Internship Proposal 2025

School - Location: CentraleSupélec, Gif-sur-Yvette (10 miles from Paris)	
Laboratory: SPMS	**Web site: https://spms.centralesupelec.fr/**
Name of the supervisor: Mehdi Adrien Ayouz and Viatchslav Kokoouline (University of Central Florida, US)	**Email: mehdi.ayouz@centralesupelec.fr**

Title: Ab Initio Potential Energy Surface and Quantum Collision Dynamics of N_2–NH_3 for Plasma-Catalytic Ammonia Synthesis

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

Engineering & Technology: Chemical engineering

Free Key words: *ab initio* calculations, potential energy surface, ammonia, cross section, rotational and vibrational quenching, AI-assisted modeling

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

Period: from February

Details for the subject:

General context:

Collisions between N_2 and NH_3 play a fundamental role in atmospheric chemistry, astrochemistry, and low-temperature molecular dynamics. These collisions are particularly relevant for understanding energy transfer processes in planetary atmospheres, interstellar clouds, and cold molecular beams [1,2]. While N_2 and NH_3 have been extensively studied individually, the N_2–NH_3 dimer has received less attention in terms of detailed potential energy surfaces (PES) and state-to-state inelastic collision data. Several studies have explored the N_2–NH_3 complex using high-level ab initio calculations, focusing on bound-state properties, van-der-Waals minima, and microwave spectra [3,4,5]. However, fully dimensional PESs suitable for quantum scattering calculations are either not publicly available or are restricted to simplified models, such as rigid-rotor approximations [6,7].

Rotational and vibrational excitation in N_2–NH_3 collisions is crucial for modeling energy transfer processes. This is especially important at low temperatures relevant to planetary atmospheres, cold molecular beams, and astrochemical environments. Some experimental data exist for rotational transitions of NH_3 in collisions with N_2 [8,9], but comprehensive state-to-state cross sections for combined rovibrational excitation of the N_2–NH_3 complex are largely missing [10,11]. Previous scattering studies often rely on approximate PESs or model potentials and therefore cannot provide high-accuracy cross sections for detailed comparison with spectroscopic, experimental, or astrochemical models.

This gap motivates the current internship: the construction of a high-quality PES for the N_2–NH_3 complex at the ab initio level, to serve as input for quantum scattering calculations using MOLSCAT. The goal is to produce state-to-state cross sections for rotational excitation, which are currently unavailable in the literature, and are essential for developing predictive models of collisional energy transfer and validating approximate theoretical methods. The internship will also assess whether simplified rigid-rotor models suffice or if a full-dimensional PES is required for accurate cross sections.

As for vibrational excitation, its effect will be explored within the adiabatic approximation using vibrationally averaged PES. This approach allows inclusion of vibrational effects in the collision dynamics at a reasonable computational cost and enables evaluation of the rigid-rotor approximation for N_2–NH_3 collisions [12,13].

Description of the work

The main objective of this internship is to compute a high-quality ab initio PES for the N_2–NH_3 dimer and to study its quantum collision dynamics. Energy points for the dimer will be calculated at the CCSD(T)-F12/aug-cc-pVXZ level (or using calibrated DFT for more extensive regions) with Gaussian, MOLPRO, or ORCA, covering relevant radial and angular configurations [3,4,5]. The resulting PES will be represented analytically via spherical harmonic expansions, splines, or machine-learning interpolation methods, ensuring smoothness and numerical stability for scattering calculations.

Using this PES, quantum non-reactive scattering calculations will be performed with MOLSCAT to obtain state-to-state cross sections for rotational and, if feasible, vibrational excitation of N_2 and NH_3 [1,6]. The close-coupling equations will be solved by propagating the log-derivative matrix, and convergence will be carefully verified with respect to the number of channels, radial grid, and propagation step. Integral and differential cross sections, as well as thermal rate coefficients as a function of temperature, will be derived. The sensitivity of the results to approximations such as the rigid-rotor model will also be assessed, and comparisons with available experimental or theoretical data will be performed [9-11].

Expected outcomes

- A high-quality PES for N_2–NH_3 suitable for scattering calculations.
- State-to-state rotational (and potentially vibrational) cross sections and thermal rate coefficients over temperatures ranging from 10–1000 K.
- A detailed report documenting methodology, convergence tests, uncertainty analysis, and recommendations for future theoretical and experimental studies.

This internship will serve as a preliminary stage for a potential PhD, which will focus on understanding microscopic mechanisms of energy transfer in N_2–NH_3 collisions. The PhD will build on this work to perform advanced theoretical studies using complementary computational techniques, providing a realistic description of rovibrational excitation processes relevant to plasma-catalytic ammonia synthesis. Results will be compared with experimental data and existing models to validate the PES and scattering calculations, guiding future research on reaction dynamics under plasma conditions.

References

[1] Hutson, J. M., & Green, S., MOLSCAT – Quantum Scattering Program, version 14, 2019.

[2] Surin, L. A., et al., Ab initio potential energy surface and microwave spectrum of the NH_3–N_2 complex, J. Chem. Phys., 152 (2020) 124301.

[3] Bowman, J. M., et al., Ab initio studies of N_2–NH_3 and related van der Waals complexes, J. Chem. Phys., 112 (2000) 3154–3165.

[4] Chaban, G. M., et al., Rotational spectroscopy and potential energy surface of the NH_3–N_2 dimer, J. Chem. Phys., 118 (2003) 10120–10128.

[5] Raghavachari, K., et al., A fifth-order perturbation comparison of electron correlation theories (CCSD(T)), Chem. Phys. Lett., 157 (1989) 479–483.

[6] MOLSCAT documentation and tutorials, IPAG Grenoble.

[7] Suenram, R. D., Lovas, F. J., Microwave spectrum and structure of NH_3–N_2, J. Chem. Phys., 94 (1991) 1661–1667.

[8] Hobbs, D., et al., Rotational energy transfer in NH_3–N_2 collisions: experiment and theory, Phys. Chem. Chem. Phys., 18 (2016) 17845–17852.

[9] Toczyłowski, R., et al., Ab initio study of NH_3 dimers and complexes, J. Phys. Chem. A, 106 (2002) 6493–6500.

[10] Faure, A., & Wiesenfeld, L., Rotational and vibrational excitation in molecular collisions, J. Chem. Phys., 143 (2015) 064303.

[11] Volpi, A., et al., Low-temperature NH_3–N_2 collisional data: experimental and theoretical review, J. Mol. Spectrosc., 300 (2014) 1–10.

[12] Quéméner, G., et al., Adiabatic treatment of vibrational excitation in weakly bound complexes, J. Chem. Phys., 136 (2012) 114302.

[13] Wang, X., et al., Quantum scattering studies of N_2–NH_3 with rigid rotor approximation, J. Chem. Phys., 141 (2014) 224301.