Internship M2 PPN

from 2026 April 1st to 2026 July 31th

Title of the project: Line-by-line analysis in silane spectra using *ab initio* calculations and symmetry-breaking effects under H → D substitutions

Supervisor(s): M. Rey, D. Viglaska

Laboratory / Department / Team : ICB / ICQ / MARS

Collaborations: V. Boudon, C. Richard

Summary:

Vibration–rotation spectroscopy remains invaluable for understanding and characterizing spectral features for the modeling of planetary atmospheres. Recent advances in highly sensitive experimental techniques now make it possible to record spectra with very high resolution, thereby increasing the need for new theoretical tools and efficient algorithms capable of accurately solving the time-independent Schrödinger equation. For the line-by-line analysis of high-resolution spectra of polyatomic molecules, whose energy levels are organized into small clusters of strongly interacting vibrational states, effective polyad models have proven relevant for decades to fit experimental data. The Dijon group has a strong expertise in the analysis of spectra of highly symmetric molecules. The Dijon formalism is based on the use of irreducible tensor operators, which are particularly well suited to fully exploit molecular symmetry properties. However, this approach may suffer from the lack of experimental information on the so-called dark states, particularly as the density of states increases, leading to a poor determination of some resonance coupling parameters. In this context, supplementary information can be obtained from *ab initio* calculations, either from variational calculations or via the derivation of effective models using appropriate transformations. Within the team, we have developed complementary theoretical tools for computing molecular spectra based on the construction of nuclear-motion Hamiltonians using ab initio potential energy surfaces (PES). *Ab initio* dipole moment surfaces are employed to compute line intensities.

The subject of this study will be the silane molecule (SiH_4) and its isotopologues resulting from H → D substitutions. Silane is used in various applications, such as semi-conductor industry. It is also one of the many species present in the interstellar medium. As such, it is important too accurately characterize and model its infrared absorption spectrum, up to excited vibrational states.

In this internship, we propose to analyze and model silane's overtone and combination bands in the 4000–5000 cm^{-1} stretching region. The analysis will benefit from an initial of set of spectroscopic parameters, to be refined, and directly derived from an accurate PES. The student will also investigate symmetry-breaking effects in silane spectra arising from H → D substitutions. In particular, she/he will focus on the band correspondences and the associated isotopic vibrational shifts between SiH_4 and SiH_3D/$SiHD_3$. Finally, variationally-computed spectra will be produced for the T_d and C_{3v} species using our home-made computer code.

Type of project (theory / experiment): Theory

Required skills: Quantum mechanics, basics of molecular spectroscopy, skills in computing