DUST, HAZES AND CLOUDS IN EXOPLANETARY ATMOSPHERES

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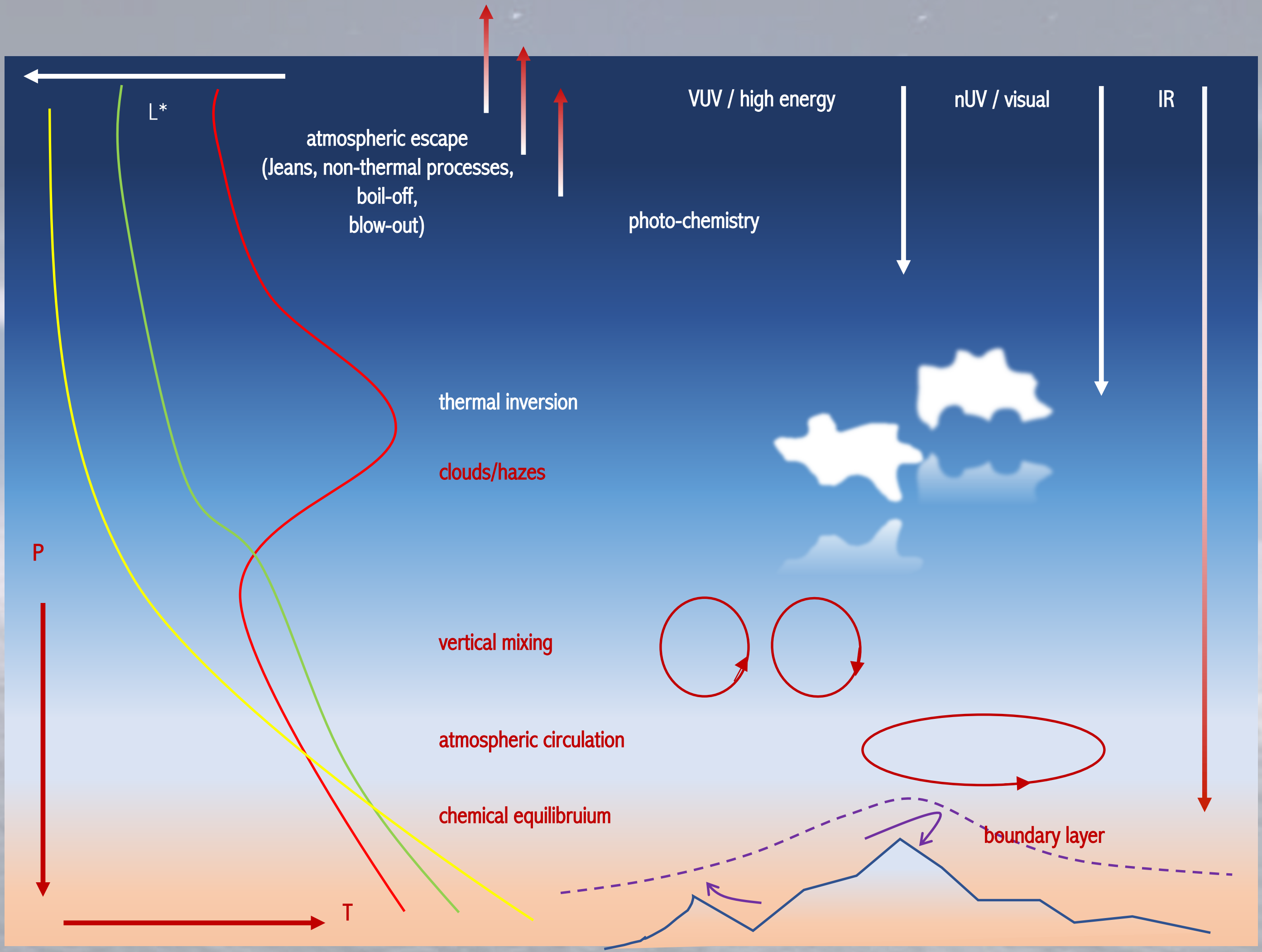
SPECULA PANORMITANA MDCCXC

- observations show that particles are common across a variety of temperatures and planetary types;
- formation and distribution of particles are inextricably connected to composition and thermal structure of an atmosphere;
- in turn the particles interfere with our probes of atmospheric composition and thermal profiles;
- a better understanding of particles leads to a better understanding of an atmosphere as a whole.

Atmospheric processes

- planet's energy balance
- cooling
- gain and loss of volatiles
- surface ⇋ interiors ⇋ atmosphere
- impact biological processes

- particles: e.g., Venus, sulphur cycle; Earth & Mars, surface climates.

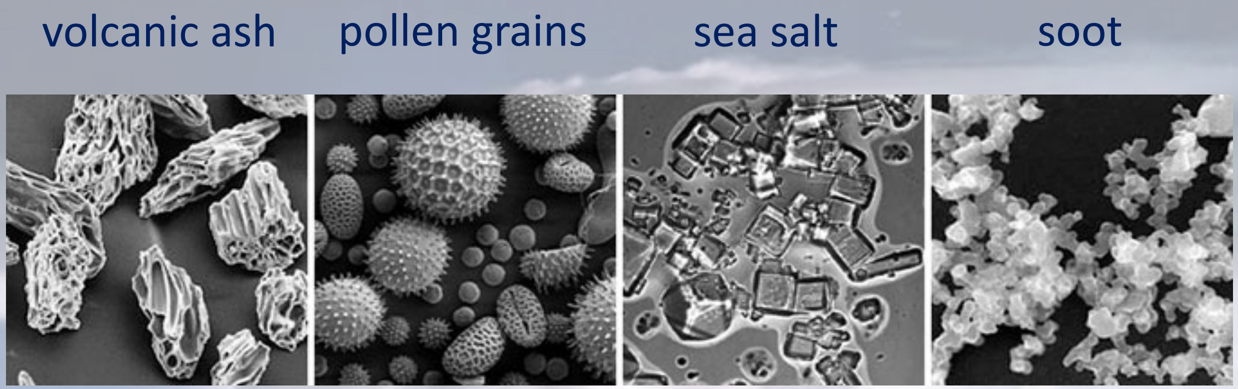


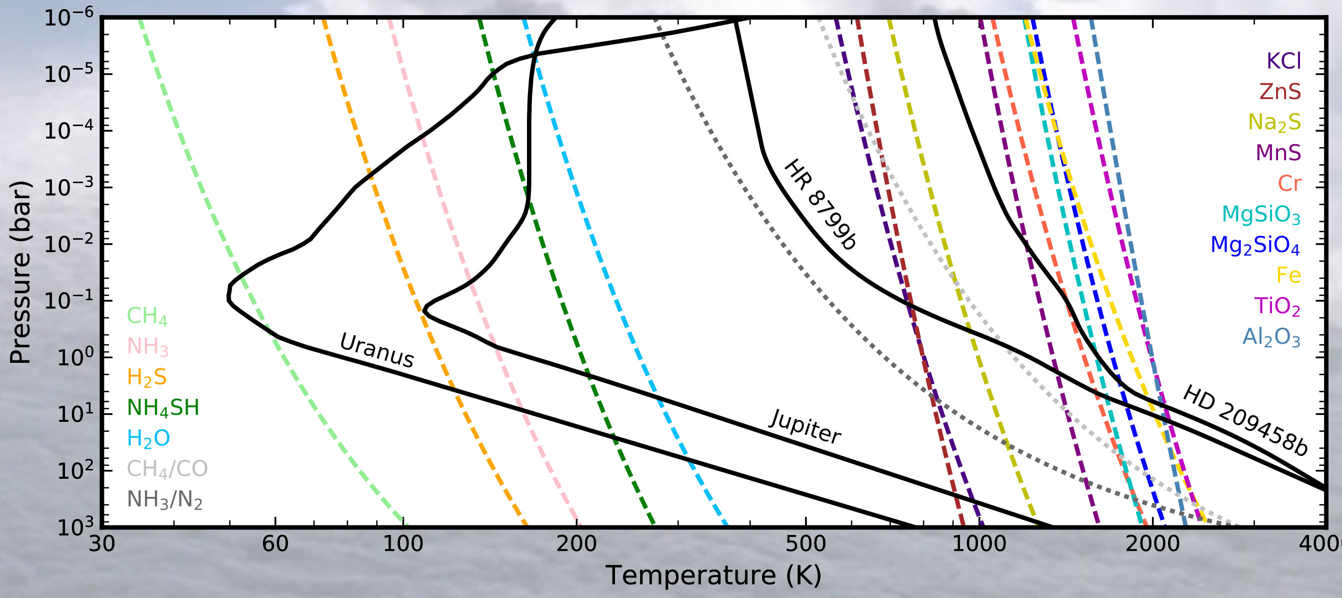
Particles are common in the atmospheres of exoplanets

- transmission spectroscopy (+ reflected light, emission photometry, phase curves)
- solar system
  - -- widespread
  - -- local and global
- clouds, hazes, and dust have something in common
  - -- particles (liquid or solid)
  - -- absorb and scatter light differently than gases

are they haze? are they clouds?

we don't really know





Particles are common in the atmospheres of exoplanets

- dust

particles lofted into the atmosphere

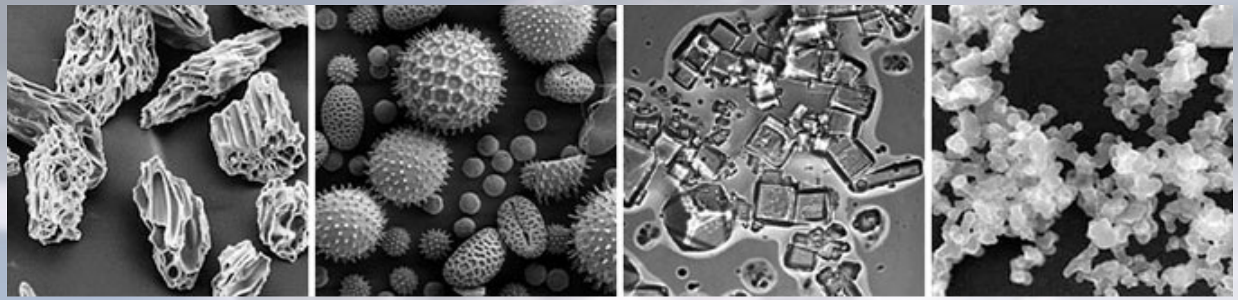
- clouds

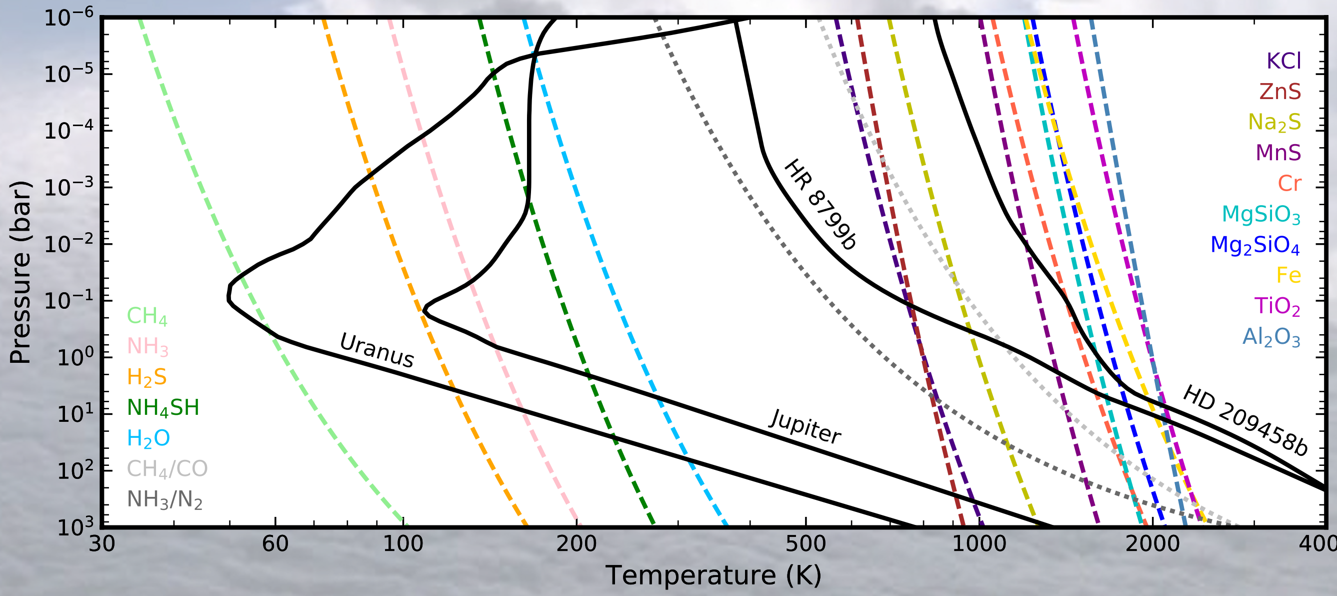
collections of particle formed in the atmosphere under thermochemical equilibrium (see dust formation in AGB stars)

- hazes

particles formed directly from photo- and radiation-chemical processes

volcanic ash pollen grains sea salt soot





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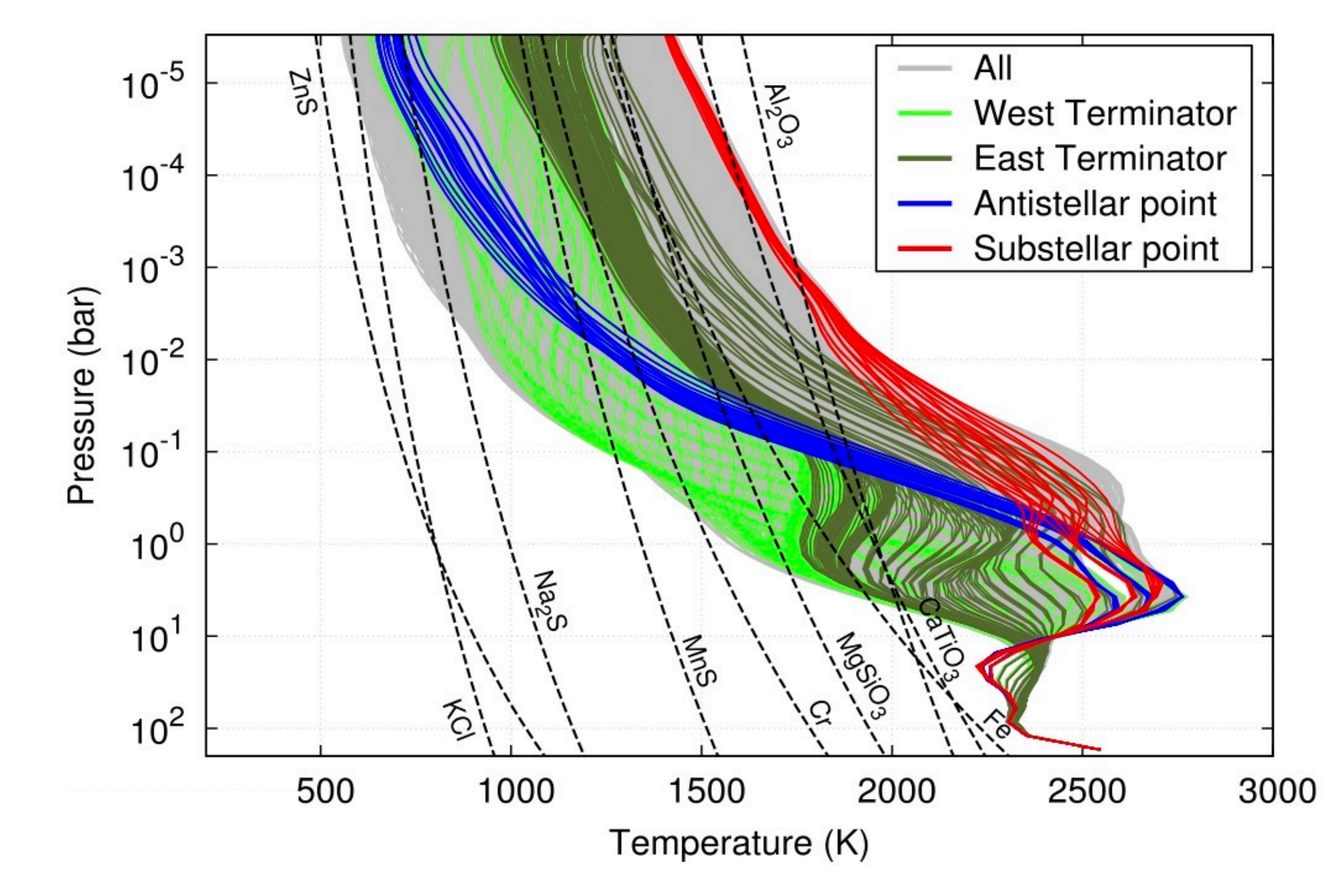

T_{eq} = 1900 K, Parmentier+16

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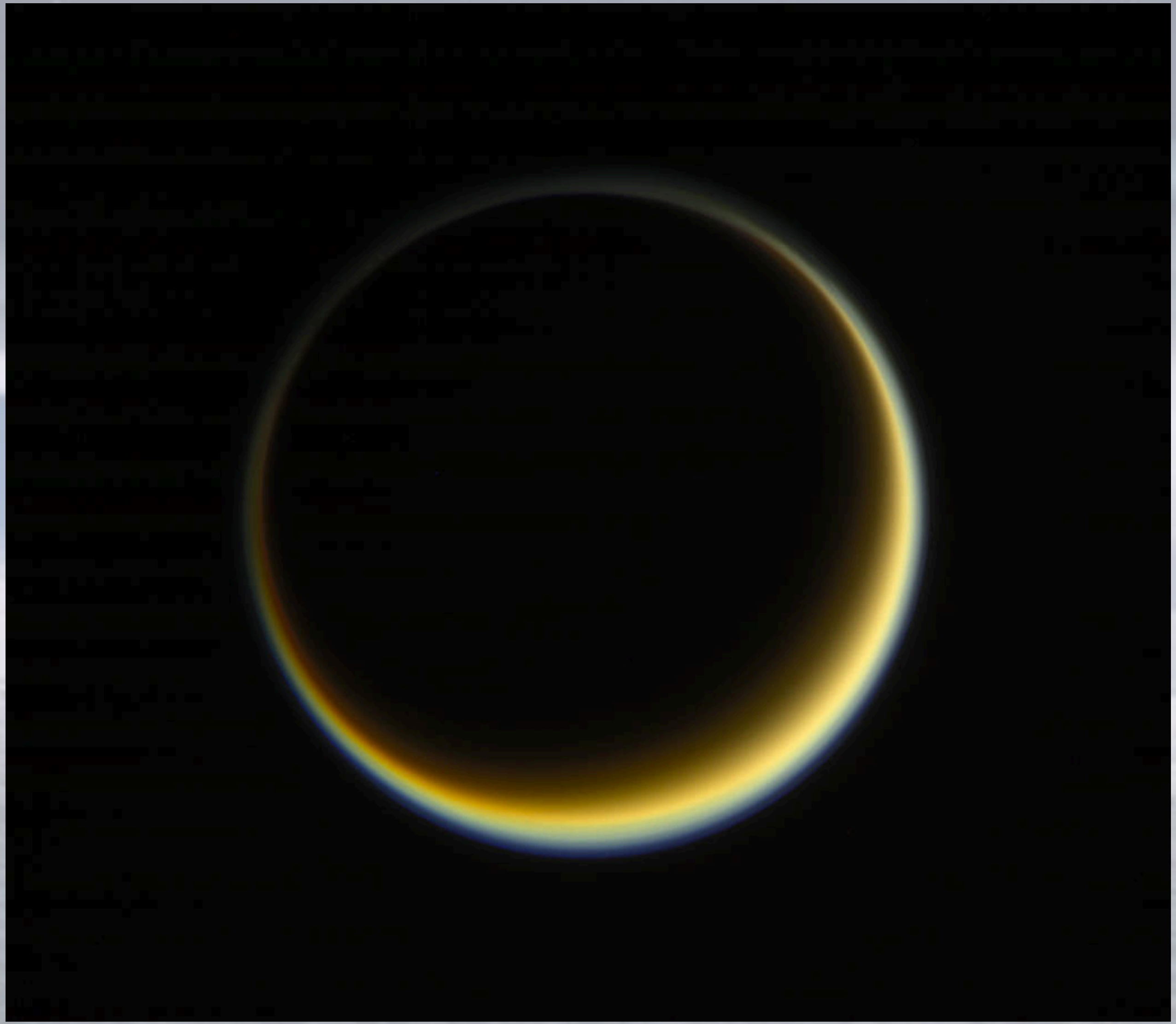


