



Exoplanet Characterisation Observatory (EChO)

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Chemical modelling of hydrogen- rich exoplanet atmospheres

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Chemical modeling of exoplanet atmospheres

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Determining the elemental composition of the atmosphere/envelope of exoplanets is one of the keys to understand their origin and evolution. In the Solar System, elemental abundances in the envelope of the gaseous giants and icy giants are not well constrained because of the condensation cold trap that removes some carriers of the main elements (in particular oxygen) from the upper atmosphere probed by observations. Interestingly, it could be easier to unveil the elemental composition of an extrasolar hot/warm- Jupiter or Neptune than that of our own Jupiter and Neptune. This, however, requires the ability to translate spectroscopic observations into molecular abundances and physical conditions (pressure and temperature) and then into an elemental composition. This second step would be relatively simple if atmospheres were at chemical equilibrium, in which case the detailed molecular composition depends solely on the temperature, pressure, and elemental composition. At the exception of the very hottest exoplanets, equilibrium does not hold due to UV photolysis, mixing, and advection. As a consequence, the kinetics of hundreds of individual reactions controls the atmospheric composition.

The diversity of exoplanetary atmospheres observable with EChO spans a broad range of physical conditions. Individual reaction rates must therefore be known at temperature ranging from below room temperature to above 2500 K and - because the deep atmospheric layers are chemically mixed with the layers probed by spectroscopic observations – at pressures up to about 100 bars. Fortunately, these conditions are also found in typical combustion experiments and explosion engines and we benefit from decades of research on the chemical kinetics needed for exoplanetary atmospheres. Through a collaboration with research departments dedicated to applied combustion, we were able to develop a kinetic model based on a network of ~2000 of reactions that has been experimentally validated over this temperature-pressure range and for gaseous mixtures of 105 species made of H, He, C, O and N. This kinetic model is now implemented into atmosphere models that can accurately simulate the chemistry of any type of atmosphere that are dominated by these elements.

1. Recent progress in 1D atmospheric chemical modeling

The first 1D models used to study the atmosphere of transiting exoplanets assumed thermodynamic equilibrium because of the high temperature of these atmospheres (e.g. Burrows and Sharp, 1999; Seager and Sasselov, 2000; Sharp and Burrows, 2007; Barman, 2007; Burrows et al., 2007, 2008; Fortney et al., 2008a). However, photodissociations by the stellar UV fluxes, and transport/mixing resulting from the dynamics powered by the intense irradiation, occur on timescales comparable or even shorter than the chemical timescales. As a consequence, planetary

atmospheres are out of equilibrium and hot/warm exoplanets are the site of a unique chemistry where thermochemistry (chemistry involving endothermic processes) competes with photolysis and gas dynamics. Departures from equilibrium have been first addressed based on timescales arguments (e.g. Lodders and Fegley, 2002; Fortney et al., 2006, 2008b; Visscher et al., 2006, 2010; Madhusudhan and Seager, 2010) or modeled by coupling the dynamical processes with some chemical reactions describing the CO-CH₄ conversion (Cooper and Showman, 2006).

Robust and versatile modeling of atmospheric chemistry requires the use of a kinetic model, including all relevant individual chemical and photochemical processes.

The first (photo)chemical models for exoplanets were adapted from Jupiter chemical schemes that did not include endothermic reactions, occurring at high temperature (Liang et al. 2003, 2004). These reactions can be neglected in Jupiter's atmosphere, but are crucial to model the atmosphere of most known transiting exoplanets. A next generation of models then included these endothermic reactions (Zahnle et al. 2009a,b; Line et al. 2010; Moses et al. 2011) consistently with the constraints of thermodynamics. These kinetics models evolve towards the chemical equilibrium when photolysis and transport are turned off. Different networks with very different individual kinetic rates can, however, evolve toward the same equilibrium provided that they use the same equilibrium constant to derive the rates of endothermic reactions from exothermic ones. In a next step, kinetic networks and their associated rates have therefore been constructed and selected by their ability to reproduce the global chemical behavior of experimentally-controlled abundances. This has been made possible thanks to a close collaboration with teams working on applied combustion who deal with mixtures whose elemental composition (H, O, C, N), temperature (300-2500 K), and pressures (up to hundreds of bars) overlap with those of exoplanet atmospheres (see for instance Bounaceur et al. 2007). The accuracy demanded when modeling the chemistry of an explosion engine exceeds by far those needed to predict the atmospheric composition of exoplanets. This experimental validation confers a great confidence on the results obtained over a very broad range of conditions. The chemical scheme by Venot et al. (2012) includes all the reactions required to model the kinetic evolution of radicals and molecules containing fewer than three carbon atoms. It involves 105 compounds, linked by ~2000 reactions. It is available to the scientific community on the database KIDA (Wakelam et al. 2012, <http://kida.obs.u-bordeaux1.fr>). A new network validated for molecules containing up to 6 carbon atoms is about to be released. This network will allow to study the chemical complexity arising in atmospheres with elemental C/O abundance ratios greater than unity.

