Séminaire de Chimie Théorique

Salle Conférence, 3eme Est, bat. A12

Mardi 17 Janvier à 11:00

Dr. Otoniel Denis Alpizar

Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Molecular collision studies at extreme temperatures relevant to the hypersonic flight regime

The NO, CO and N^{2+} molecules play a major role in the chemistry near the surface of vehicles for atmospheric re-entry in the hypersonic flight regime. Therefore, the reactive and inelastic collisions of these systems with the most common atmospheric gasses must be considered in the design of spacecraft. At the extremely high temperature typical of this regime, the experiments are difficult and expensive. Consequently, the theoretical studies became vital for the correct comprehension of the energy transfer of such molecular collisions. The vibrational relaxation of CO($\nu = 0 \leftarrow \nu = 1$) in Ar is considered for validating a computational approach to determine the vibrational relaxation time using an accurate, fully dimensional potential energy surface (PES). For lower temperatures, direct comparison with experimental data shows very good agreement whereas at higher temperatures comparisons with an empirically modified model confirm its validity for CO in Ar. Additionally, the calculations provide insight into the importance of $\Delta\nu > 1$ transitions that are ignored in the Landau-Teller framework. The collision of N^{2+} with Ar is studied also using quantum and classical methods. Comparison with multi-reference MRCI+Q calculations establishes that UCCSD(T)-F12a is a sufficiently high level of theory for this problem. Results from quantum close coupling and quasiclassical trajectory calculations agree favorably and the rates for inelastic collisions are lower than those from Langevin theory. This differs from previous calculations on a zero point-corrected PES. Nevertheless, previous experimental rate coefficients for N^{2+} ($\nu = 0$, $j = 6$) colliding with Ar suggested that the rotational quantum number is conserved. This can not be confirmed from any of the simulations and calls for new single molecule experiments. Furthermore, the $N(^4S)+NO(^2\Pi)$ and $N(^2D)+NO(^2\Pi)$ reactions are investigated using classical and quantum methods to describe the nuclear dynamics. New PESs were developed from ab initio energies at the MRCI level represented as a reproducing kernel. Thermal rate coefficients are determined in the 100-20000 K temperature range. The new rates are compared with available experimental and previous theoretical data. In the nitrogen exchange reaction, the rates increase with temperatures which emphasizes the importance of this channel for a correct understanding of the reaction mechanism.

Contact : pascal.larregaray@u-bordeaux.fr