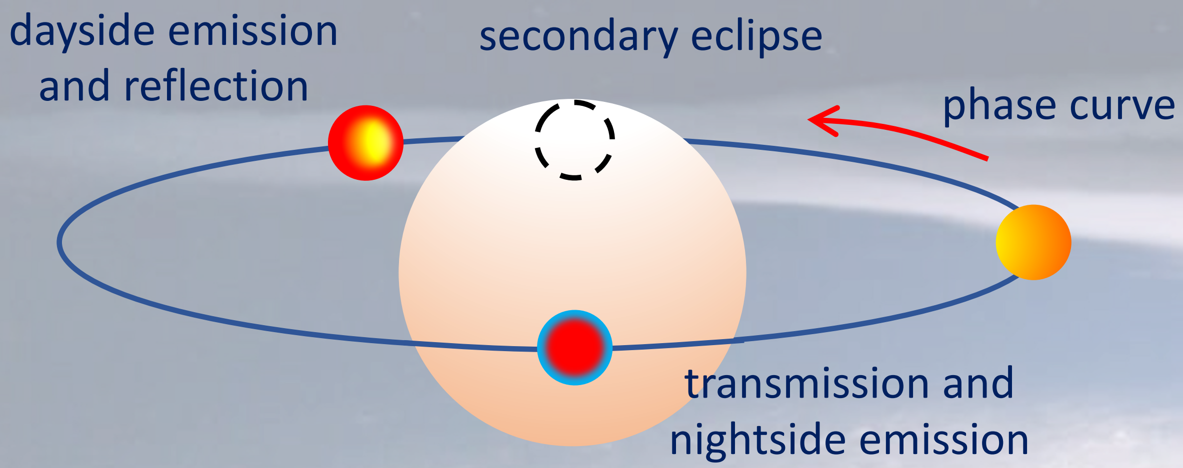
A touch of exoticism

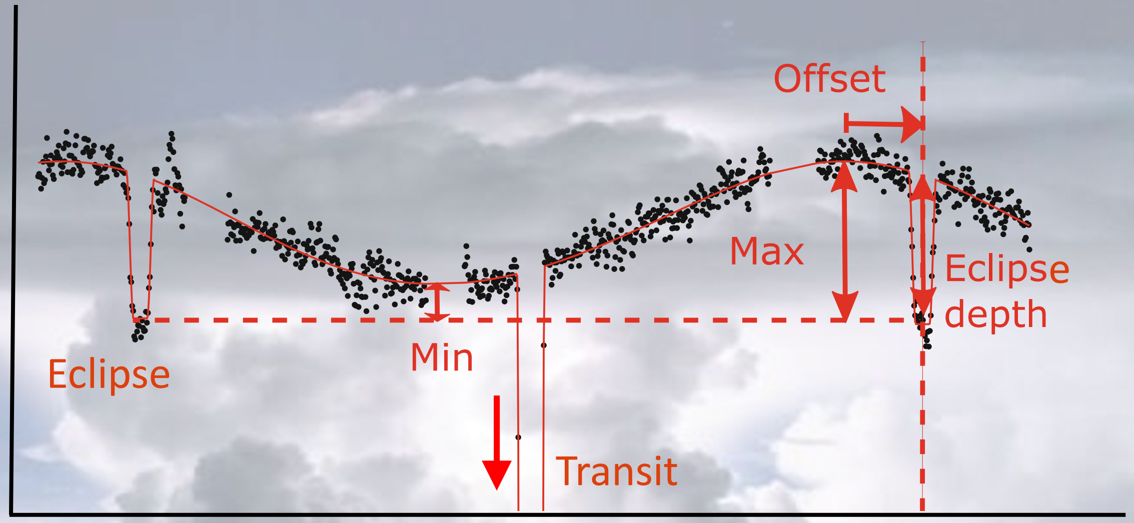
- Venus shows a thick envelope and haze system that is mostly made up of sulfuric acid and sulfuric dioxide;
- Earth's atmosphere water and water ice clouds are abundant, as well as high altitude sulfuric acid hazes;
- In Mars, there are water and CO2 ice clouds, which may use the abundant red dust in its atmosphere as nucleation sites;
- Jupiter and Saturn are covered in clouds of water, ammonia, and possibly ammonium hydrosulfide, with overlying hydrocarbon photochemical hazes; visible Jupiter > Saturn, fewer hazes; Saturn in the infrared is more structured than in visible;
- Titan: substituted PAHs;
- exoplanets: transmission spectra are frequently featureless in the near–infrared; inability of stellar photons to reach depths in the atmosphere below the cloud top;

exotic materials, such as salts, sulfides, rocks, metals, and hydrocarbon «soots»

particles often clump together to form complex mixtures

Particles impact every method of exoplanet atmosphere characterization

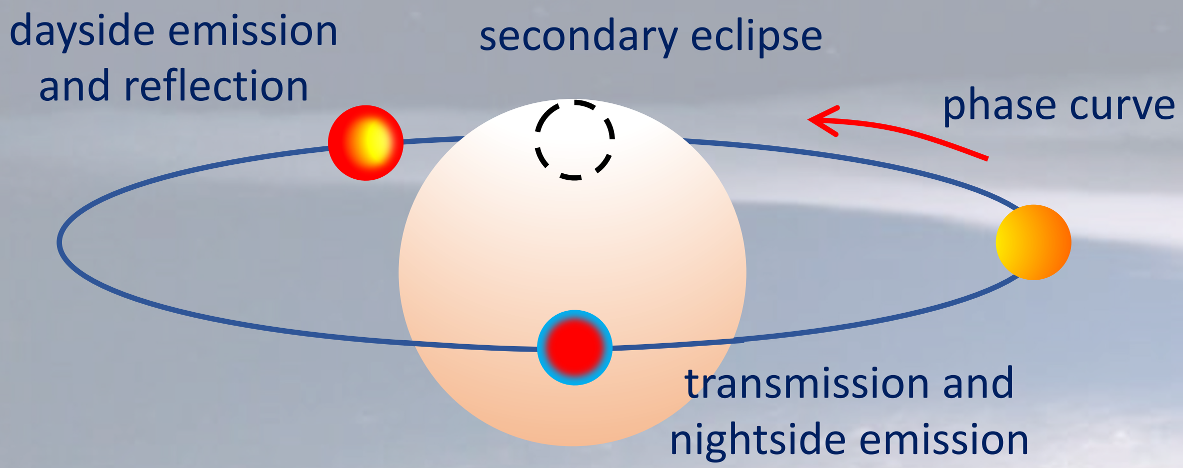




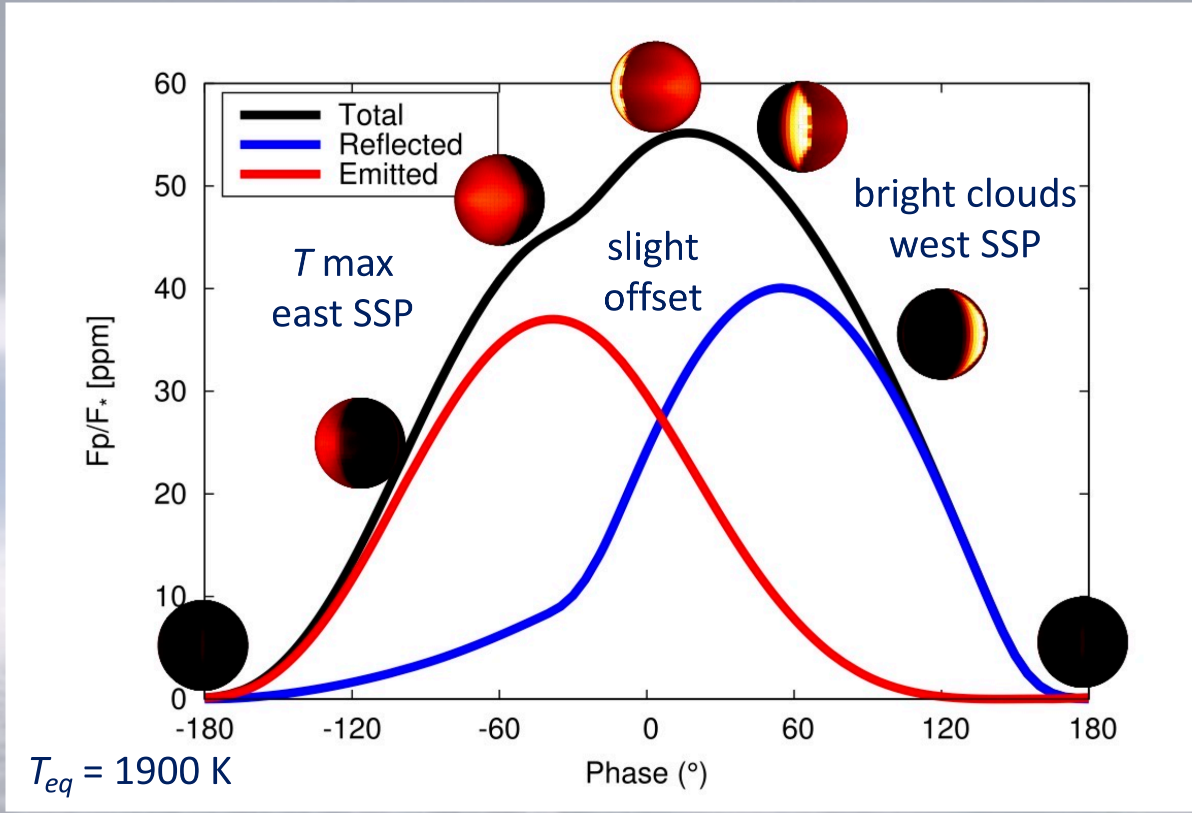
- transmission: straightforward interpretation
- phase curve: 3 observables; secondary eclipse depth, phase curve offset, phase curve relative amplitude

when ignored, spatial inhomogeneities can lead to a biased interpretation of transiting and secondary eclipse observations

Particles impact every method of exoplanet atmosphere characterization



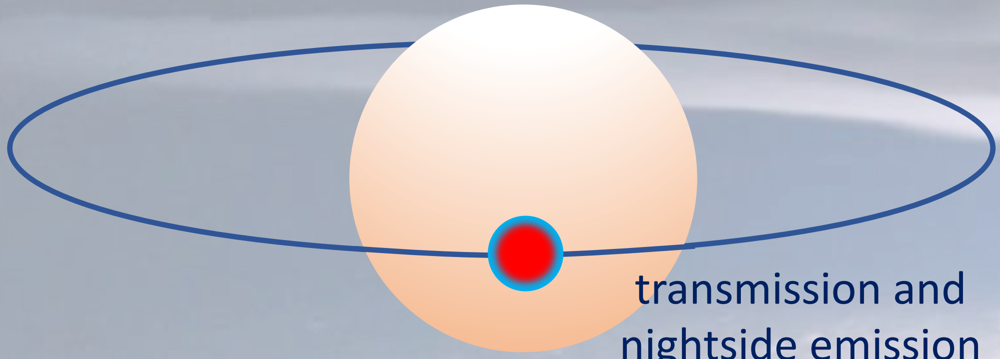
Parmentier & Crossfield 2018

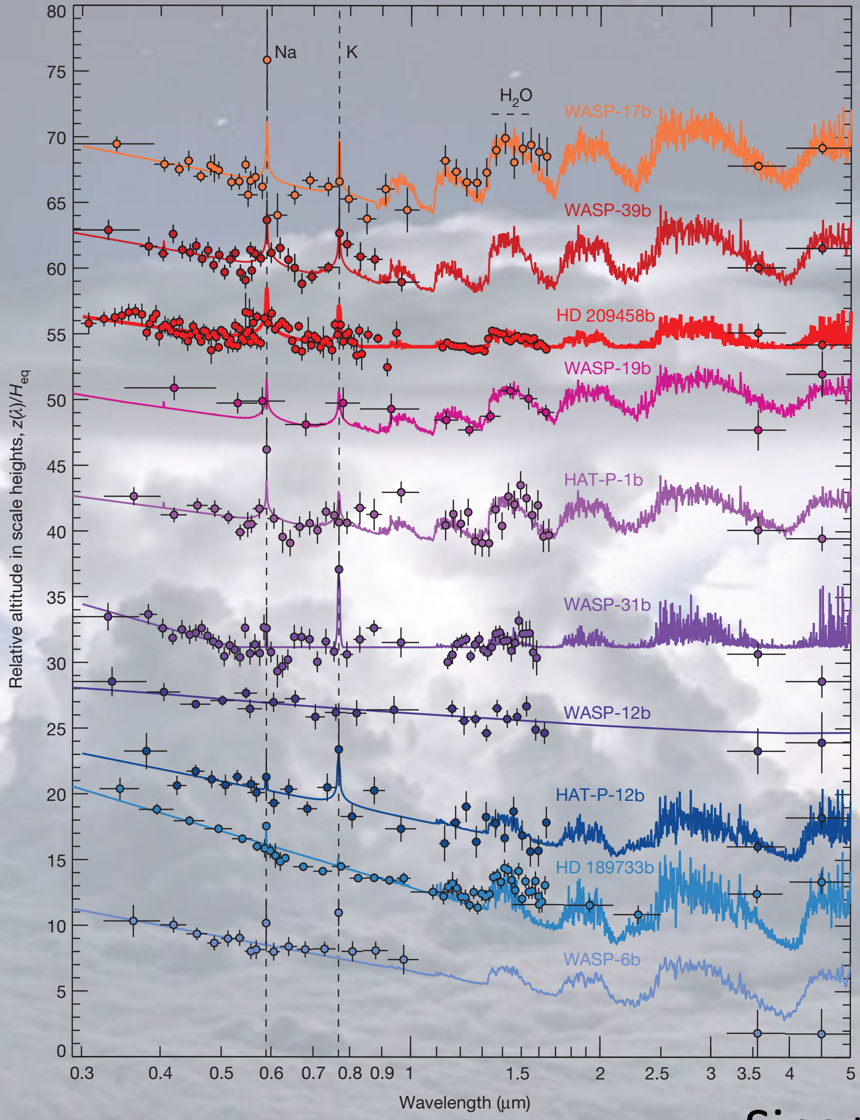


- optical → albedo; infrared → thermal emission
- cooler planets: reflected light dominates over emission (negative offset)
- hotter planets: the opposite

when ignored, spatial inhomogeneities can lead to a biased interpretation of transiting and secondary eclipse observations

Transmission





Sing+16

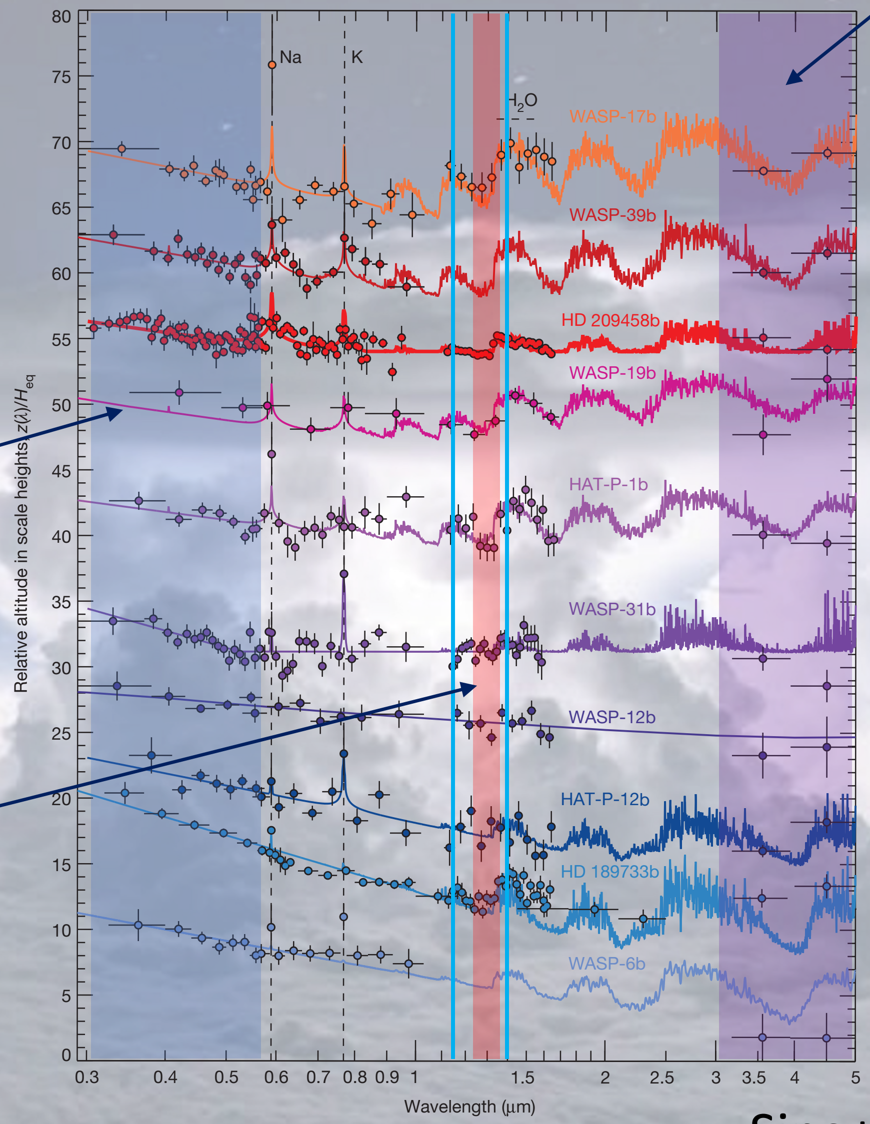
Transmission

strong H_2O, CO and CH_4 absorption bands

strong water bands

dominated by scattering for clear, cloudy and hazy exoplanets

hazy, cloudy and highly sub-solar models; H_2O continuum (near solar)