2. Applications to hot Jupiters and warm Neptunes

Chemical models of exoplanetary atmospheres have largely focused on the study of the hot Jupiters HD 209458b and HD189733b, as these two objects have been widely observed at primary transit and secondary eclipse conditions, leading to important constraints on their

atmospheric chemical composition (Zahnle et al. 2009a,b; Line et al. 2010; Moses et al. 2011; Venot et al. 2012). The degree of departure from chemical equilibrium is different in the atmosphere of these two exoplanets, as illustrated in Figure 1. In the case of HD 189733b, one can clearly notice the larger effect of photolyses and vertical mixing on the chemical composition, with all species affected, except the main reservoirs (H_2 , H_2O , CO , and N_2), showing important departures from chemical equilibrium.

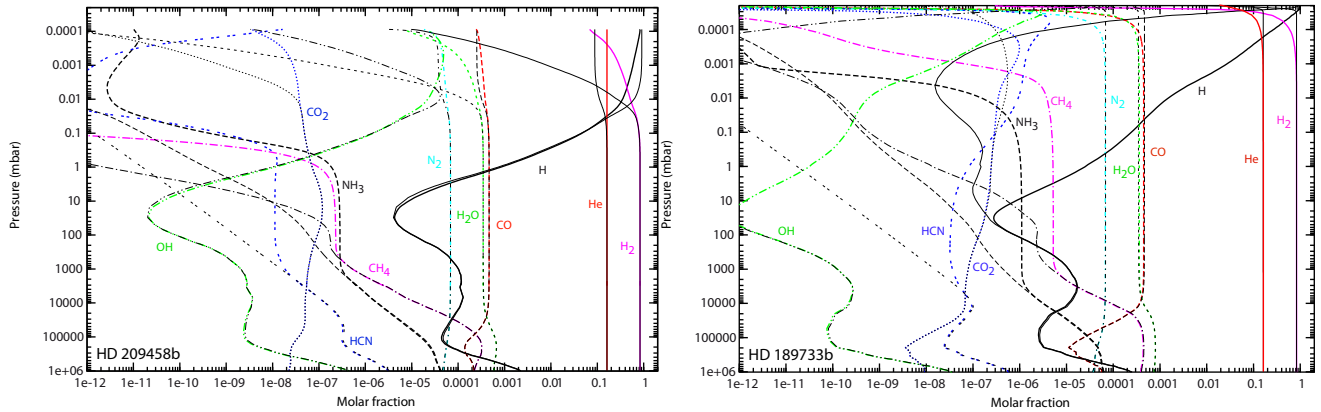


Figure 1: Steady-state composition of HD 209458b (*left*) and HD 189733b (*right*) calculated with a non equilibrium model (color lines), compared to the thermodynamic equilibrium (thin black lines). From Venot et al. (2012)

The atmospheres of hot and warm Neptunes are also very interesting sites to be studied with chemical models (Line et al. 2010; Moses et al. 2013, Agúndez et al. 2013b, Venot et al. 2013b). The warm Neptunes GJ 3470b and GJ436b have an equilibrium temperature lower than hot Jupiters and their atmospheres are more sensitive to disequilibrium processes. Using these two planets as study cases, we have investigated the effect of vertical mixing and UV flux, but also the metallicity of the envelope (which can be much higher for these planetary masses) and the thermal profile. As illustrated on Figure 2, these four parameters have an important influence on the abundance of species. In these two cases, the C-bearing species is dependent on the metallicity and the temperature.

