Internship 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 study of the nitrogen-based molecule collisions by electron impact as support for modeling ammonia synthesis by plasma-assisted catalysis

Scientific field (one among the list- remove other choices):
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 visit to the University of Central Florida
Period: from now (for 6 months)

Details for the subject:

General context:

Ammonia (NH_3) is the primary ingredient in fertilizers, and also widely used for the production of base chemicals (urea, ammonium salts, etc.) [1]. More recently, NH_3 was proposed as H2 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 NH3 synthesis and H2 production, reflecting its current CO_2 footprint (1.2 % of the global annually produced CO2). NH3 today is almost exclusively (>96%) produced by thermal catalysis, the Haber-Bosch (H-B) process [3], which is high energy consuming due to severe operating conditions, i.e. T>500°C and P>150 bars [4]. From a thermodynamic point of view, NH3 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 in order 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 NH3 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 ambient. This non-thermal distribution of energy allows overcoming the kinetic and thermodynamic limitations of thermal catalysis (H-B process), and 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 more 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 a great importance for modeling such plasma.

Description of the work:
This internship project aims to investigate the vibrational collision of NH_3 and NH_3^+ by electron impact. Bas on previous studies [7,8,9] (HeH^+, CH^+, CF_3^+, $CH_2NH_2^+$, NH_2CHOH^+, BF_2^+, etc.), the ab inito calculations will be performed, with the help of Molpro [10], to compute the normal modes of the taget molecules. These findings will be then employed to perform the scattering calculations using the R-matrix code [11]. Different tests will be carried out by varying the scattering model parameters such as the basis set and complete active space.

This preliminary work will be followed by a PhD. devoted to provide the cross sections and related rate coefficients for the dissociative recombination (DR) and vibrational excitations (VE) processes of NH_2^+, NH_3^+, NH_2 and NH_3, with development of model including electronically-excited states of the target molecules.

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 with the US institution is planned during the internship.

References:
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[3] C. Smith et al., vol. 13 (2020), 331–344.
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[7] C H Yuen, M A Ayouz, N Balucani, C Ceccarelli, I F Schneider, V Kokoouline, Monthly Notices of the Royal Astronomical Society, Volume 484, Issue 1, Pages 659–664 (2019).
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[10] H. J. Werner ; et al., Molpro package, WIRES Comput. Mol. Sci. 2012, 2, 242–253.
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