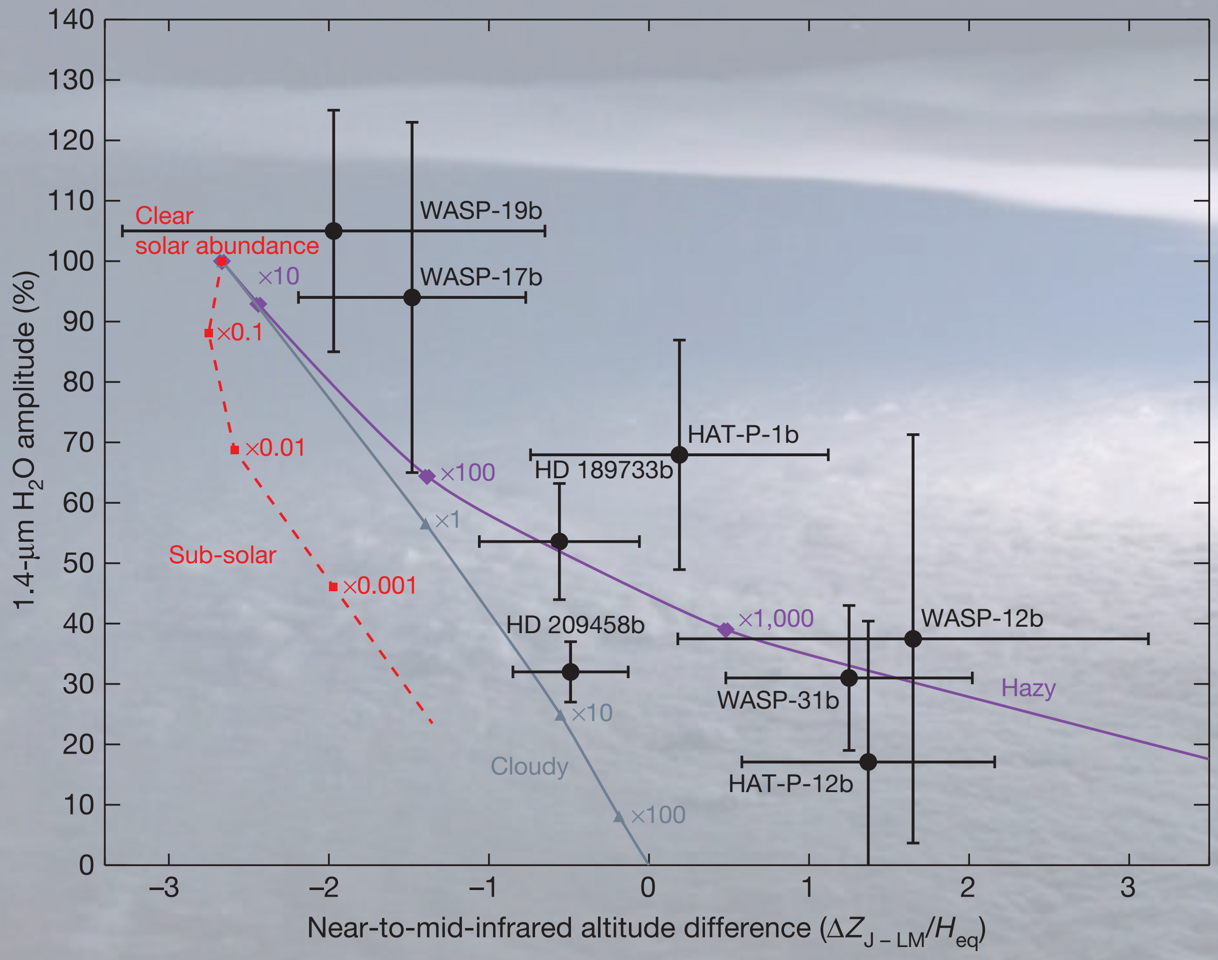


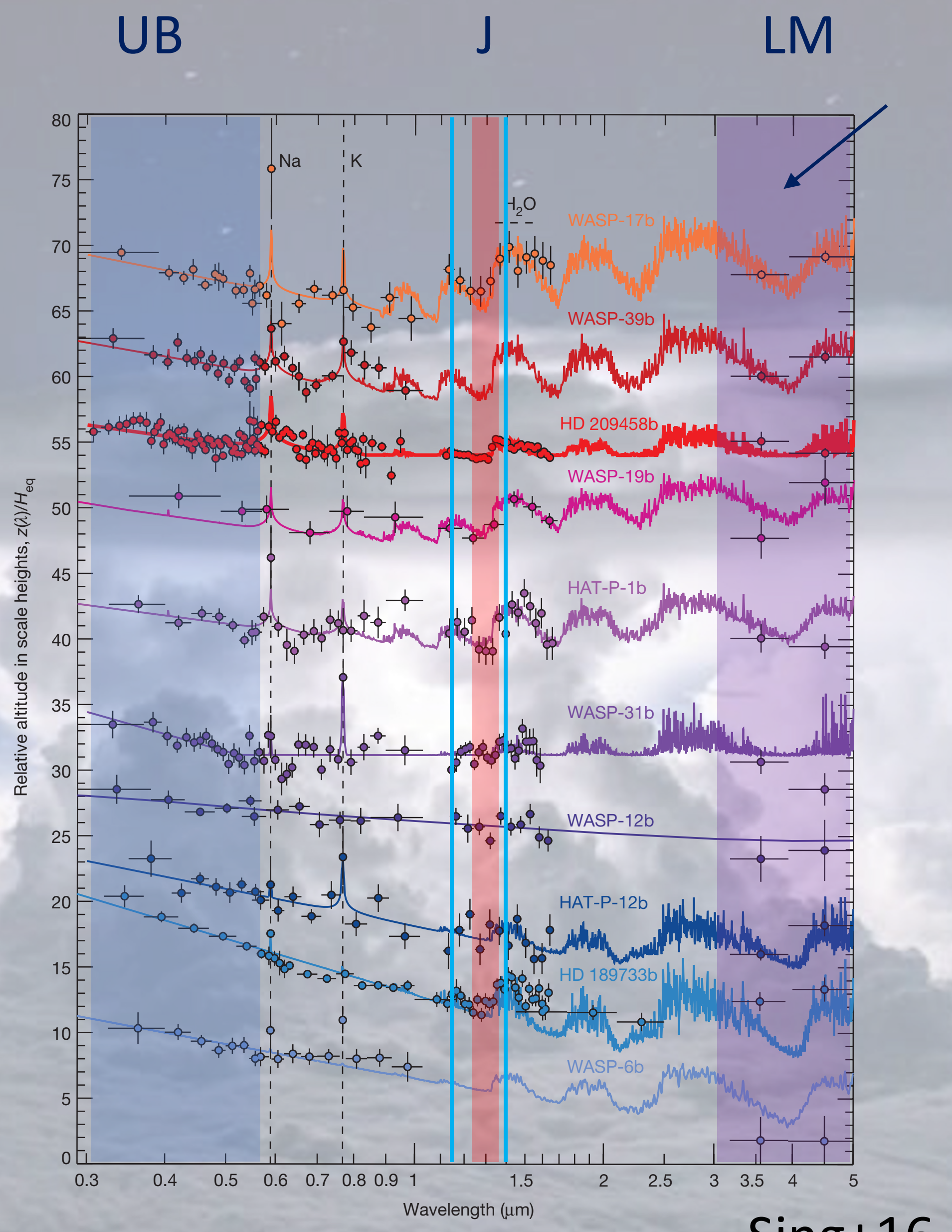
Sing+16

Transmission

$$z(\lambda) = H\ln\left(\frac{nP\sigma(\lambda)}{\tau}\sqrt{\frac{2\pi R_P}{kT\mu g}}\right)$$

wavelength-dependent transit-measured altitude





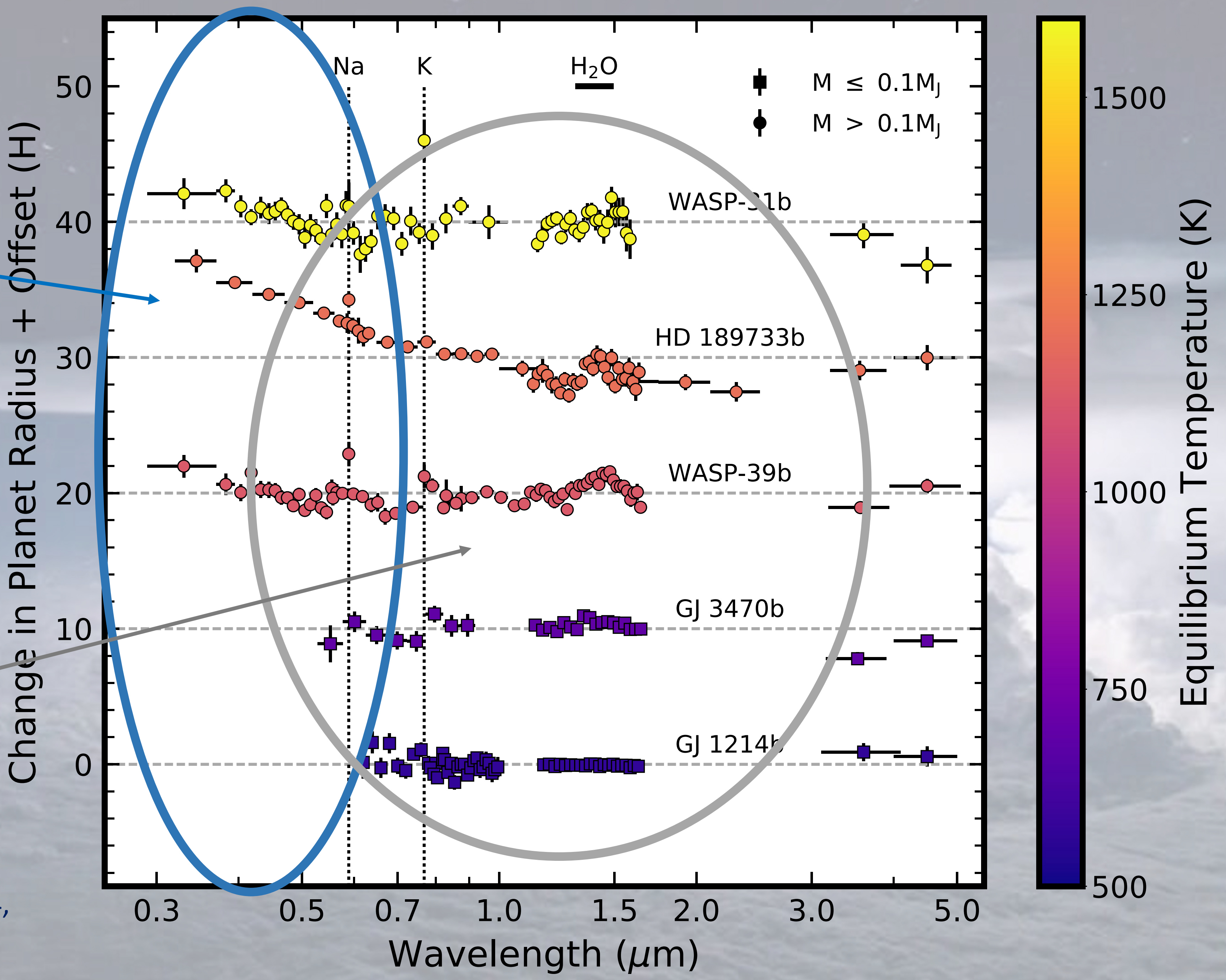
Sing+16

Transmission

scattering (hazes)

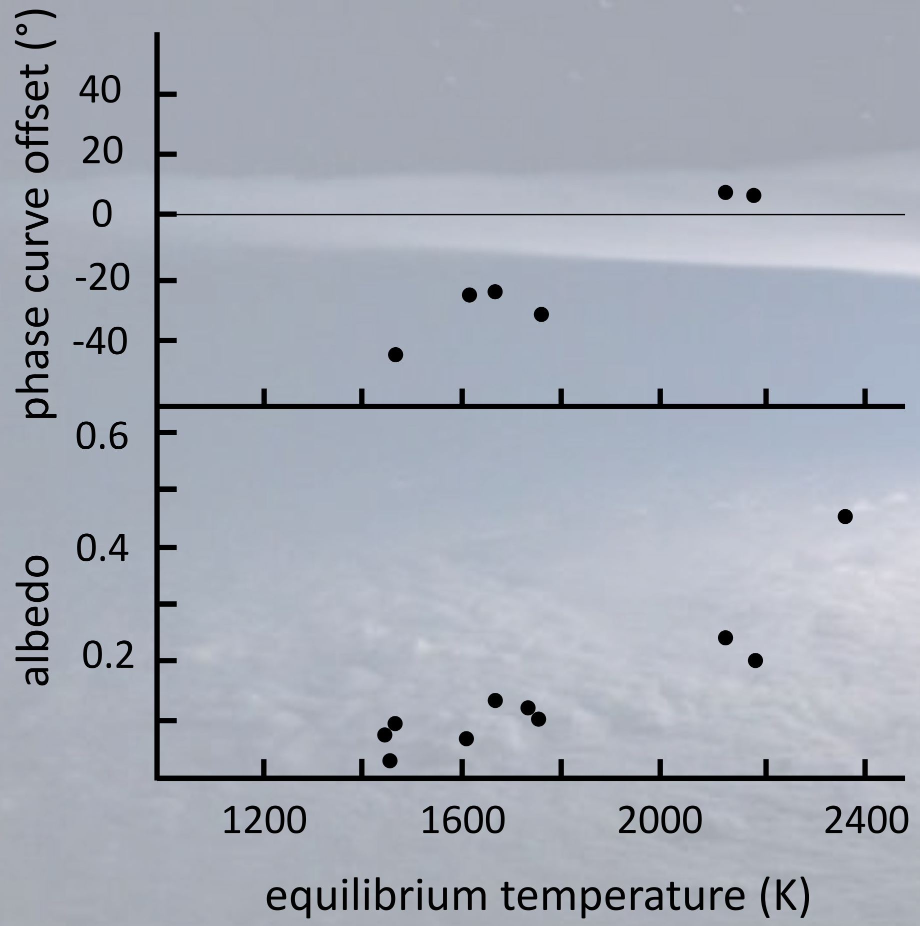
frequently
clouds = grey body
hazes = Raileigh

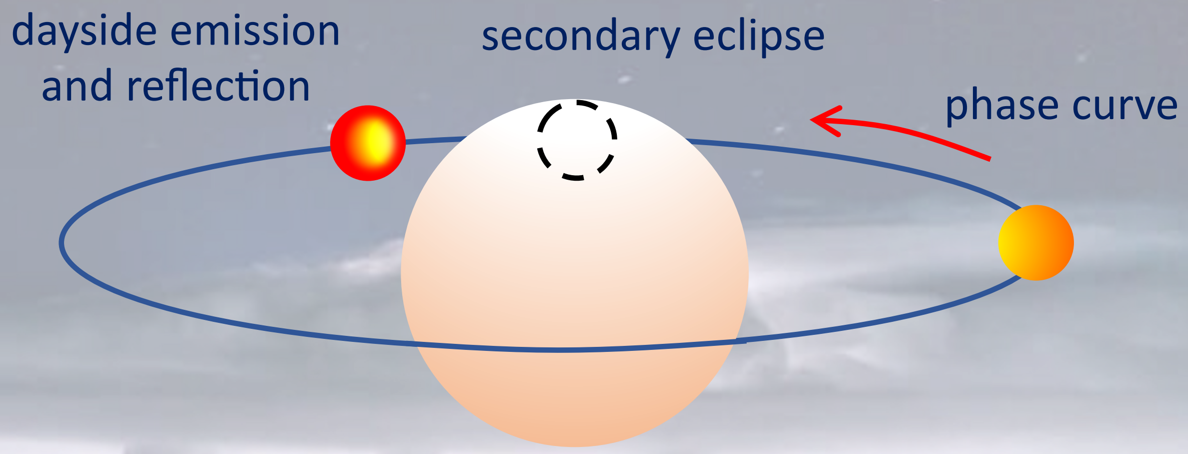
damping (clouds)



Bean+11, Désert +11, Kreidberg+14,
Benneke+19, Wakeford+21

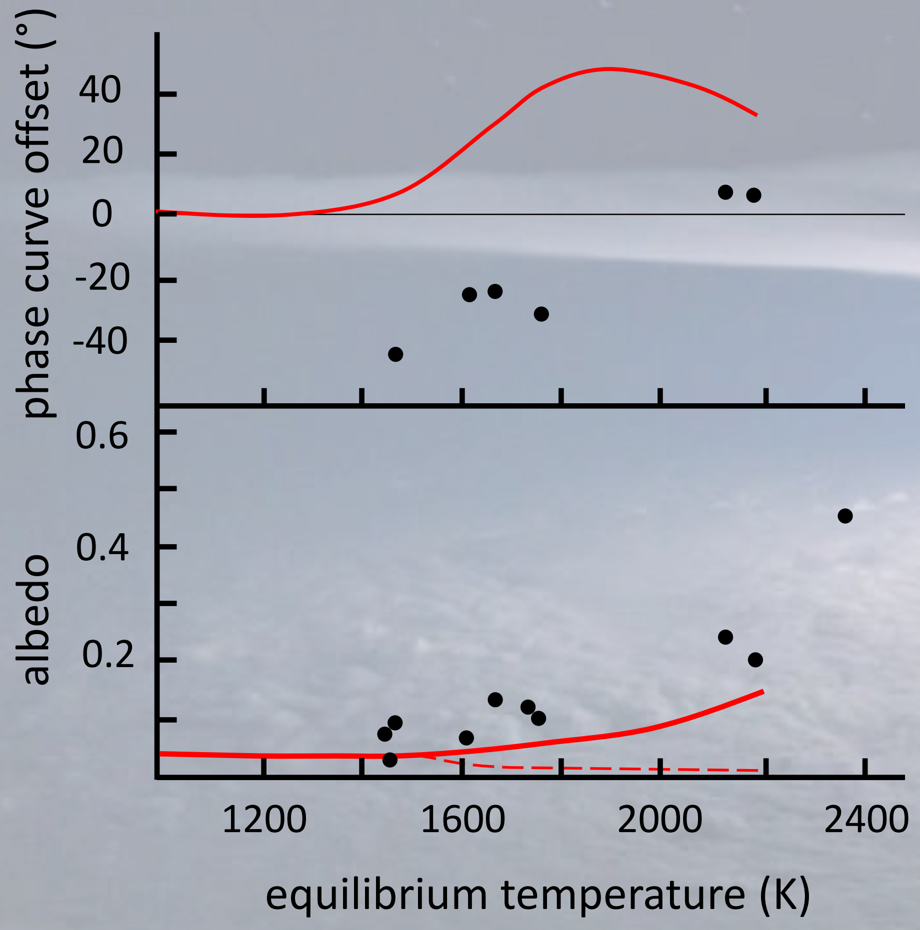
Phase curve shifts

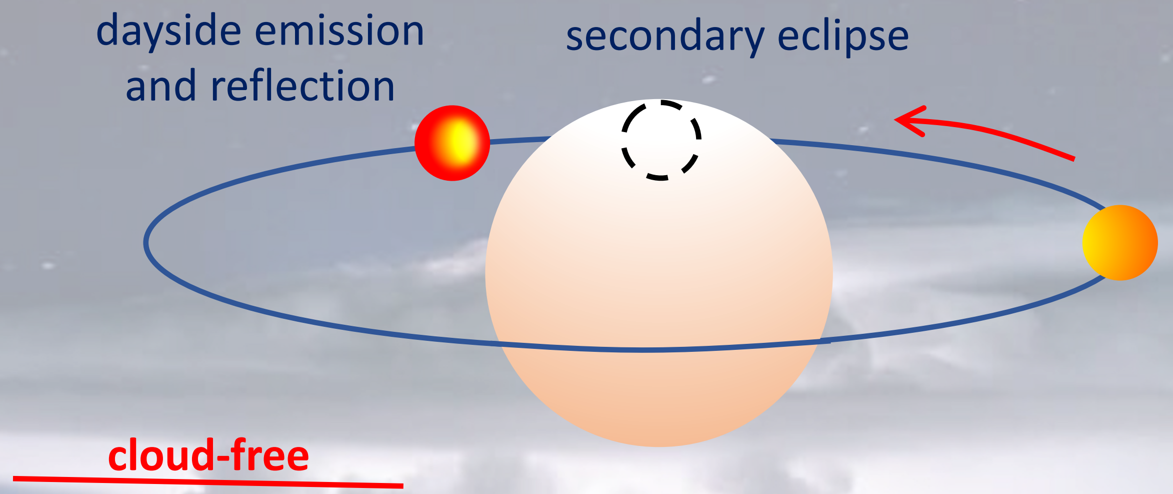




data: Kepler; models: Parmentier+16

Phase curve shifts





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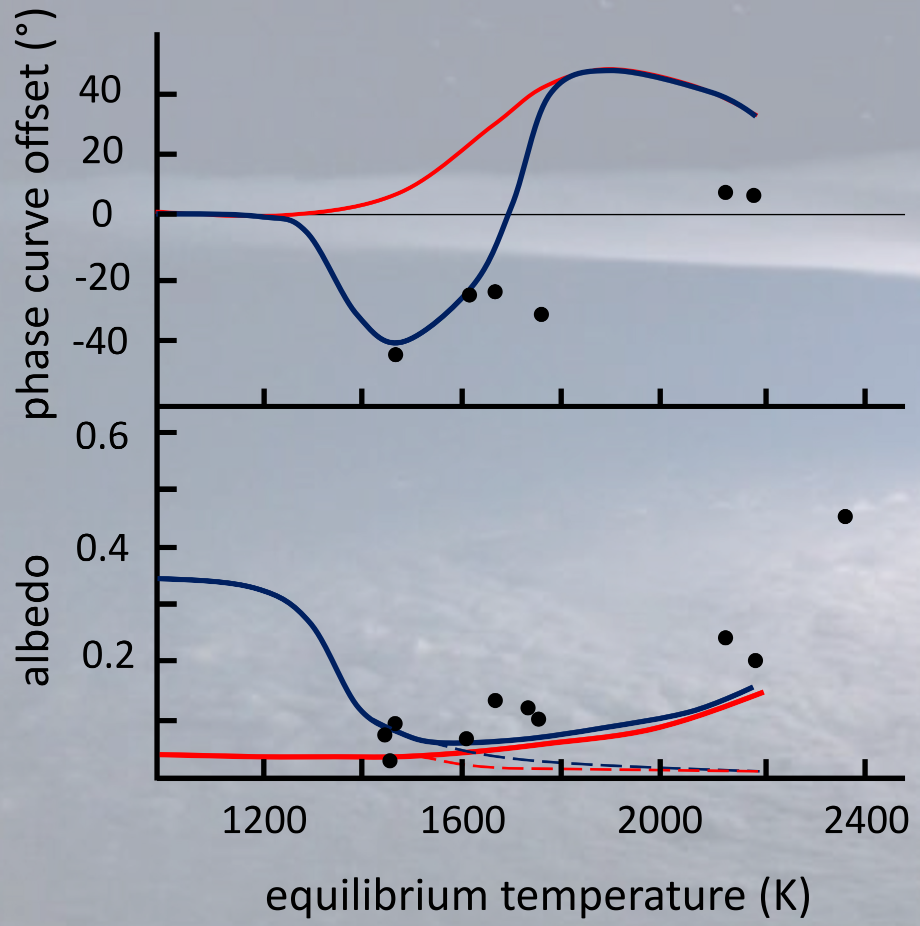