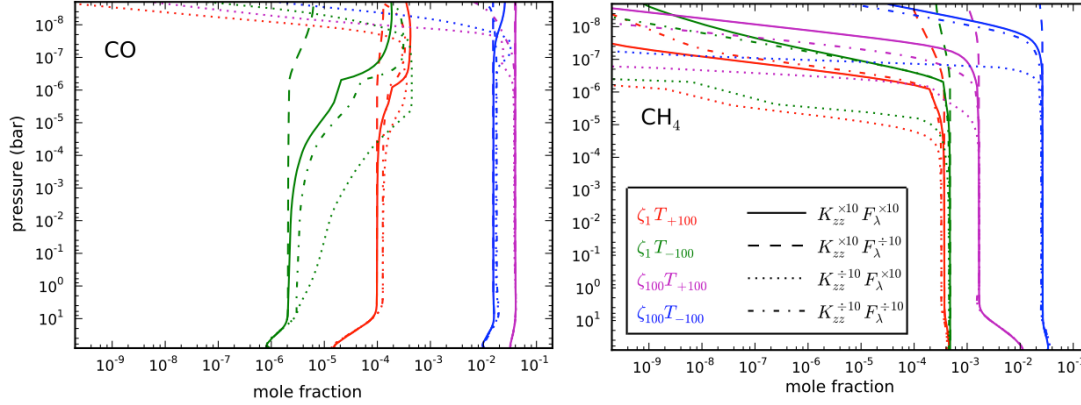


Figure 2: Vertical distribution of the abundances of CO and CH₄ as calculated through 16 models of GJ 3470b in which the space of parameters of metallicity (ξ), temperature (T), eddy diffusion coefficient (K_{zz}), and stellar UV flux (F_{λ}) are explored. Each colour corresponds to a set of metallicity and temperature, and each line style to a set of eddy diffusion coefficient and stellar UV flux. From Venot et al. (2013b)

3. Beyond one-dimensional models

Hot Jupiters and Neptunes orbit close to their host star and are thus expected to be tidally locked, showing permanent day and night sides (Guillot et al. 1996). The unequal heating of the planet maintains a strong temperature contrast between the day and night sides. These temperature gradient and the fact that photochemistry is switched on in the irradiated dayside and off in the non-irradiated nightside might drive important variations in the chemical composition of the atmosphere with longitude and latitude.

These inhomogeneities can be alleviated, or even almost suppressed, by the strong horizontal winds present in the atmospheres of these planets, which tend to redistribute the heat from the day to the night side and to homogenize the chemical composition among the different regions of the atmosphere. Evidences of strong winds, with velocities of a few km s⁻¹, in the atmosphere of hot Jupiters and Neptunes come from both general circulation models (GCMs), which predict that circulation is dominated by a strong equatorial superrotating jet (Cho et al. 2008; Showman et al. 2009; Lewis et al. 2010; Dobbs-Dixon et al. 2012; Rauscher & Menou 2013; Parmentier et al. 2013) and observations of phase curves showing an offset between the hot spot and the substellar point (Knutson et al. 2007) and Doppler shifts in spectral lines attributed to day-to-night winds (Snellen et al. 2010).

Therefore, on the one hand, the uneven irradiation of these planets tend to produce an atmosphere with a non homogeneous distribution of temperature and chemical composition, and on the other, horizontal winds tend to homogenize temperature and molecular abundances among the different regions of the planet. Whether the atmosphere shows an irregular or rather uniform structure is the result of these two competing factors. The subject can be studied theoretically and constrained with observations of the emission spectra of exoplanets at different phases and

transmission spectra acquired at the transit ingress and egress, a type of observations which are especially well suited for EChO.

The 3D temperature structure of hot atmospheres has been investigated theoretically to a great detail by numerous groups, mainly in the context of general circulation models. An illustration of the important variations of temperature as a function of longitude in the atmosphere of the hot Jupiter HD 209458b is given in Figure 3. For a detailed description of how such inhomogeneities can be probed by EChO we refer to the Technical Note by Parmentier, Showman, and de Wit.

