PhD Proposal 2021

School: École Centrale de Paris (CentraleSupélec)/ University of Central Florida	
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Collaboration with other partner during this PhD: In USA : Prof V. Kokoouline at University of Central Florida	

Title: Electron-driven reactivity of greenhouse gas molecules by electron impact: the NO_2/CO_2 prototype for control and reduction of atmospheric pollution.
Scientific field: Atmospheric chemistry, Chemical physics, basis on mathematical modelling and simulation, applied physics and chemistry, engineering sciences, quantum physics
Key words: depollution process, electron molecule collisions, atmospheric chemistry

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 NOx 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 NO2 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).

In a recent work (Liu's PhD, 2017-2020), we reported the first theoretical results on vibrational excitation and de-excitation of the NO_2 molecule in collisions with a low-energy electron [H. Liu, et al. (2019)]. This study could be valuable in kinetic studies of low-temperature NO_2-containing plasma. Latter, we applied our developed theoretical approach to N_2O and we obtained the rate coefficients for vibrational excitation and de-excitation of the molecule. These outcomes have been compared and validated with the available experimental data [H. Liu, et al. (2020)].

Research subject, work plan:

The aim of this project is to contribute to enrich the cross sections database for excitation of NO_2 molecules by electron impact and pursue the former studies. This PhD would allow developing a prototype model on NO_2 taking into account its electronically-excited states and further its rotational structure. The theory and the conclusions suggested in this work would serve as a route towards studying another important greenhouse molecule such as CO_2.

The cross sections will be evaluated using the electron-molecule scattering codes. In particular, the UK R-matrix [J. Tennyson et al., (2007)] will be used and combined to the frame transformation procedures to obtain the scattering matrices describing the transition amplitude for one level to another of the target molecule. The obtained S-matrices will be employed to deduce the cross sections that will be used for modeling the dynamics of destruction of NO_2, for instance. The PhD work consists of three main tasks:

Task 1 – Following Liu's PhD work (see Fig.1), we will adapt the developed model to e-molecule collisions in which S-matrix is energy-dependent. Choosing a different normalization factor for the scattering electron wave function, the energy dependence of S can be removed. Then, the renormalized S is energy-independent so that vibrational frame transformation (VFT) can be employed. After VFT, the renormalization factor is multiplied back, and the energy dependence is recovered to compute the cross sections. These data will be compared to those already published and obtained with previous treatment, viz. the use of the smooth S-matrix for e-NO_2 collision energies below the first resonance < 1.6 eV of the $^3B_1$ symmetry. The developed procedure could be further applied to a variety of systems for which the S-matrix for electron-molecules collisions is energy-dependent such as CO_2.

Task 2- Another approach would be needed were there to exist electronic resonances or a sufficiently high total energy of the system for all collision channels to be open for ionization. Similar to the "closed channel elimination" procedure used in standard theories (and in former studies such as Jiang's PhD, 2017-2020. See Ref.[Jiang, et al. (2019)]), we will adapt this procedure in combination with the Breigt-Wigner formula so that the e-NO_2 scattering physics below the first electronic state can be represented using an energy-independent multichannel scattering matrix evaluated above.

Task 3- The above-mentioned developments will be generalized and applied to CO_2. The obtained results will be compared and validated with experiments performed in laboratory, in collaboration with Prof. Christophe Laux at EM2C (Centralesupélec). 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 in close collaboration with US theoretical group of Prof .V. Kokoouline at UCF. An exchange and long term stay in the institution is planned during the PhD.

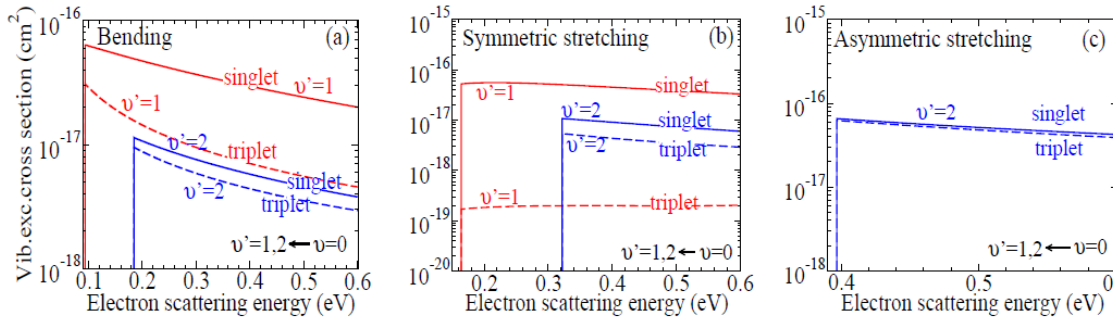

Fig.1: Calculated cross sections as functions of the electron scattering energy for the vibrational excitation of NO_2 being initially in the lowest vibrational state v = 0 for the three normal modes (see the text for detailed discussion): (a) cross sections for v ' = 1, 2 ← v = 0 transitions for bending mode; (b) for symmetric stretching mode; (c) for asymmetric stretching mode. See Ref. [H. Liu, et al. (2019)] for more details.

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