

PhD subject proposal – 2019

Title: Molecular excited states in extreme conditions – Application to exoplanets.

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Scientific department: ICQ

Research group: SMPCA

Co-supervisor: Robert GEORGES, Institut de Physique de Rennes

General scientific context:

Excited rovibrational levels play a central role in the molecular processes taking place in various regions of the universe. One can cite one example in which the researchers of the SMPCA team are interested, and which is proposed for this PhD work: the chemistry and the spectroscopy of the atmospheres of exoplanets.

The subject is part of the new and expanding context of the study of the properties of exoplanets. If the first extrasolar planet was discovered a little more than 20 years ago only, it is the very recent instrumental developments which allow today to study its composition, that it is using spectrometers (SPHERE, GPI, ...) on large terrestrial telescopes (VLT, ...) or using space missions either in progress (Kepler, ...) or upcoming (Ariel, JWST, ...). It is already possible to perform spectroscopic measurements on some of these atmospheres. This is particularly the case of giant planets orbiting near their star or young stars still in formation. In both cases, these are high temperature objects (500 to 2000 K), containing a lot of methane (CH₄).

This subject, which is fiercely competitive, is innovative in that it aims to perform a particularly complex modeling of spectra involving highly excited states of the molecule under consideration, using state-of-the-art experimental techniques (emission spectroscopy with intensity measurements, hypersonic jet CRDS spectroscopy) and advanced theoretical methods specific to the SMPCA group (symmetry-adapted formalism, quantum chemistry calculations). In other words, the unique theoretical model developed in Dijon on the basis of experimental spectra produced in Rennes under extreme temperature conditions, with no equivalent, is a tool of unparalleled precision to date. Our ambition is to extend its area of validity to all infrared region so that this can be integrated into the atmosphere models of hot exoplanets to better constrain their thermal structure.

In addition to methane, the atmosphere of exoplanets also contains hydrogen, helium, carbon, nitrogen, oxygen atoms ... Its composition evolves as a function of the chemical reactions between all those species, including molecules in highly excited rovibrational levels. Knowing precisely the state-to-state cross sections and rate coefficients of those reactions in a wide range of temperatures is therefore necessary to model the kinetic evolution of the atmospheres of exoplanets. Due to the difficulty to measure experimentally such state-to-state quantities, theoretical predictions are particularly relevant in that context. The computed rate coefficients will feed astrophysical databases like KIDA (<http://kida.obs.u-bordeaux1.fr/>), and will serve as input for atmospheric models describing the dynamical evolution of the atmosphere. The project will be done in the collaborative framework of CNRS program PCMI (Physico-chimie du milieu interstellaire), gathering many researchers all over France.

In this context, the SMPCA group has internationally recognized expertise in the modeling of CH₄ spectra. It benefits from fruitful collaborations with groups of innovative experimentalists in Rennes (absorption and emission spectroscopy at high temperature, in flow or in hypersonic jet), in Brussels (intensity measurements), as well as with theoreticians in Reims and planetologists in Meudon. Work on high-temperature spectra has been initiated recently at master's lectures and an ongoing post-doctoral internship. It is part of the ANR e-PYTHEAS contract (2017-2020, see: <http://e-pytheas.cnrs.fr>). The SMPCA team also possesses an internationally recognized knowledge in the modeling of gas-phase reactive collisions using a full quantum formalism based on the resolution of the time-independent Schrödinger equation in hyperspherical coordinates. These calculations require large numerical capacities that are provided by the Computing center of the University (CCUB).

Objectives:

The first objective of the project is to obtain an accurate modeling of the absorption and emission spectra of methane in the mid infrared (between 2 and 10 μm), for a range of temperatures between 500 and 2000 K. In particular, the aim will be to produce lists of lines usable by the planetologists, and in strong interaction with them, for radiative transfer calculations in exoplanetary atmospheres. The second objective will be to study the atom-diatom reactions, $A + BC \rightarrow AB + C$, with AB and BC in arbitrary rovibrational levels. Cross sections and rate coefficients will be computed in a wide range of collision energies and temperatures (up to thousands of kelvins), using the time-independent formalism of reactive collisions based on hyperspherical coordinates. The reactions that will be studied involve the atomic and molecular species mentioned above. The computed rates will then be employed by our collaborators in France and in Europe (Grenoble, Montpellier, Le Havre ...), in order to model the composition of the atmospheres of exoplanets.

Proposed work:

From recent work developed within the SMPCA group, the first step is to analyze in detail the emission data (positions and intensities) obtained in Rennes for the region around 2.1 μm (called "Octad") of methane. The hot bands will have to be assigned and included in a global fit of the methane lines, on the model of the recent work of B. Amyay (see B. Amyay *et al.*, J. Chem. Phys. **148**, 134306, 2018). The intensity data will be extracted in collaboration with J. Vander Auwera at the ULB (Brussels) where student stays are envisaged and new spectra should be recorded.

In addition, the collaboration with Rennes will continue on thermodynamic out-of-equilibrium spectroscopy by CRDS in a hypersonic jet (see M. Louviot *et al.*, J. Chem. Phys. **142**, 214305, 2015). This technique makes it possible to obtain vibrationally very hot spectra, but with a simplified rotational structure and is very promising for the study of very excited complex states. It is being improved at the Institute of Physics of Rennes and student stays in this laboratory are planned to participate also in these experiments.

The student will also focus on the reactions $O + NO$ and $C + NO$ in a wide range of temperatures. In particular, he/she will study the reaction involving NO in excited rotational and vibrational levels. Comparisons for these collisional processes will be made with experimental results obtained from French groups (Rennes, Bordeaux).

The subject will also benefit from important exchanges with the theoreticians of the GSMA laboratory in Reims and the planetary scientists of the LESIA laboratory in Meudon, as part of the ANR e-PYTHEAS. The work will be supervised by Vincent Boudon in Dijon and Robert Georges in Rennes. It should be noted that it will benefit from the support of a computer research engineer recently recruited in Dijon, particularly as regards the uploading of data produced via the MeCaSDa database of the European VAMDC consortium (see <http://vamdc.org>).

Required knowledge:

Solid knowledge in quantum mechanics, theoretical molecular spectroscopy, computer science. Knowledge in mechanics of rarefied fluids and in collision physics would be appreciated.

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