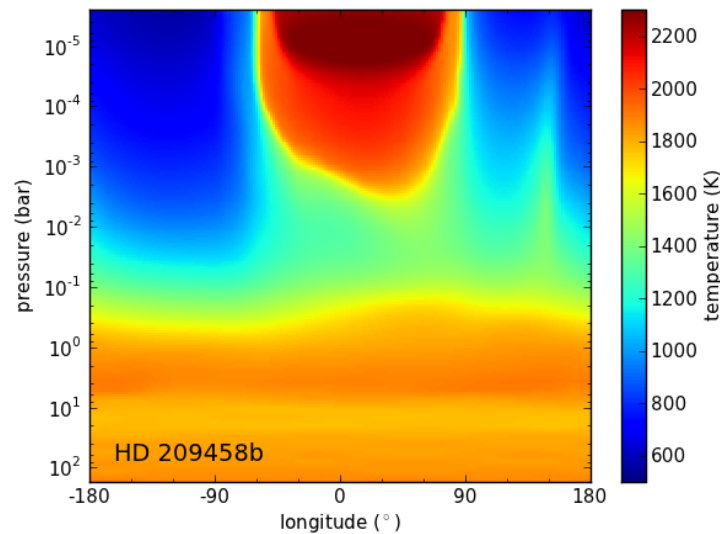


Figure 3. Temperature structure averaged latitudinally over 20° around the equator of HD 209458b, as calculated with a GCM simulation (Parmentier et al. 2013). Note the existence of strong temperature contrasts between the day and night sides, with a extremely hot dayside stratosphere above the 1 mbar pressure level.

Here we focus on how atmospheric constituents are distributed in the atmospheres of hot Jupiters and Neptunes according to theoretical calculations. It is clear that to investigate the subject, one-dimensional models need to go one step further toward two- and three-dimensional models to properly deal with the longitude and/or latitude dimensions. Significant contributions to the subject have been made in recent years. A first attempt to understand the interplay between dynamics and chemistry was undertaken by Cooper & Showman (2006), who coupled a three-dimensional general circulation model of HD 209458b to a simple chemical kinetics scheme dealing with the interconversion between CO and CH₄. These authors found that, even in the presence of important temperature gradients, the mixing ratios of CO and CH₄ are homogenized throughout the planet's atmosphere in the 1 bar to 1 mbar pressure regime. A different approach was adopted by Agúndez et al. (2012), who coupled a robust chemical kinetics scheme to a simplified dynamical model of HD 209458b's atmosphere, in which the atmosphere rotates as a

solid body, mimicking a uniform zonal wind. This exploratory study neglected vertical mixing and photochemistry but was able to identify the main effect of zonal winds of the distribution of molecules, which we may summarize as “the zonal wind tends to homogenize the chemical composition, bringing molecular abundances at the limb and nightside regions close to chemical equilibrium values characteristic of the dayside”.

A step further has been recently taken by Agúndez et al. (2013a) with a pseudo two-dimensional model of the atmospheres of HD 209458b and HD 189733b, which takes into account simultaneously thermochemical kinetics, photochemistry, as well as vertical and horizontal transport, the latter modeled as a uniform zonal eastward wind. The distribution of the chemical composition with altitude and longitude in the atmosphere of these two hot Jupiters is found to be quite complex because of the interplay of the various physical and chemical processes at work. In the main, much of the distribution of molecules is driven by the strong zonal wind and the limited extent of vertical transport, resulting in an important homogenization of the chemical composition with longitude. In general, molecular abundances are quenched horizontally to chemical equilibrium values of the hottest dayside regions, and thus the composition in the cooler nightside regions is highly contaminated by that of warmer dayside regions. The abundance of some molecules such as CO and H₂O show little variation with either longitude or altitude, while others such as CO₂ experience significant abundance variations with longitude (see Figure 4). In general, the cooler the planet the largest the homogenization of the chemical composition with longitude. Moreover, in cooler planets such as transiting Neptunes orbiting M dwarfs, the temperature contrast between the day and night sides is less severe because the cooling rate scales with the cube of temperature, and therefore the composition is expected to be even more homogeneous with longitude than in warmer planets such as HD 209458b and HD 189733b. The important homogenization of the chemical composition predicted for hot Jupiter and Neptunes possesses important constraints on how the planetary emission spectrum varies with phase and on the differences between the transmission spectrum of the planet probing each of the two meridians of the planet terminator during the transit ingress and egress. Most such variations in the spectra are expected to be due to differences in the temperature structure rather than to differences in the chemical composition between different regions of the planetary atmosphere, and this can be readily tested with the observations that EChO will be able to carry out.