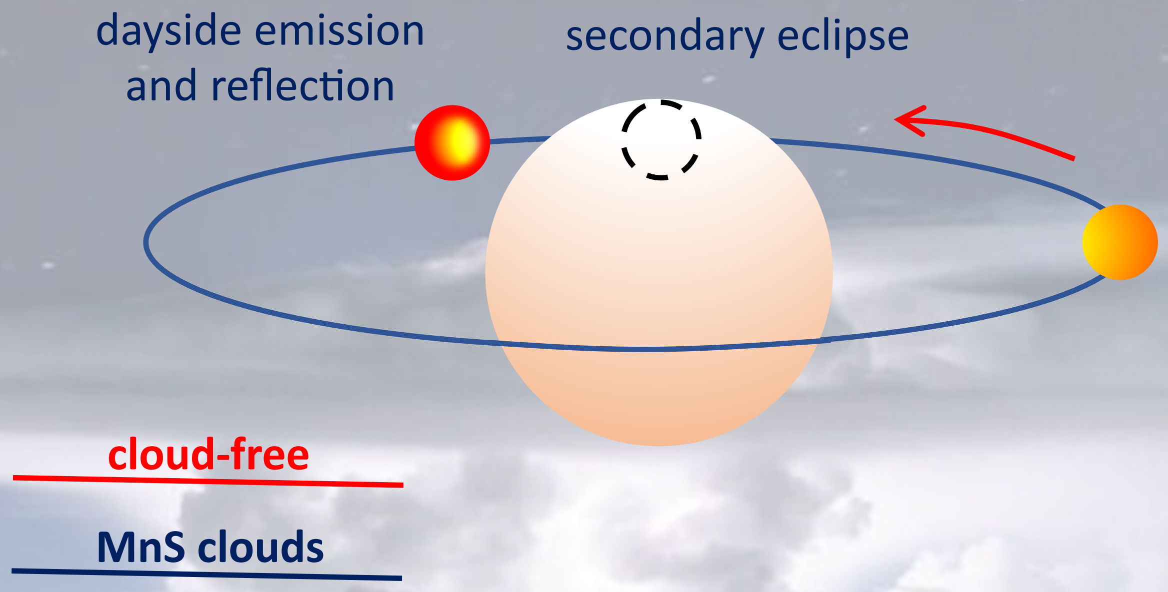

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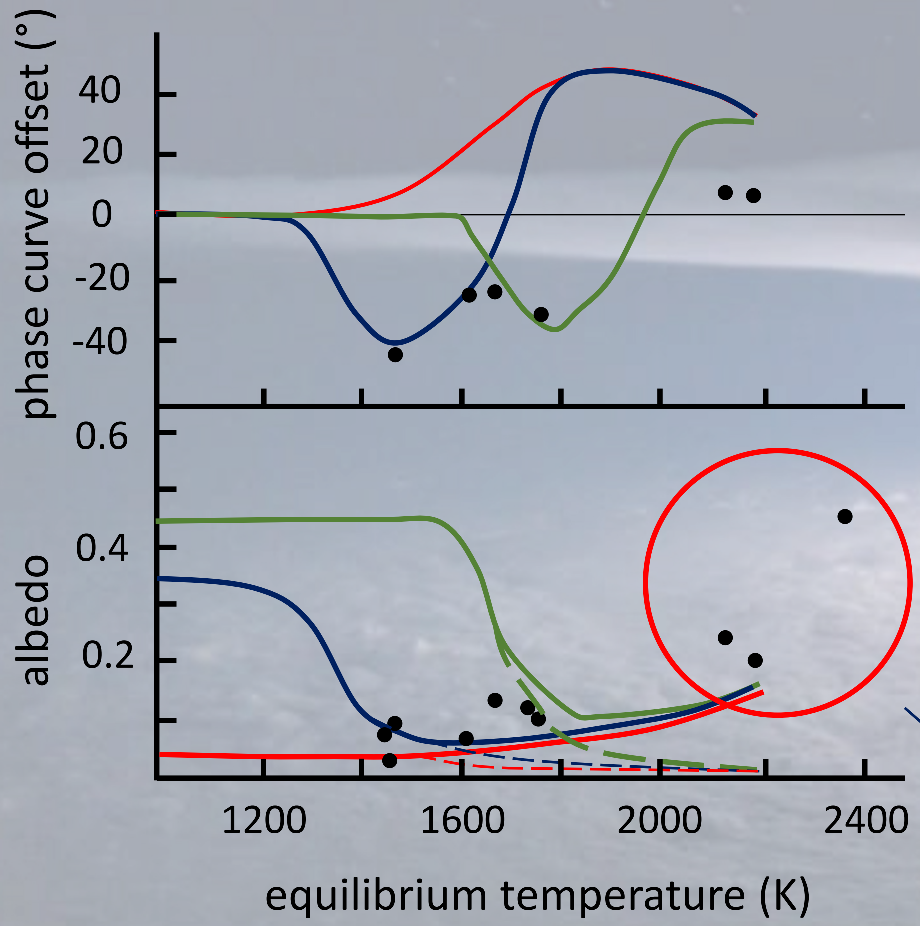
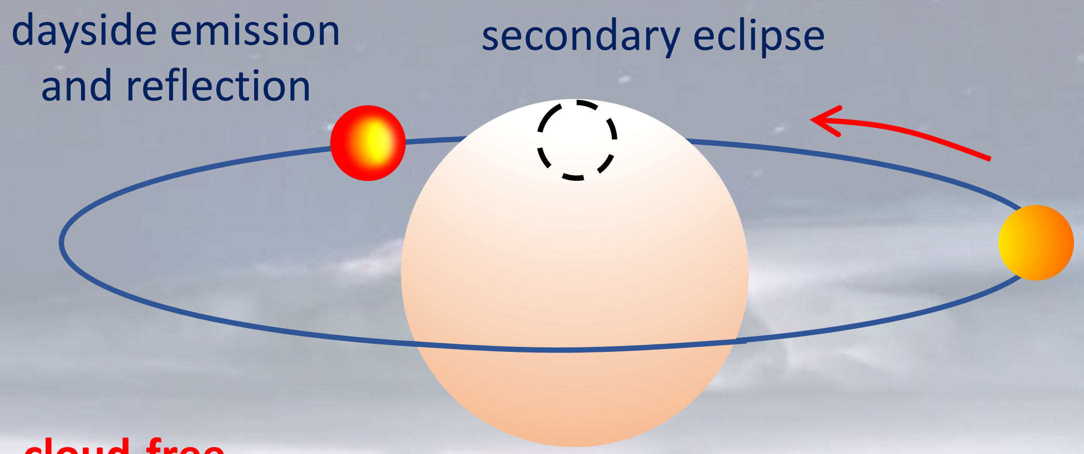




cloud-free

MnS clouds

$MgSiO_3$ clouds

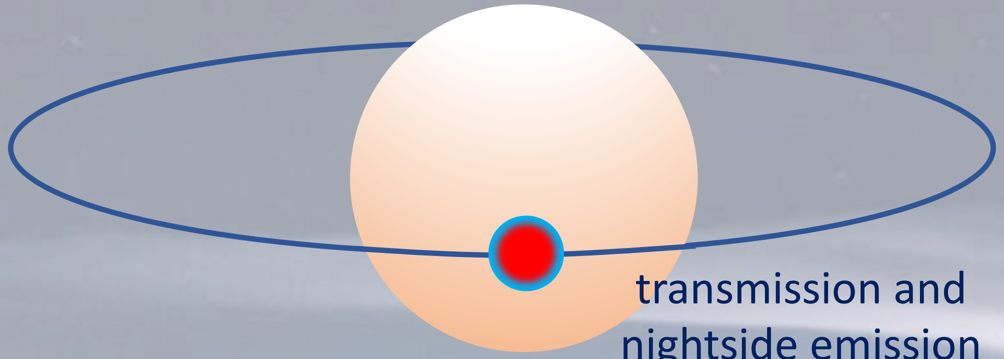
negative phase shifts → daysides cloudy

low albedos → daysides only partly cloudy

mostly thermal emission

data: Kepler; models: Parmentier+16

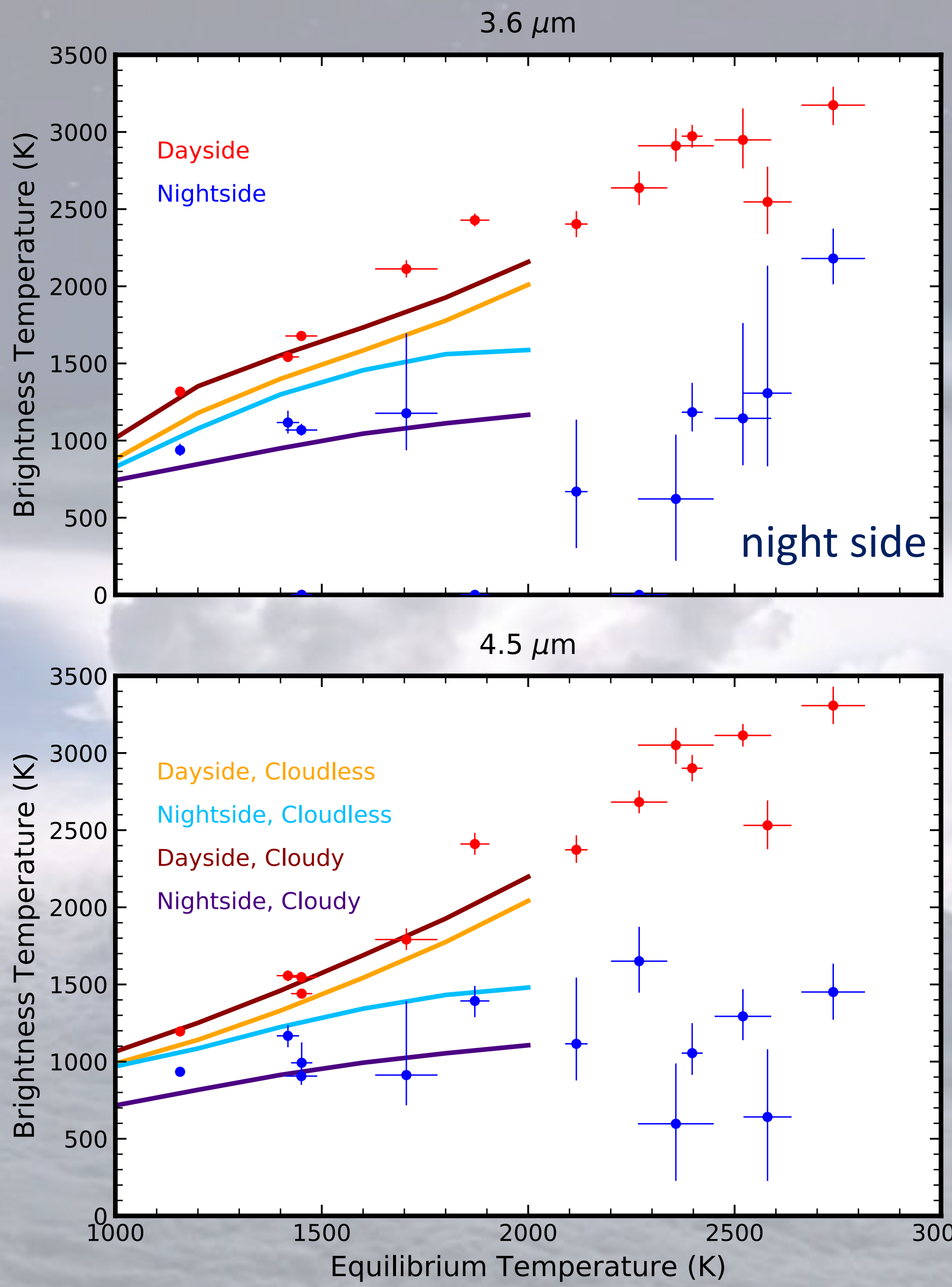
Phase curve shifts



nightside at near-infrared wavelengths probe the top of a cloud layer that persists on all transiting exoplanets

↓

nightside brightness temperature is tied to the condensation temperature of that cloud



The need for laboratory measurements and numerical modelling

- limited information on the micro-physical properties, i.e. particle composition, size, shape, number density of scattering particles;
- consequence: exoplanet atmospheric models capable of interpreting the upcoming observations are limited by insufficiencies in the laboratory and theoretical data that serve as critical inputs to atmospheric physical and chemical tools;
- models rarely treat rigorously the scattering and absorption of light by particles of complex morphology;
- condensate clouds or photochemical hazes: ambiguity is difficult to solve from theory alone, and requires a laboratory approach;

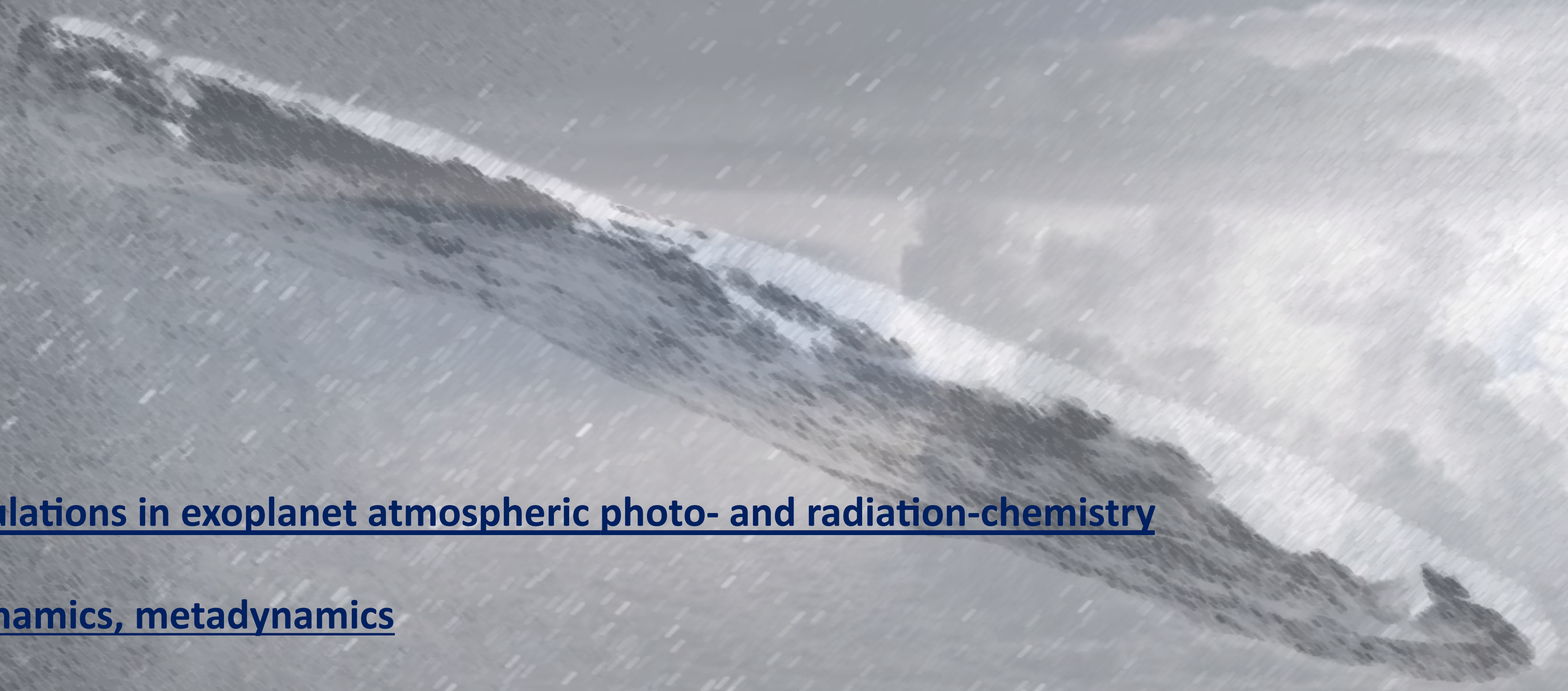
these critical gaps are regrettable as models can provide consistent, temporally and spatially resolved information about atmospheric particle properties, and related effects in an entirety which, at the current stage, is not accessible by observations

planned missions: from «taxonomy» to «understanding»

<u>status</u>: coaction of different (frequently distant) fields to provide a global description of phenomena naturally occurring on extremely different size scales;

<u>approach:</u> bridging both classical and quantum optics calculations + laboratory simulations; testing in radiative transfer calculations

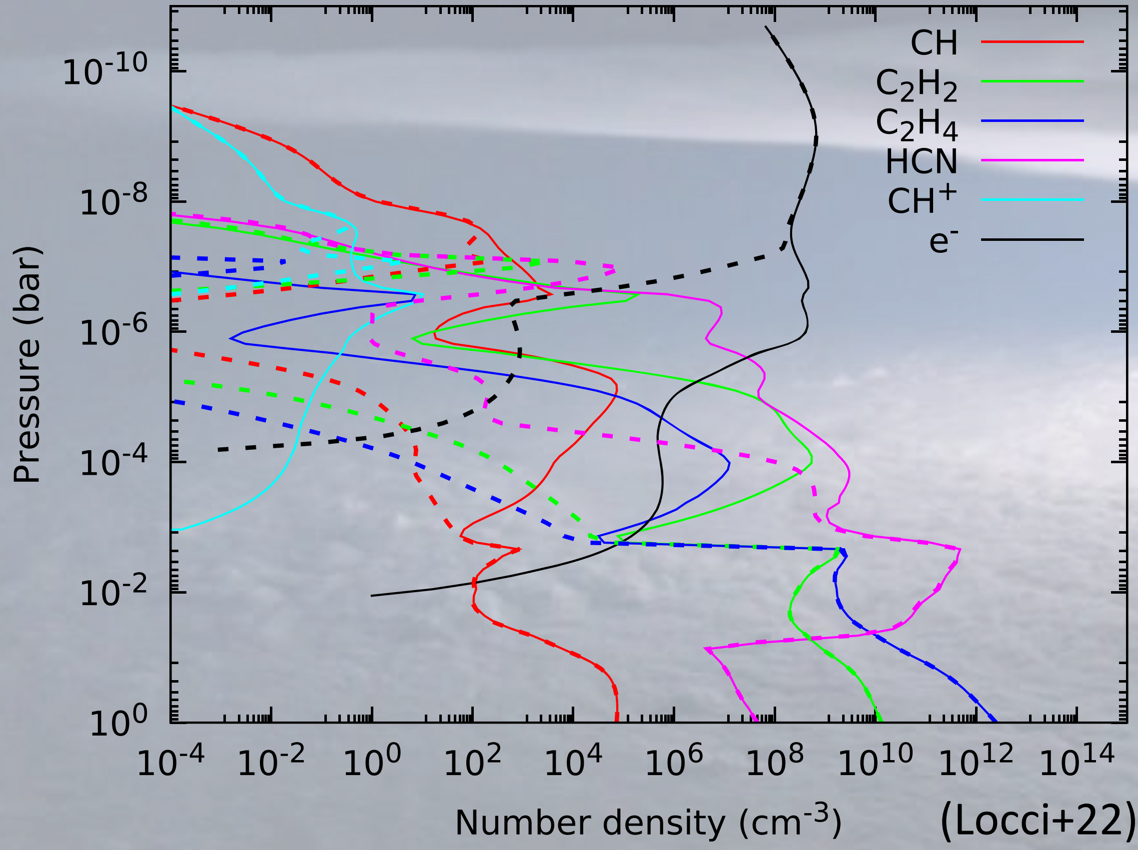
The need for laboratory measurements and numerical modelling



- *ab-initio* calculations in exoplanet atmospheric photo- and radiation-chemistry
- molecular dynamics, metadynamics
- laboratory haze and dust simulation experiments in alien atmospheres
- optical modelling of morphologically complex particles

Ab-initio calculations

CH_4 photochemistry generates hydrocarbons such as C_2H_2, C_2H_4, C_2H_6 that polymerize into more complex hydrocarbon species, some of which form aerosols; nitroaromatic in presence of NO_x;



(Locci+22)

