerate reactions that are slow, including the N≡N bond cleavage. Energetic electrons from the non-thermal plasma are capable of producing excited species, ions, and radical species through effective collisions (not accessible in thermal catalysis) and provide external catalyst activation. Thus, reaction mechanism and

selectivity in reaction quite differ from conventional catalysis (H-B process), and thermodynamic limitations encountered in H-B are no longer existing. In plasma-assisted catalysis, non-thermal plasma generates excited and charged species which react further with the solid catalyst. Knowing cross sections and rate coefficients for various processes (e.g. dissociative recombination, vibrational excitation, and so on) is of great importance for modeling such plasma.

Description of the work:
In this PhD, we will investigate various electronic collisional processes including neutral and positively-charged targets. It is part of a large project, PEPR-Spleen PLASMA-N-ACT, aiming to better understand N_2 activation under plasma for ammonia synthesis. The studies conducted will allow computing cross sections and related rate coefficients for support of plasma modeling.

Task 1 – Based on previous studies [7,8,9] (HeH^+, CH^+, CF_3^+, $CH_2NH_2^+$, NH_2CHOH^+, BF_2^+, etc.) and the developed models, we will investigate the process of dissociative recombination (DR) and vibrational excitations (VE) of e-N_3^+, e-NH_2^+, and e-NH_3^+. Our theoretical approach combines the normal mode approximation, obtained from the MOLPRO software [10], for the vibrational states of the target ions and the UK R-matrix [11] code to evaluate electron-ion scattering matrices for fixed geometries of ions.

Task 2—In the continuation of the preceding task, we will employ our model which has been adapted to neutral molecules such as H_2O, SO_2, etc. [12,13,14,15], to determine the VE of e-N_3, e-NH_2, and e-NH_3. Data obtained from these studies will be used in kinetic plasma modeling studies, conducted by the partner of the consortium.

Task 3- Electronically-excited states of the target play an important role in the modeling of plasma-assisted catalysis. Thus, we will adapt our models to include the excited states of the targets in the calculation of the cross sections. We will develop a new approach that combines normal mode approximation of ground and electrically excited states of the targets.

This work will be carried out in close collaboration with the US theoretical group of Prof. Kokoouline at the University of Central Florida. An exchange and long-term stay in the US institution is planned during the PhD.

References:
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