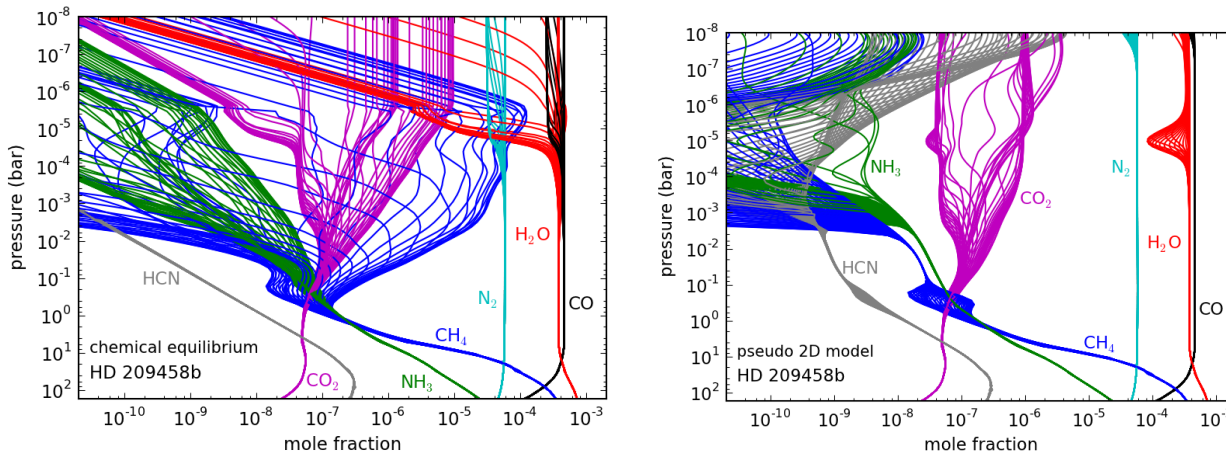


Figure 4. Vertical cuts of the abundance distributions of some of the most abundant molecules at longitudes spanning the 0-360° range, as calculated with chemical equilibrium (left panel) and with a pseudo two-dimensional chemical model (right panel) for HD 209458b's atmosphere. Note that the large longitudinal variations of the abundances predicted by chemical equilibrium are attenuated to an important extent in the more realistic pseudo two-dimensional model. From Agúndez et al. (2013a)

4. Ongoing developments

More elements, more species

Although they have much smaller cosmic abundances, elements like Sulfur, Phosphorus or Chlorine can play a role in the chemistry and the radiative budget of atmospheres and could be included. These species are less relevant for applied combustion and therefore less data is currently available but we are currently working on this question on the specific case of Sulfur.

Self-consistent coupling between the 1D thermal structure and the composition

The chemical composition depends on the temperature in the atmosphere but the temperature depends on the molecular abundances of species that absorb the incident stellar radiation and/or the planetary thermal emission. Iterations between radiative-convective calculations and chemical models are thus required. This has already been tested in 1D (Agúndez et al., 2013b) and is possible provided enough computing time is available.

Phase changes & clouds

There is a growing evidence of cloud signatures in exoplanet spectroscopic observations (Pont et al., 2013) and there are theoretical reasons to believe that condensation should occur. For instance, VO and TiO are expected to be exchanged between the gaseous and solid phase with important consequences on the thermal profile (Spiegel et al. 2009). Phase changes are therefore being implemented into the kinetic models.

Coupling 3D hydrocodes and kinetics

Current GCM can only include chemical kinetic models based on a very small network of reactions and species. One possible way to deal with this issue is to derive small chemical networks that provide a reasonably good description of the kinetics of a reduced group of species for a specific range of physical conditions and chemical background. For instance, for an atmosphere consisting of Solar abundances and with temperatures in the 800-1400K range, it may be possible to produce a network of less than 20 budget reactions with modified rate coefficients that is able to describe the behaviour of the few species important for the radiative transfer in the atmosphere (H_2O , CO , CH_4 , CO_2). It is our objective to produce, test and release such reduced networks.

High temperature UV cross sections

Photodissociations by UV play an important role in atmospheric chemistry. Available cross sections are derived from ambient or low temperature measurements. Data corresponding to the high temperatures found in hot Jupiter atmospheres (around 1000 K) are very rare. When some data exist, they have been usually done for combustion studies, on monochromatic beams or restricted wavelength ranges, usually above 190 nm while the 100-200 nm range is extremely important. It is known (e.g Koshi et al., 1991; Schulz et al., 2002; Oehlschlaeger et al., 2004) that the absorption of the UV flux is supposed to increase at wavelengths above 160 nm together with the temperature. So, when using room temperature data to model hot atmospheres we underestimate the absorption of the UV flux and photolysis rates. Consequently, it is crucial to have data corresponding to the temperature of warm exoplanets. In the context of EChO, this lack of data is now addressed by measuring absorption cross section and their temperature dependency for the important molecules of planetary atmospheres in the VUV wavelength range (115 – 230 nm). Thanks to several campaign of measurements at the synchrotron BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) and at the LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques), the absorption cross section of CO_2 (Venot et al., 2013a) has been determined up to 800 K. It can be seen on Fig. 5 that the absorption cross section of CO_2 varies significantly, increasing by several orders of magnitude together with the temperature.