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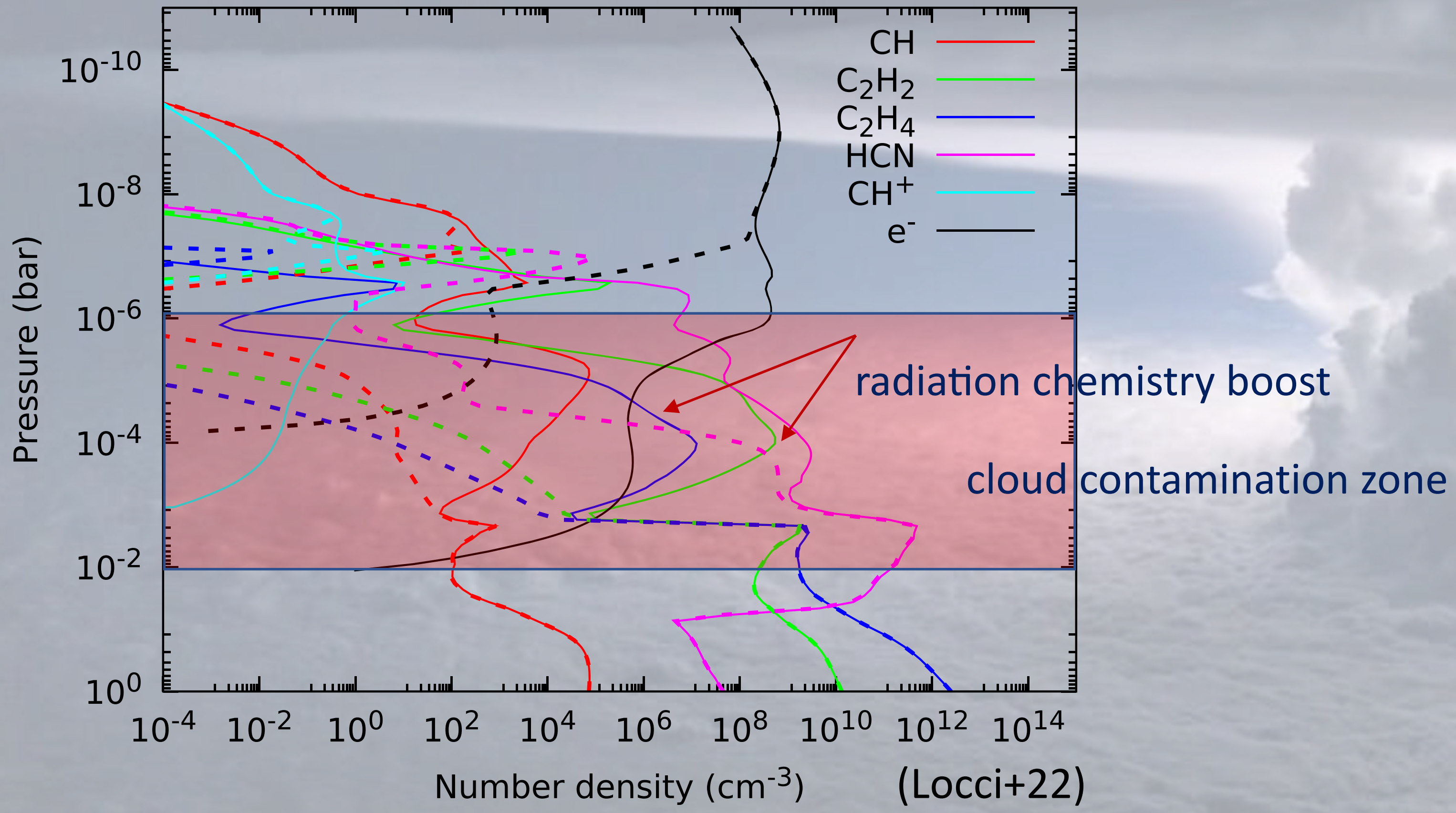

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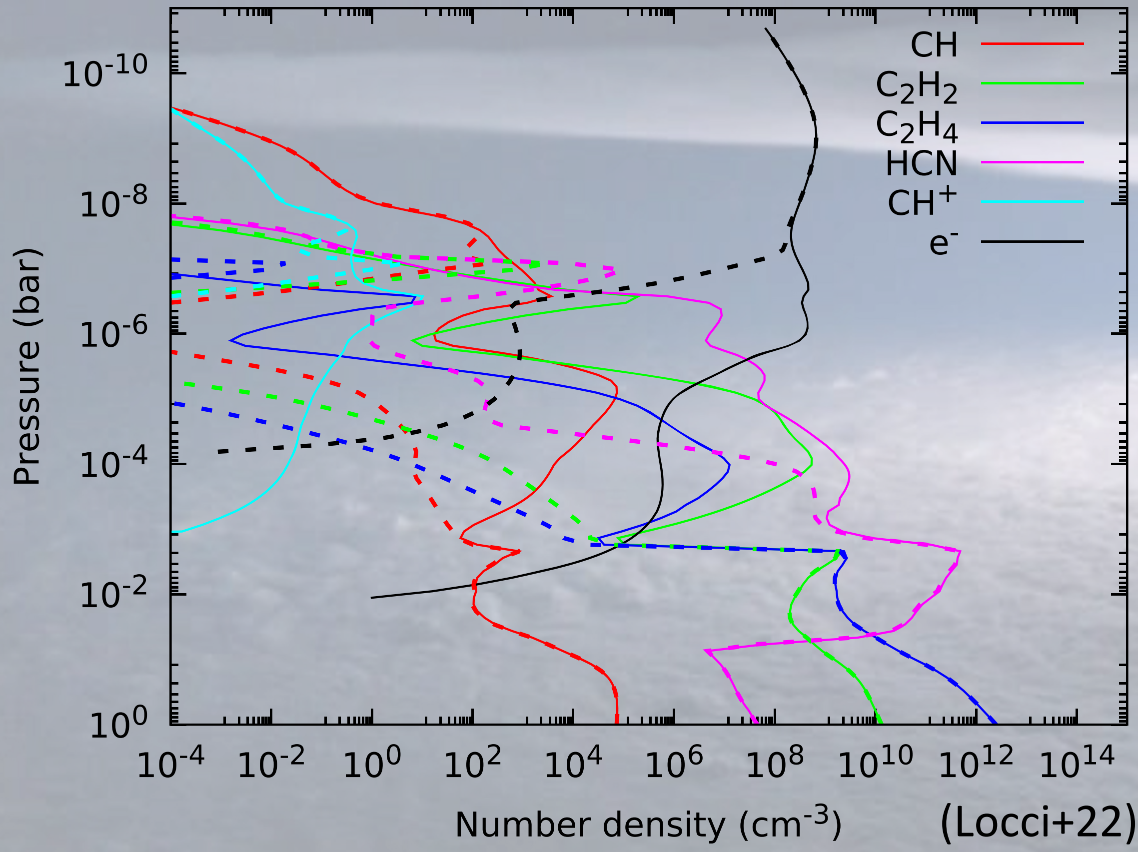
Ab-initio calculations

CH_4 photochemistry generates hydrocarbons such as C_2H_2, C_2H_4, C_2H_6 that polymerize into more complex hydrocarbon species, some of which form aerosols; nitroaromatic in presence of NO_x; aromatics good UV absorbers;



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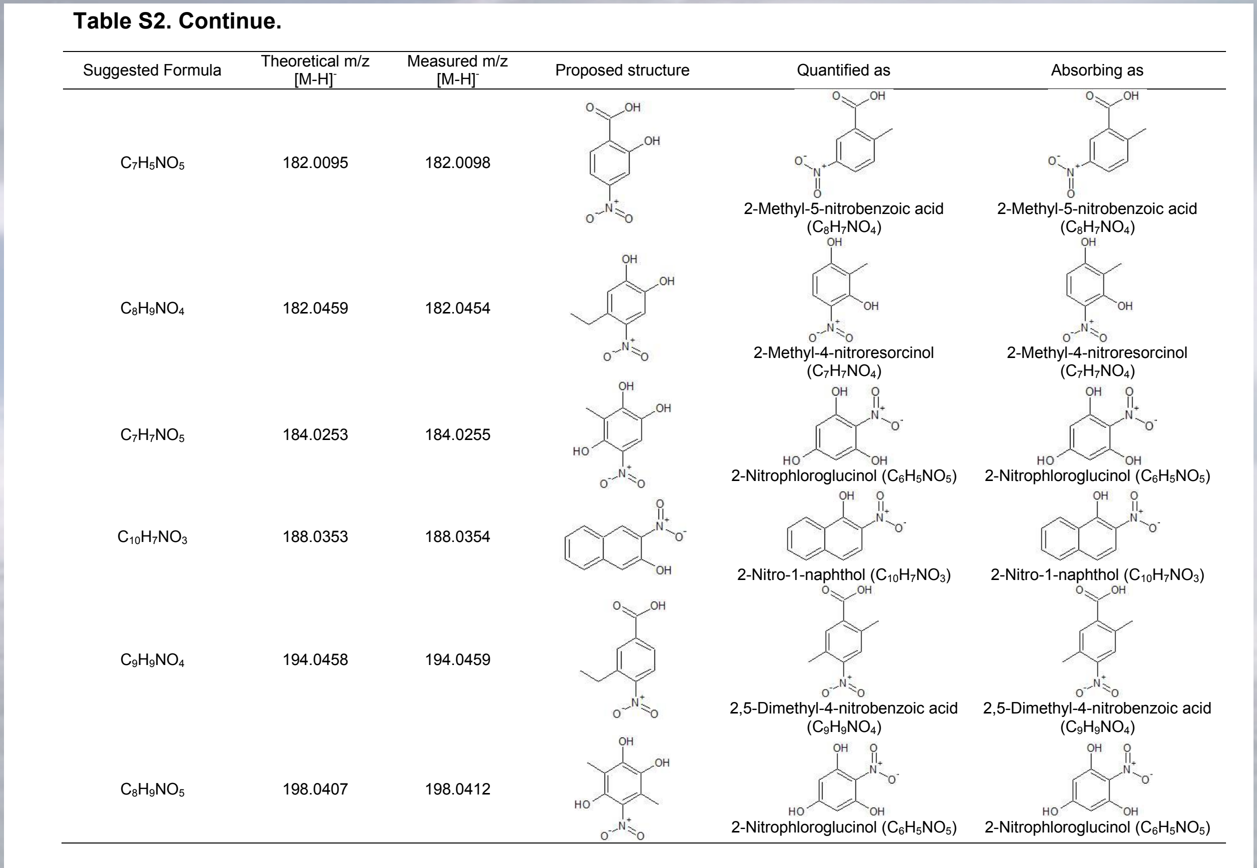
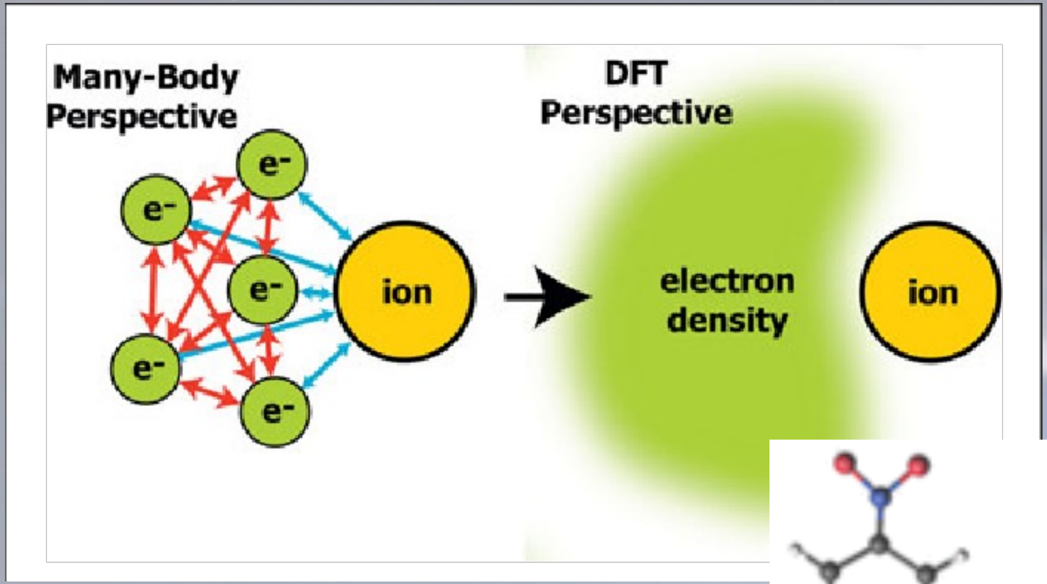


Table S2. Continue.

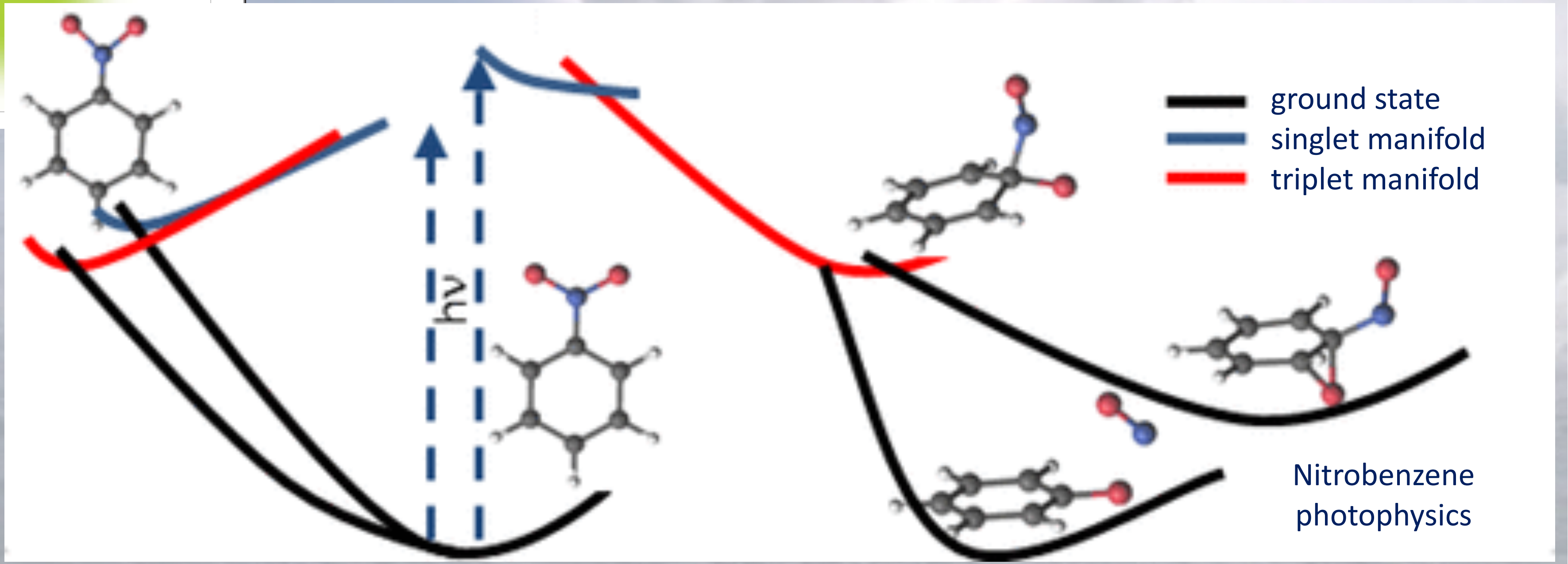
Suggested Formula	Theoretical m/z $[M-H]^-$	Measured m/z $[M-H]^-$	Proposed structure	Quantified as	Absorbing as
$C_7H_5NO_5$	182.0095	182.0098		2-Methyl-5-nitrobenzoic acid ($C_8H_7NO_4$)	2-Methyl-5-nitrobenzoic acid ($C_8H_7NO_4$)
$C_8H_9NO_4$	182.0459	182.0454		2-Methyl-4-nitroresorcinol ($C_7H_7NO_4$)	2-Methyl-4-nitroresorcinol ($C_7H_7NO_4$)
$C_7H_7NO_5$	184.0253	184.0255		2-Nitrophloroglucinol ($C_6H_5NO_5$)	2-Nitrophloroglucinol ($C_6H_5NO_5$)
$C_{10}H_7NO_3$	188.0353	188.0354		2-Nitro-1-naphthol ($C_{10}H_7NO_3$)	2-Nitro-1-naphthol ($C_{10}H_7NO_3$)
$C_9H_9NO_4$	194.0458	194.0459		2,5-Dimethyl-4-nitrobenzoic acid ($C_9H_9NO_4$)	2,5-Dimethyl-4-nitrobenzoic acid ($C_9H_9NO_4$)
$C_8H_9NO_5$	198.0407	198.0412		2-Nitrophloroglucinol ($C_6H_5NO_5$)	2-Nitrophloroglucinol ($C_6H_5NO_5$)

(Xie+17)

Ab-initio calculations



density functional theory (time-dependent) to study the complex polarizability
↓
optical properties



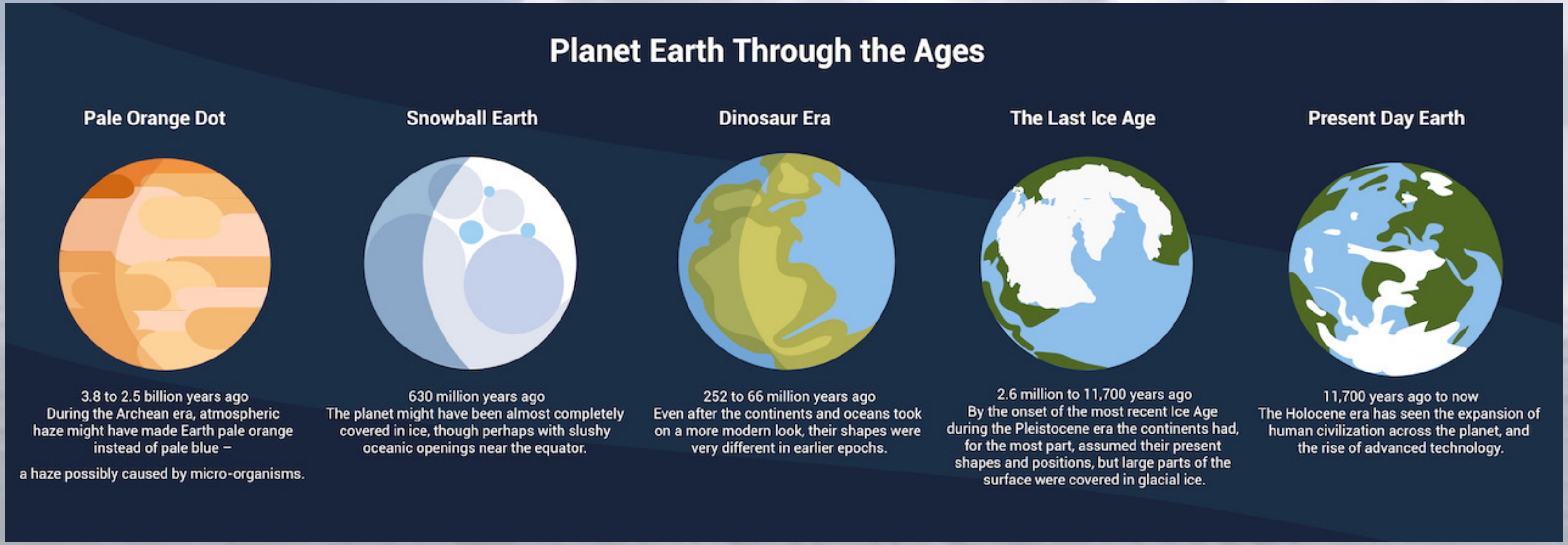
Ab-initio calculations

a noteworthy example: the pale orange dot

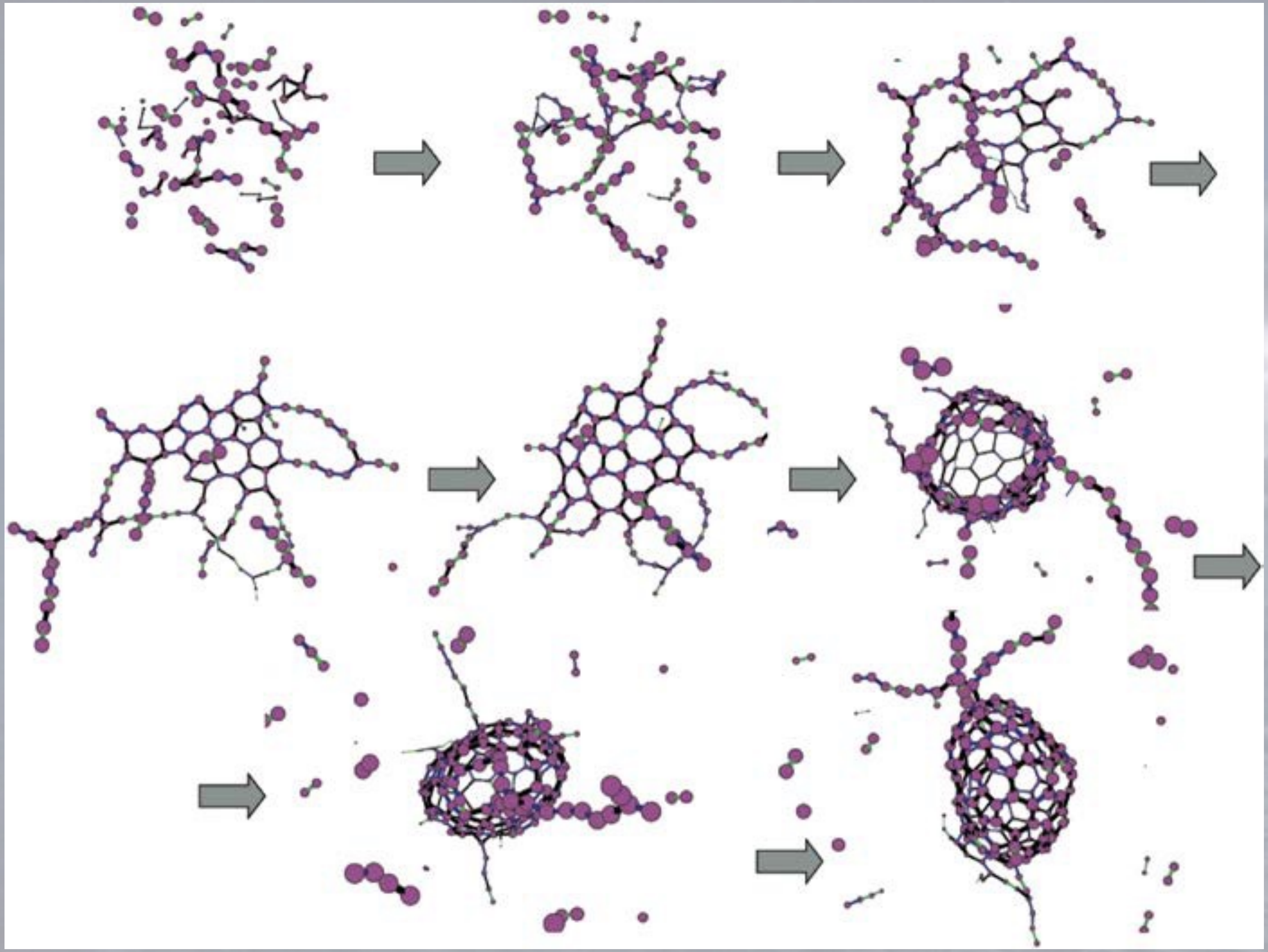
the vastly different conditions that have existed on planets' long habitable histories have been largely ignored

an anoxic environment could have supported the formation of biologically mediated —via methane photolysis— organic hazes

habitability conditions of the Archean Earth: organic hazes would have absorbed ultraviolet light so well as to effectively shield the Archean Earth (about 2 ½ billion years back) from deadly radiation before the rise of oxygen and the ozone layer, which now provides that protection; the haze was a benefit to just-evolving surface biospheres on Earth, as it could be to similar exoplanets (Hamey+16)



Molecular dynamics, metadynamics



the formation of fullerene molecules from ensembles of randomly positioned C_2 molecules in a periodic boundary box

3 steps:

1. nucleation of polycyclic structures,
2. growth by ring condensation of attached carbon chains,
3. cage closure

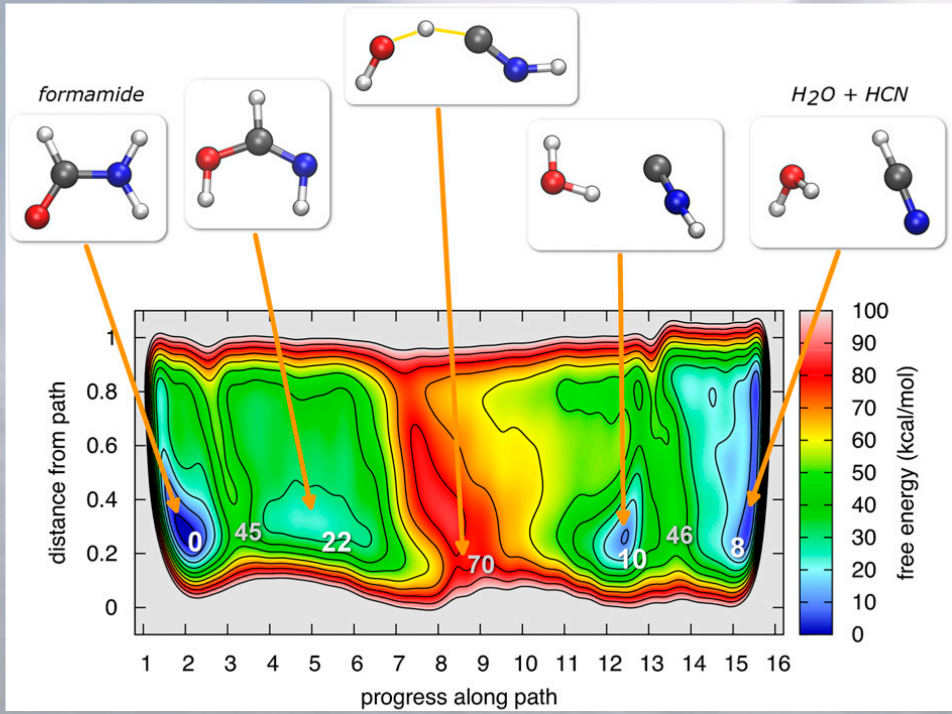
Molecular dynamics, **metadynamics**

potential energy surface (PES),: an energetic "landscape" in which different directions represents the geometrical parameters of molecules in the process of transforming themselves into products

Metadynamics

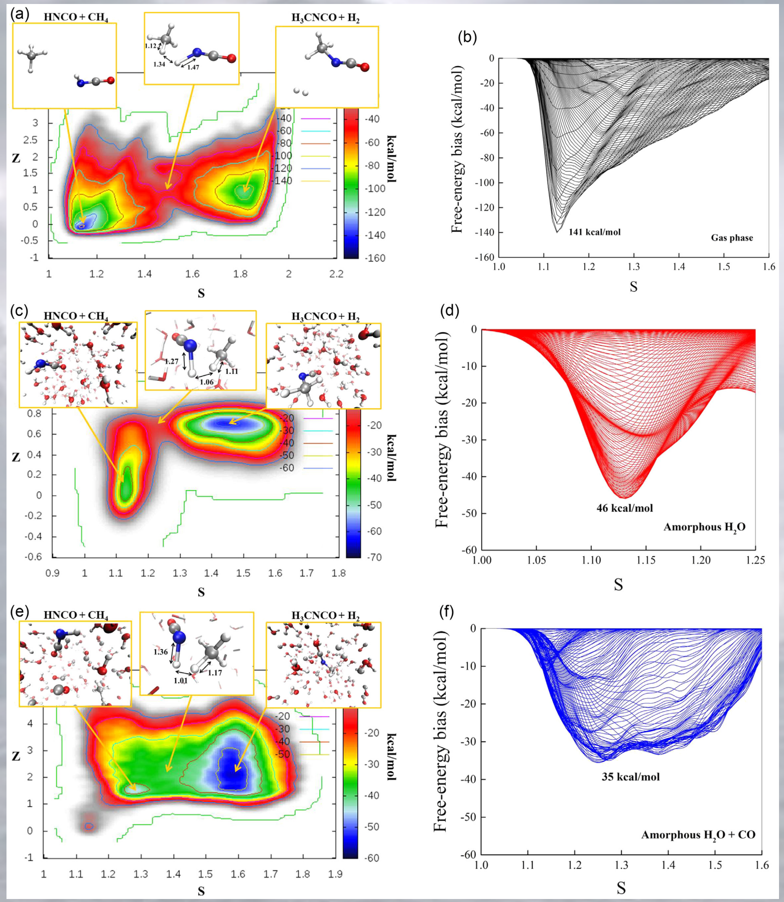
- iterative exploration of PES by applying a perturbation;
- overcome the serious problem of remaining stuck in only one probability maximum;
- drawback: very high computational costs.

Miller experiment in silico



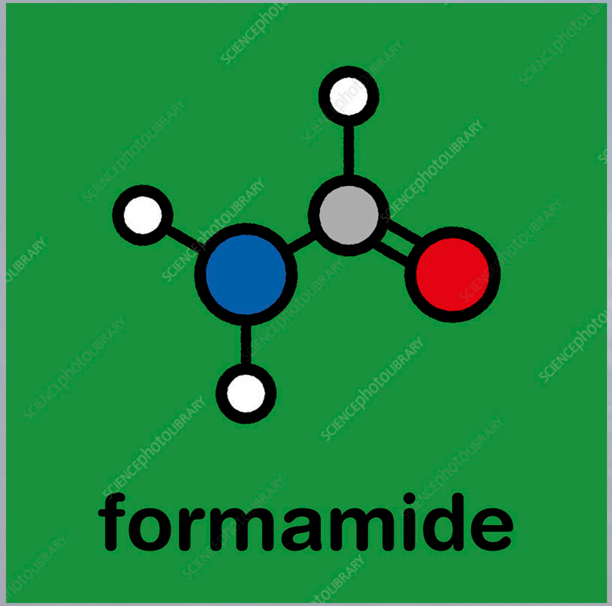
Saitta & Saija 2015

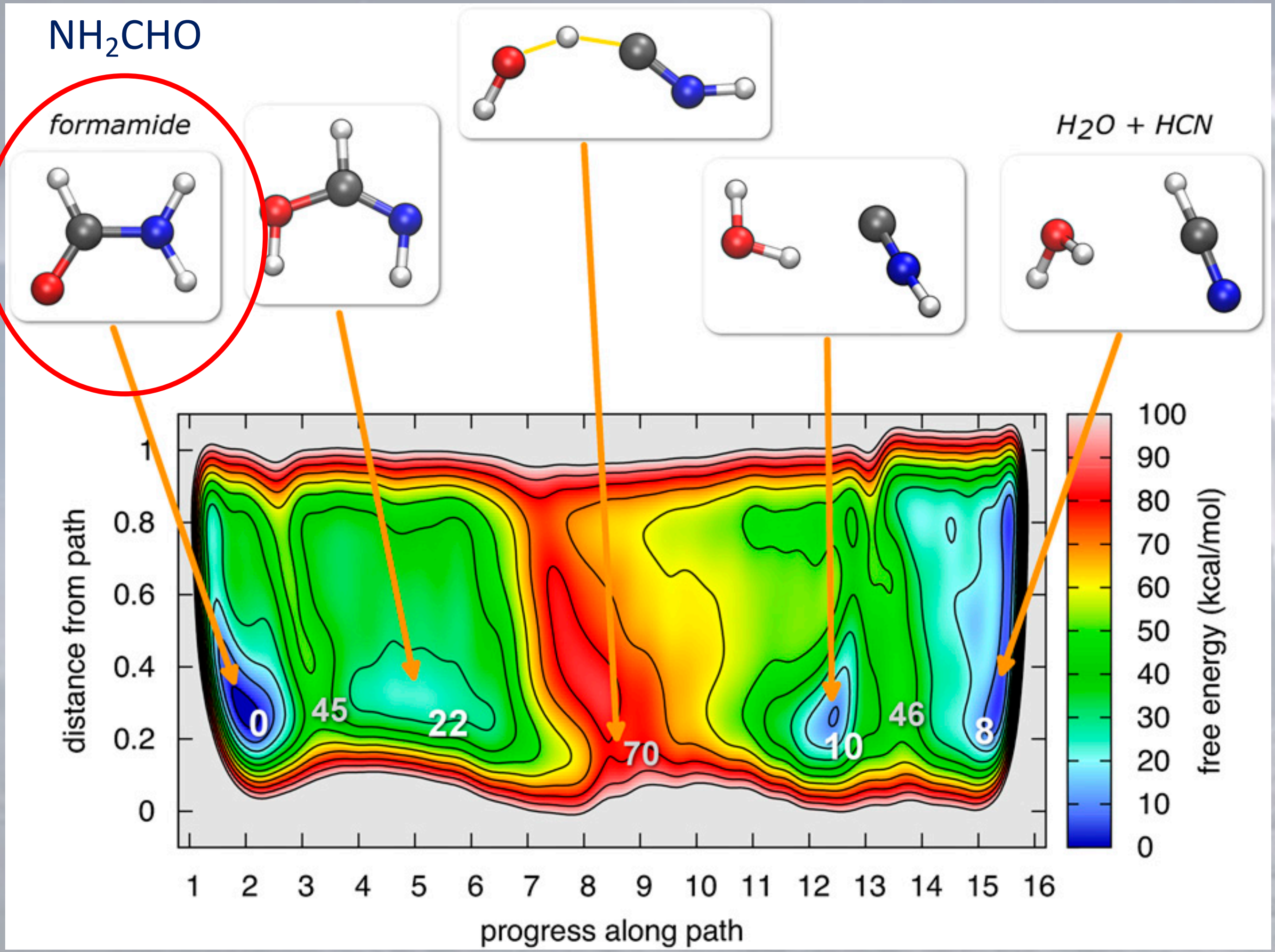
formation of methyl isocyanate



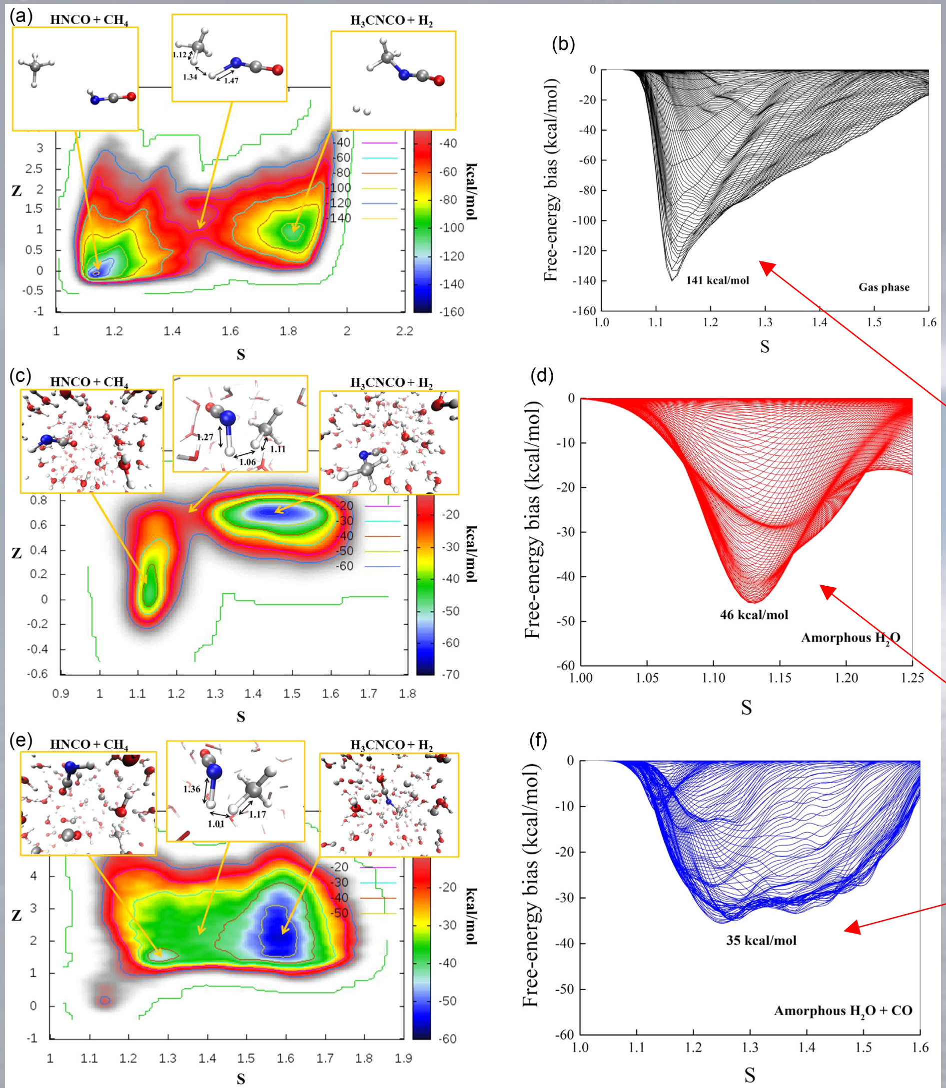
Cassone+2021

Molecular dynamics, **metadynamics**



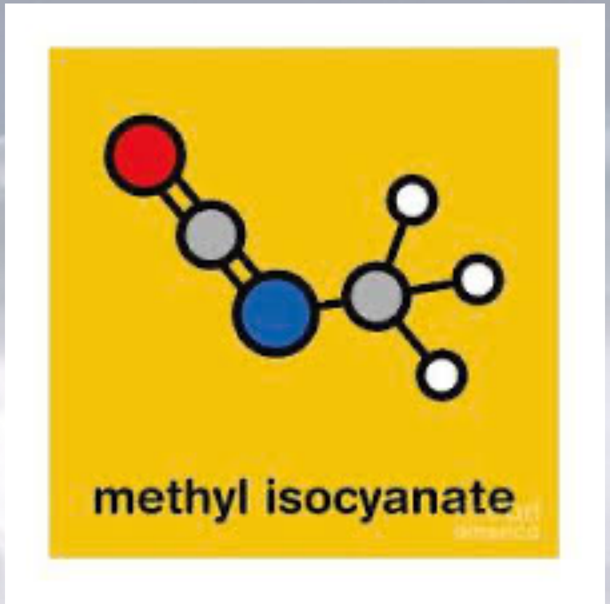


Molecular dynamics, **metadynamics**



$CH_4 + HNCO \rightarrow CH_3NCO$

a broken road



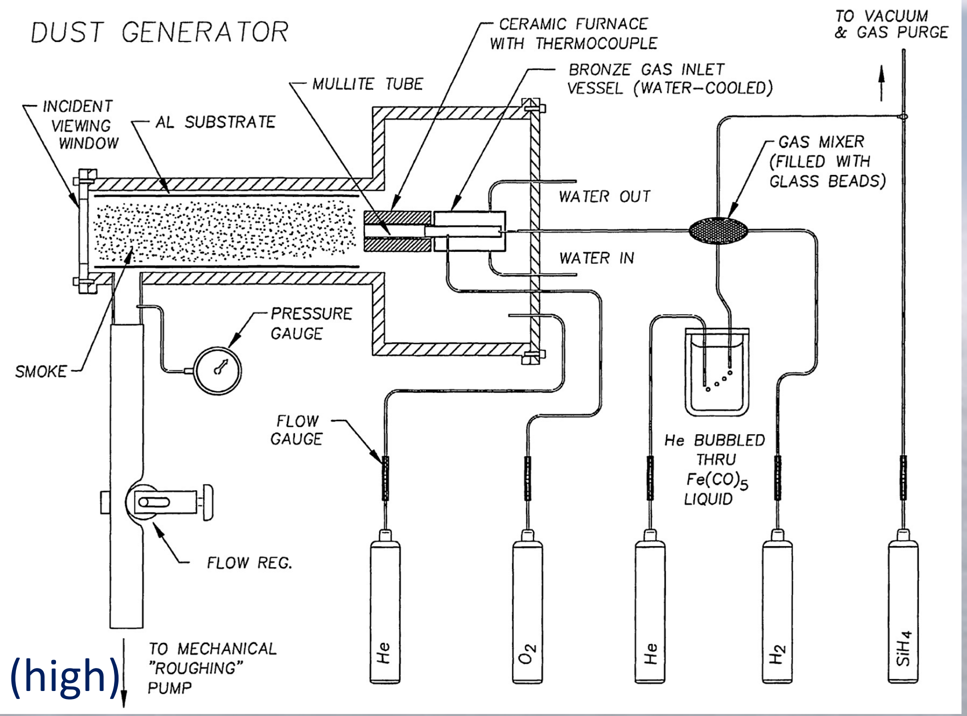
gas-phase: superbarrier!

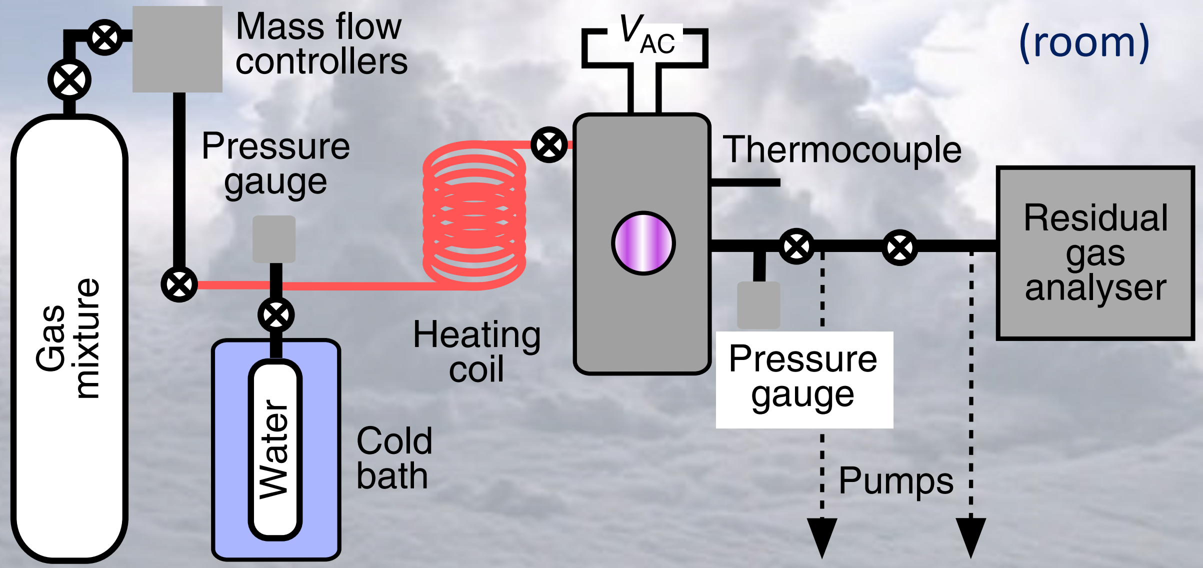
condensate: on the nature of the ice
(ices smooth barriers)

Laboratory simulations of haze and dust

- high (condensate), room (spark+radiation), cryogenic (particles) temperatures

- high: AGB stars, exotic planets (55 Cancri?);
- room (< 800 K): particles in cooler (< 800 K), smaller (< 0.3 × Jupiter's mass) exoplanets (especially with enhanced atmospheric metallicity and/or enhanced C/O ratios; super-Earths and mini-Neptunes;
- cryogenic: moons around giants (weather), super cold and thin atmospheres (Triton and Pluto).