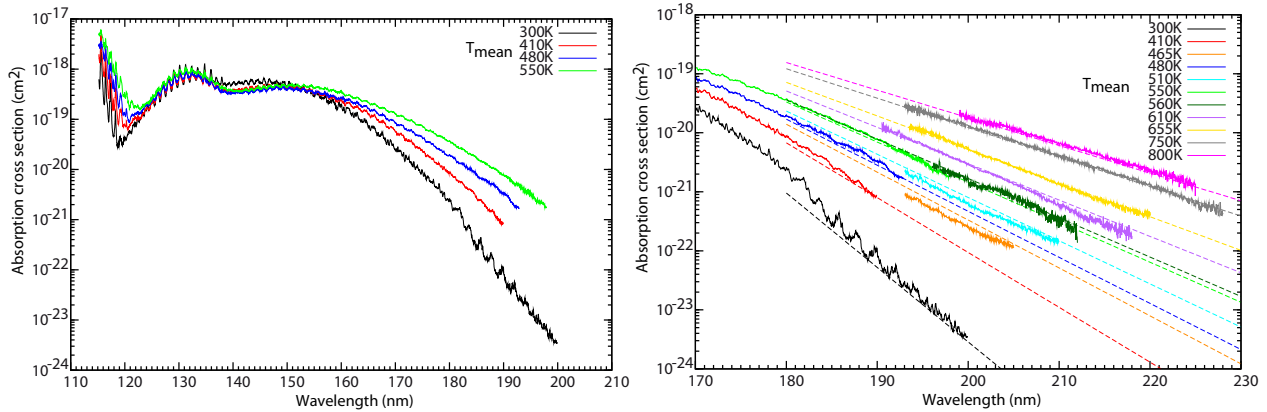


Figure 5: (*left*) Absorption cross section of CO₂ at T=300 K (black), 410 K (red), 480 K (green) and 550 K (blue) for wavelengths between 115 and 200 nm. (*right*) Absorption cross section of CO₂ for wavelengths longer than 195 nm at 465 K, 510 K, 560 K, 610 K, 655 K, 750 K, and 800 K, plotted with the cross section at ambient temperature (black). The absorption cross sections calculated with the parameterization are plotted with the same color coding.

The impact of the temperature dependency of the CO₂ cross section on exoplanet atmospheres has been studied by Venot et al. (2013a) on a prototype planet whose characteristics are similar to those of the hot Neptune GJ 436b.

Conclusion: chemical modeling and EChO

Robust chemical modeling is a key requirement for EChO or any instrument aiming at understanding the nature of exoplanetary atmospheres.

Chemical modeling is required to derive the atmospheric elemental compositions from spectroscopic observations. For giant planet envelope, this elemental composition can be described in terms of metallicity and C/O but for planets of a more terrestrial nature, whose atmospheres are outgassed from accreted solids, a much broader range of composition is expected (see Tech. Note by Leconte et al.).

Chemical models do also provides the link between composition and spectral features but also a way to explore the diversity of exoplanet atmosphere and associated signatures before the mission and to prepare the field of research to this diversity.

It is indirectly required to interpret observations (for instance orbital spectrophotometry) in terms of circulation/dynamics. Indeed, the chemical longitudinal gradients can influence the shape of the lightcurve and the detailed composition determines the pressure of the layers probed by observations. An atmosphere with the same 3D thermal structure can exhibit either strong or negligible phasecurve variations at a given wavelength depending on the actual distribution of infrared absorbent in the atmosphere.

Studying the diversity of chemical regimes in the atmospheres of EChO targets is a

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necessary step to prepare one of the most exciting goal of XXIst century science: the search for signatures of life on extrasolar worlds. It is indeed crucial to understand all the types of abiotic (=without life involved) out-of-equilibrium processes and associated signatures that physics and chemistry can produce in planetary atmosphere before considering identifying those that life and only life can generate.

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