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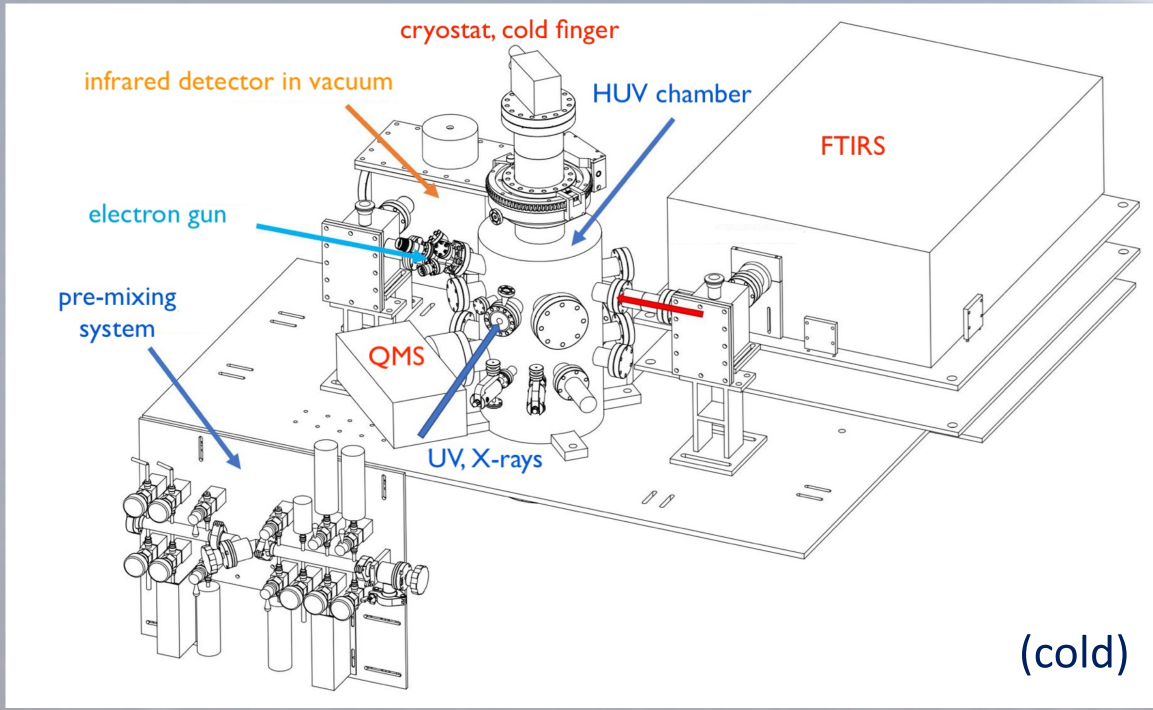
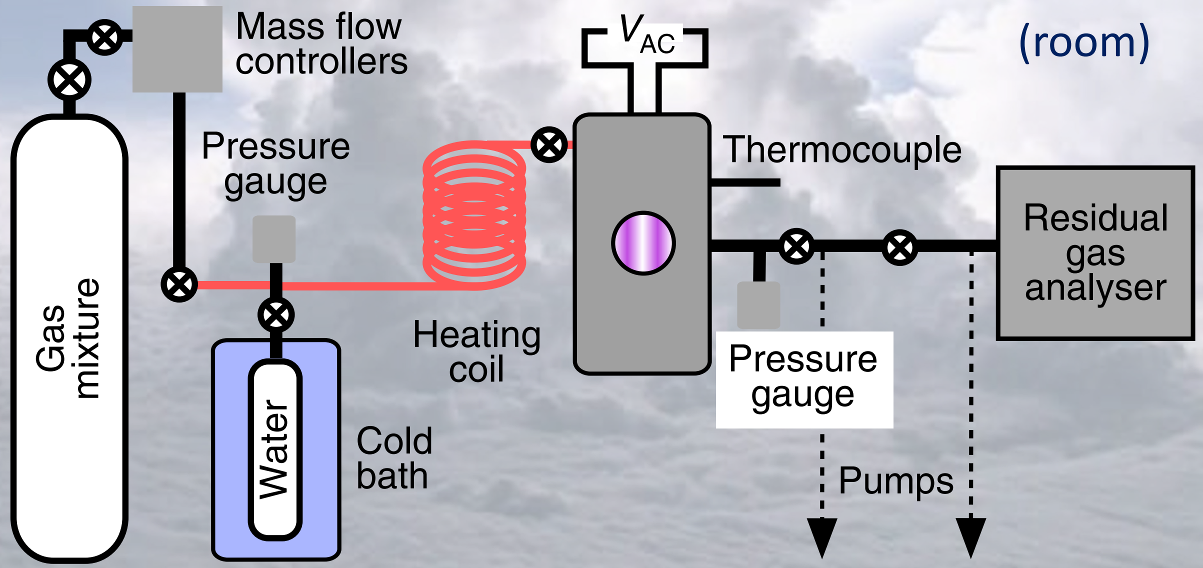
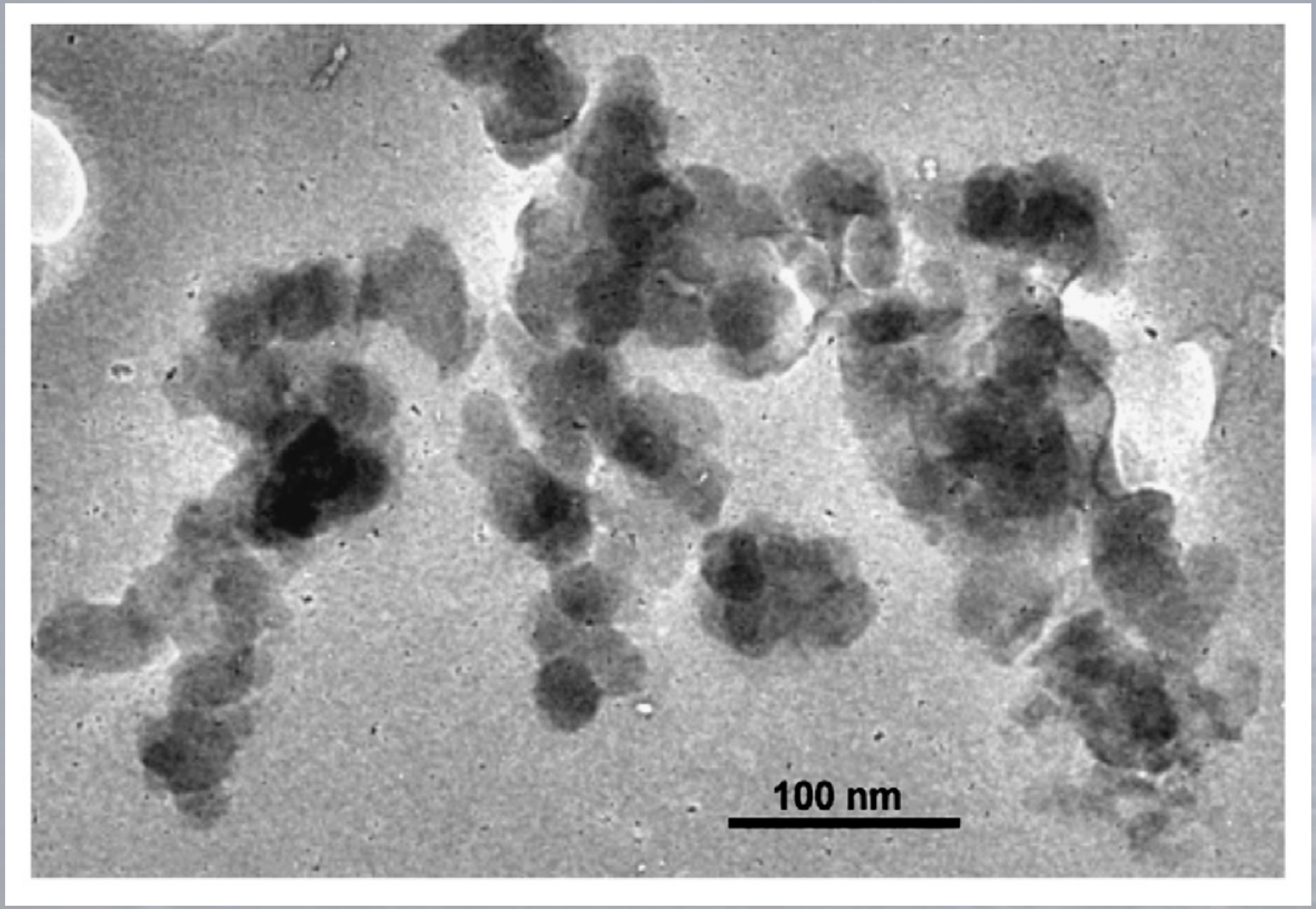
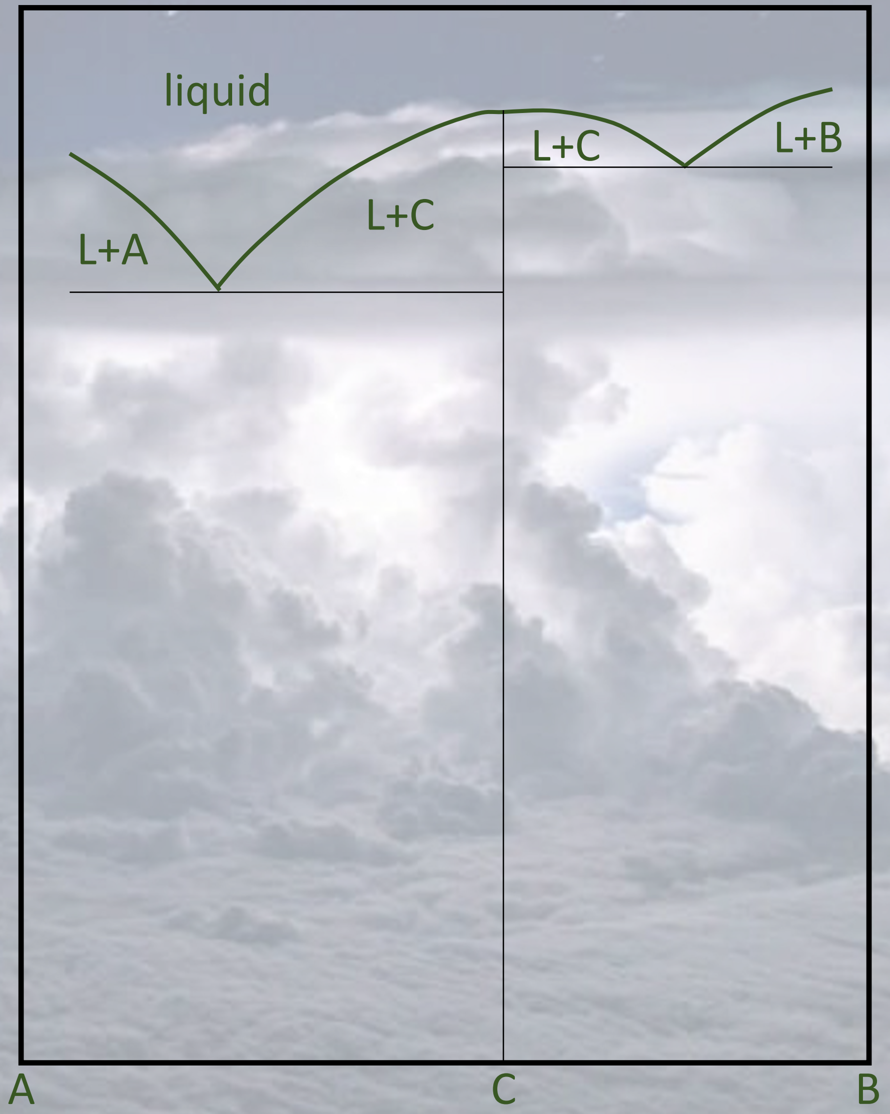




Laboratory simulations of haze and dust

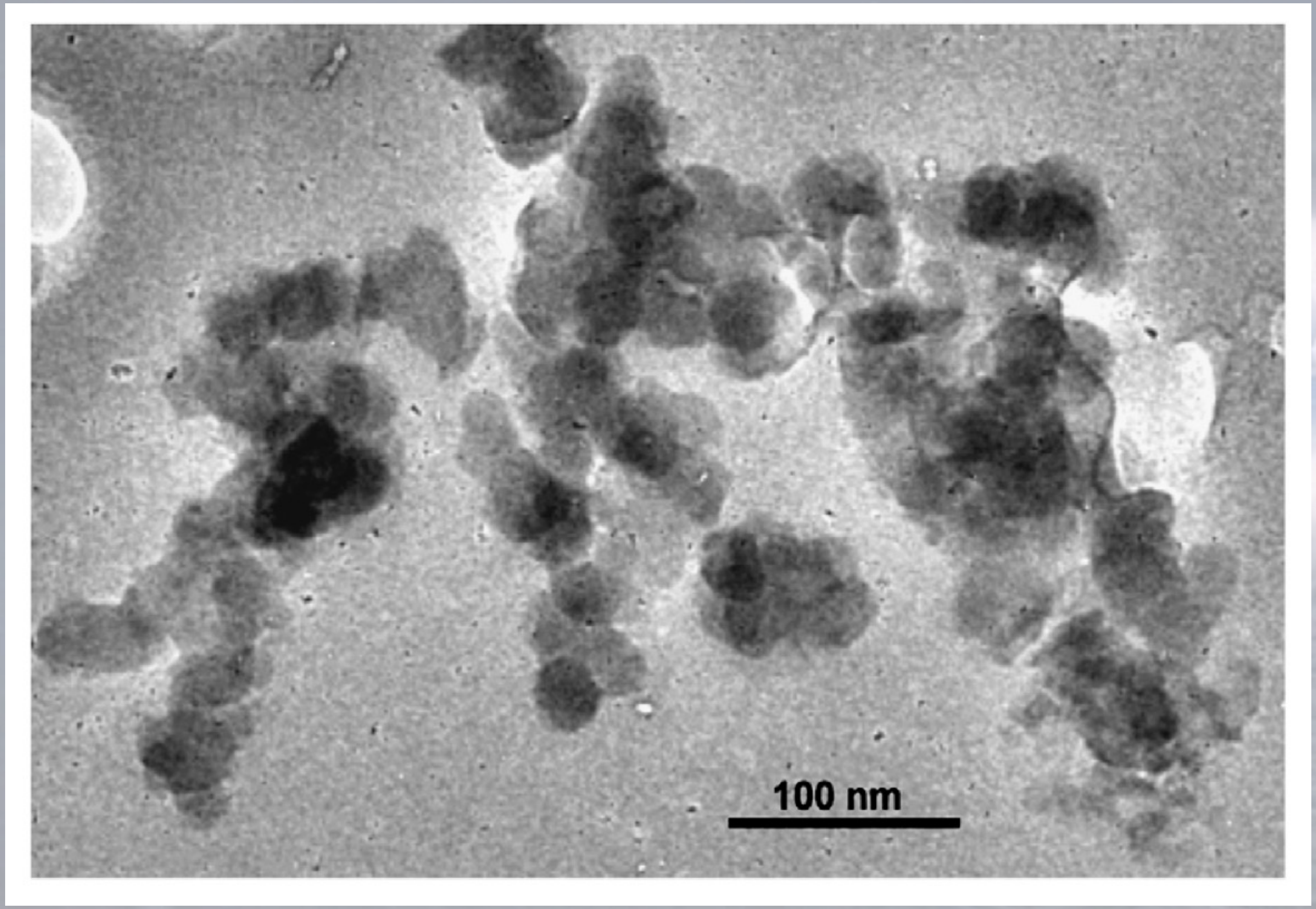
- high (furnace)

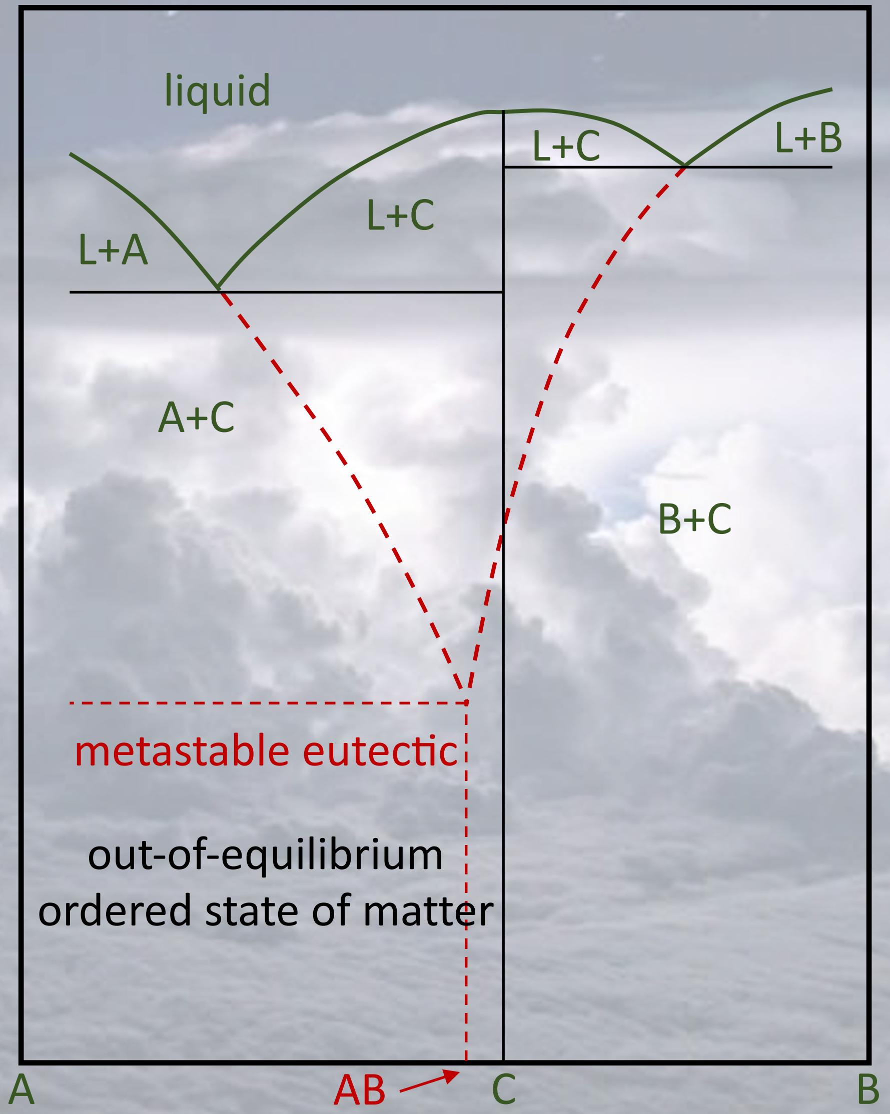




Laboratory simulations of haze and dust

- high (furnace), fast cooling





Laboratory simulations of haze and dust

- high (condensate), cooling not so fast, much simpler equilibrium calculations

if a molecule of composition $A_iB_jC_k$... is formed from free atoms of A, B, C, ... then its partial pressure in chemical equilibrium is

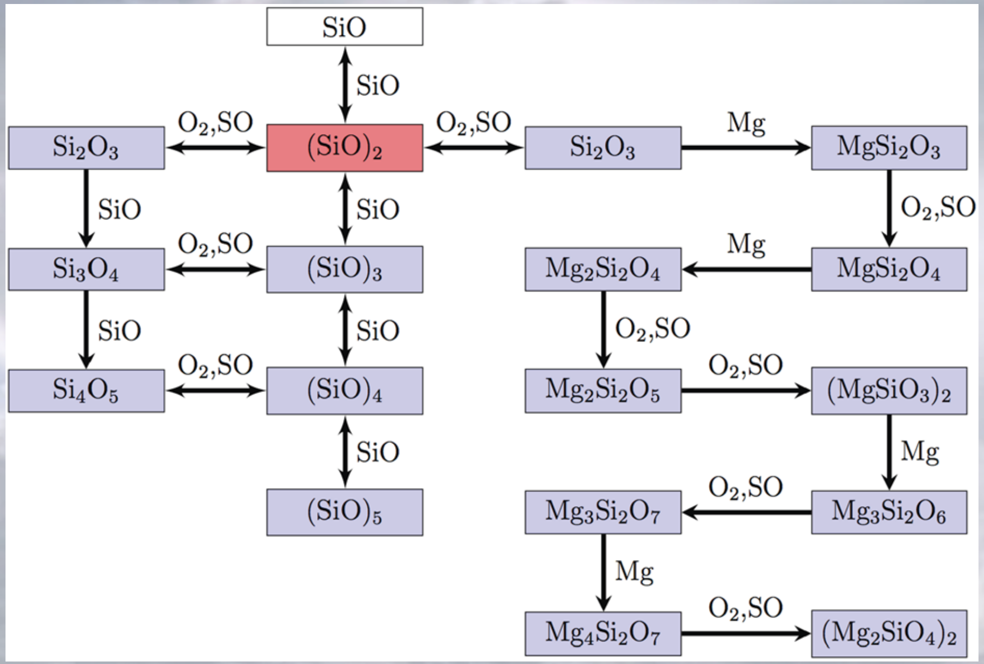
$$p(A_iB_jC_k\ldots) = p^i_A p^j_B p^k_C \ldots \exp(-\Delta G/RT)$$

If a solid with the same composition is formed from gas phase atoms, this solid is in equilibrium with the gas phase if

$$1 = a^c(A_iB_jC_k\ldots)_{..} = p^i_A p^j_B p^k_C \ldots \exp(-\Delta G/RT)$$

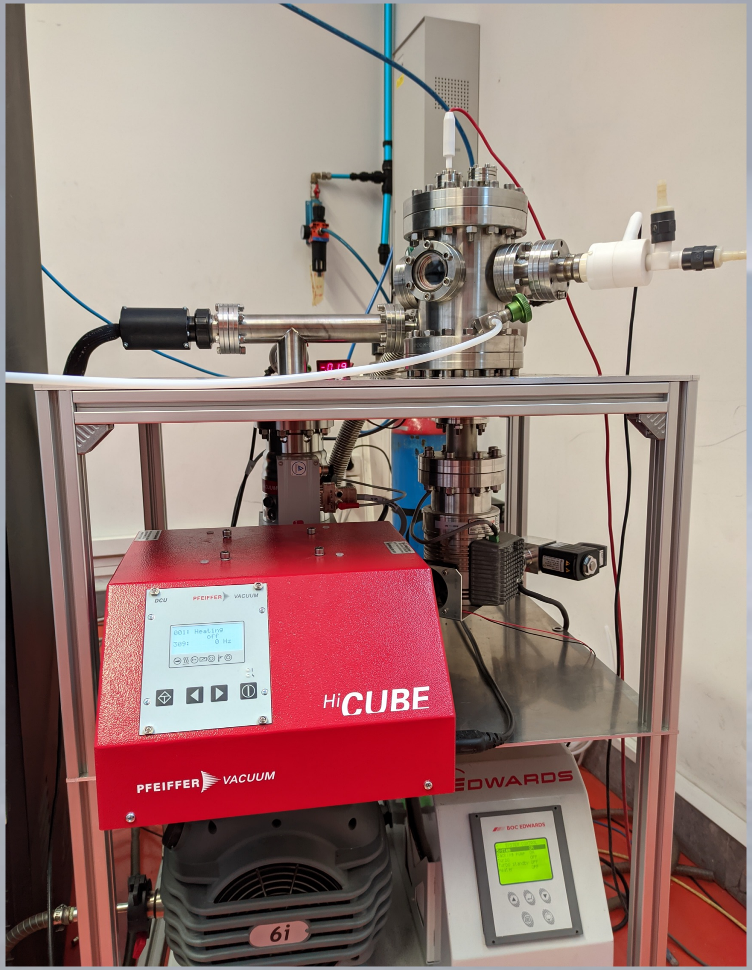
ΔG change in free enthalpy a^c are called pseudo activities, they define

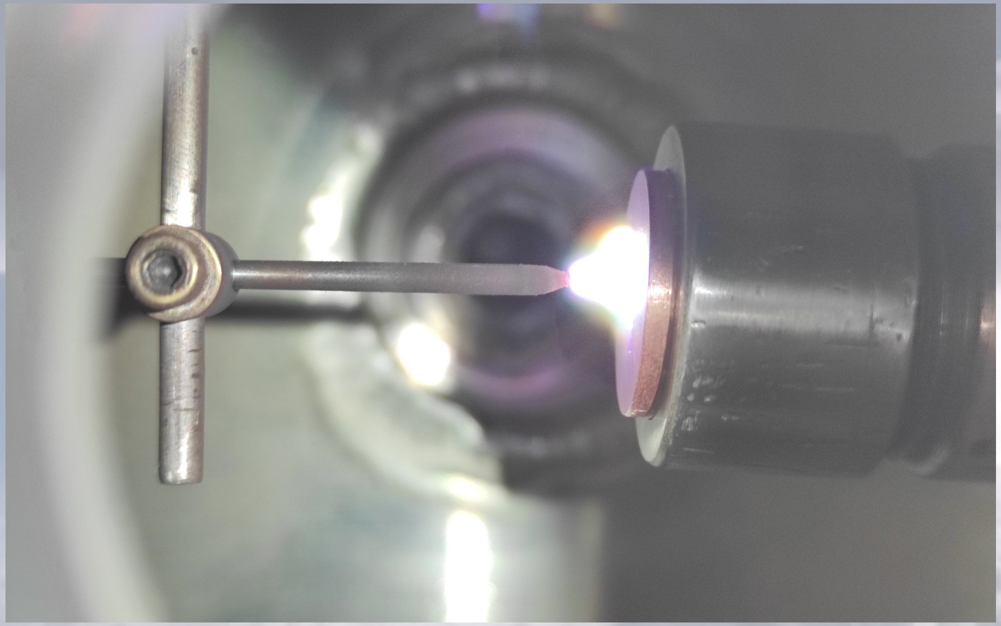
equilibrium (= 1), growth (> 1) or decline (< 1) in the nucleation cluster.



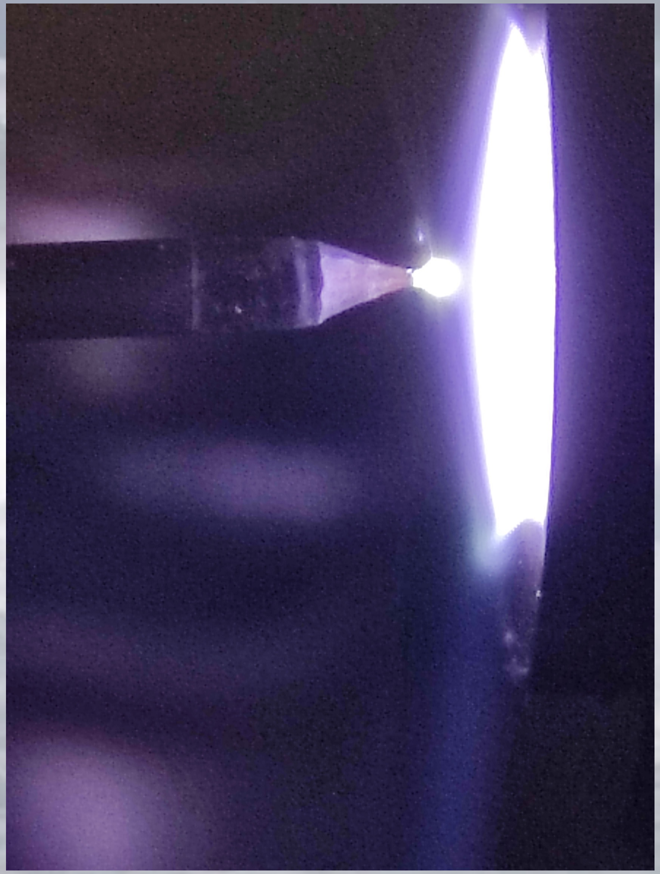
SPLASCH@OAPa (prototype)

- room (sparks & plasma)





spark

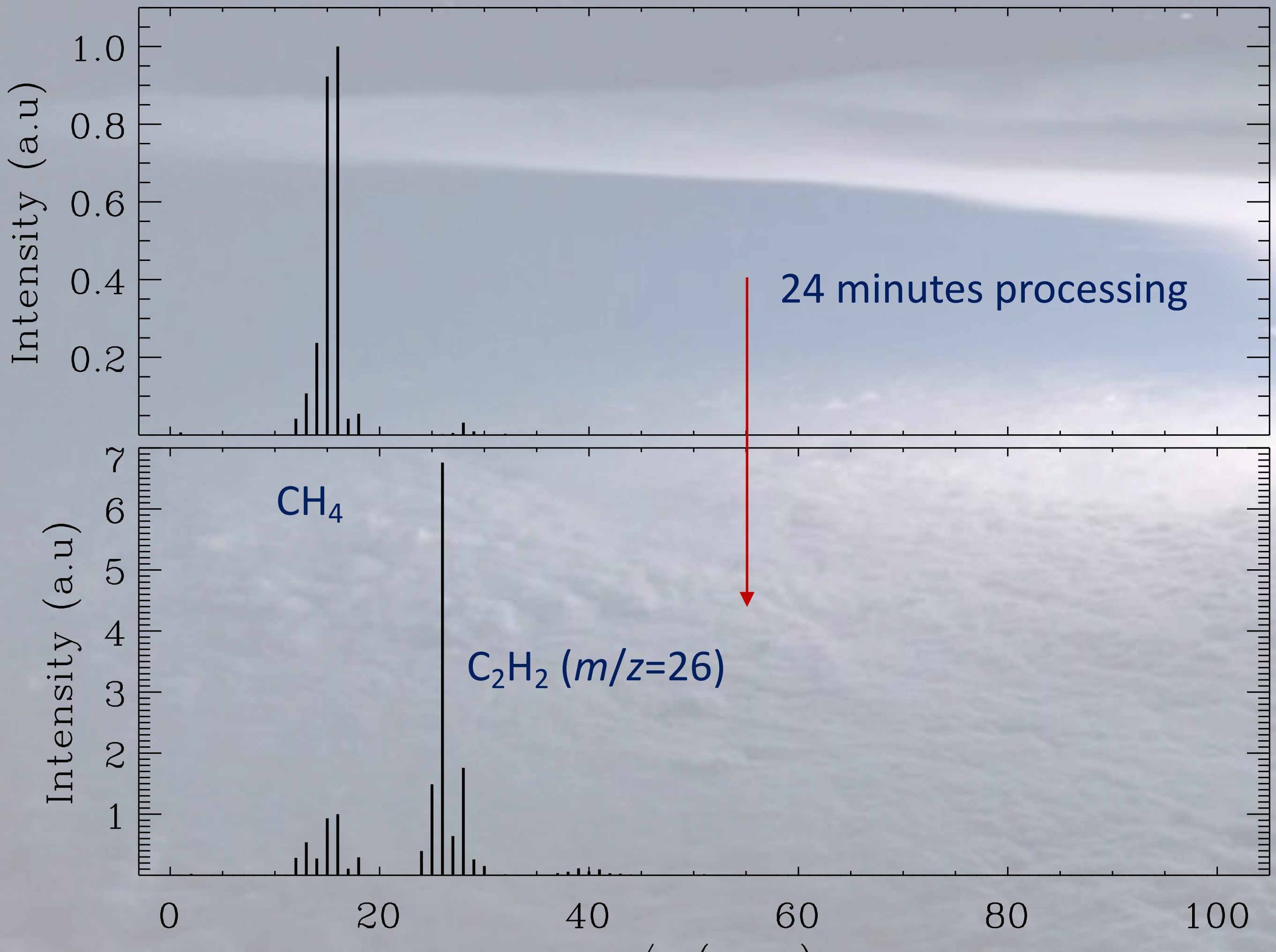


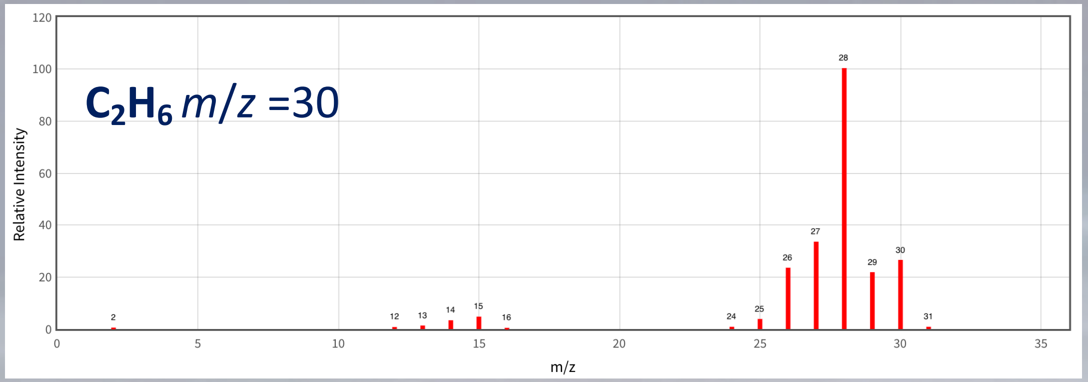
plasma

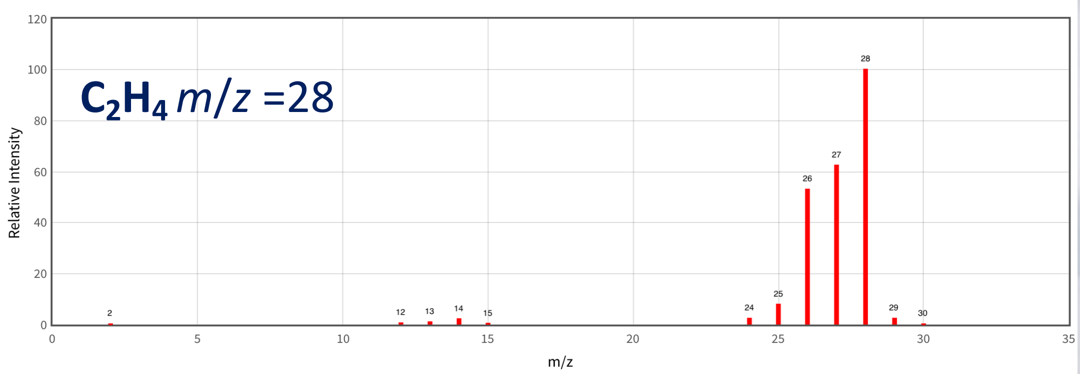
- 3kV generator
- MDHL UV lamp
- Electron-impact X-ray source
- QMS
- IR spectrometre
- UV spectrometre
- gas mixer

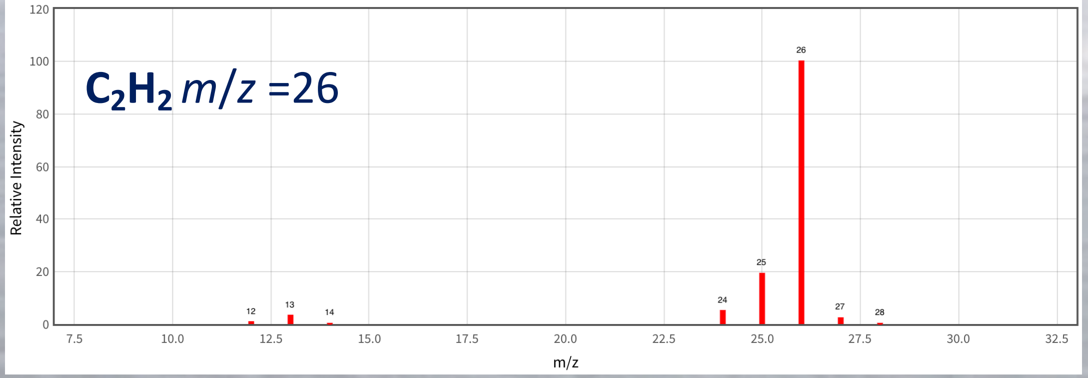
SPLASCH@OAPa (prototype)

- room (sparks & plasma), Mass spectroscopy



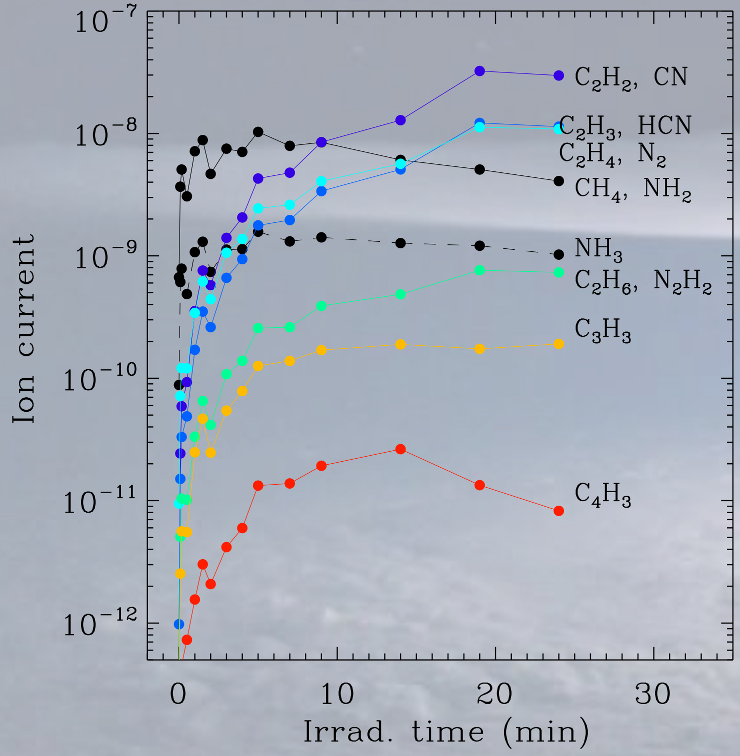




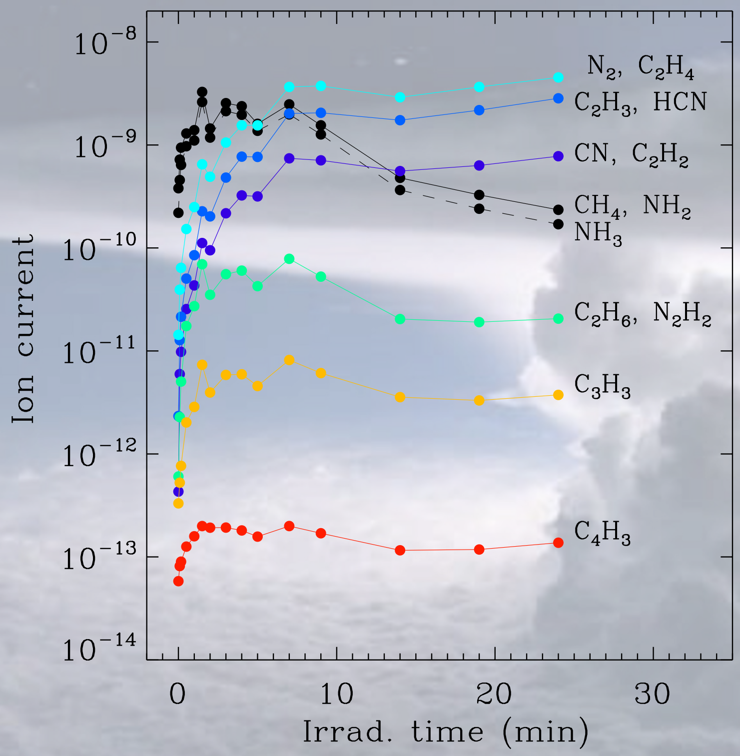


SPLASCH@OAPa (prototype)

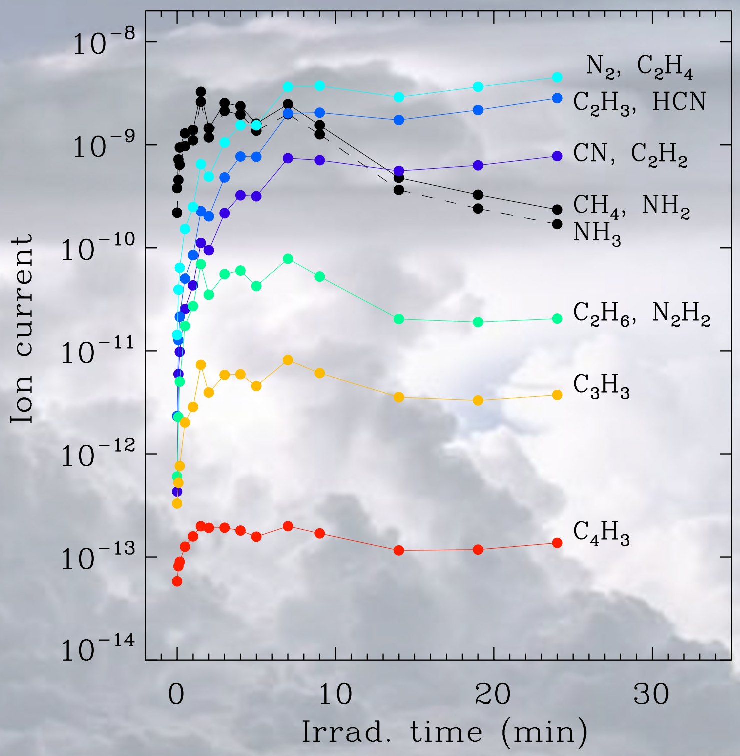
- room (sparks & plasma), gas chemical evolution



$CH_4 : NH_3$ (4:1)



$CH_4 : NH_3$ (2:1)

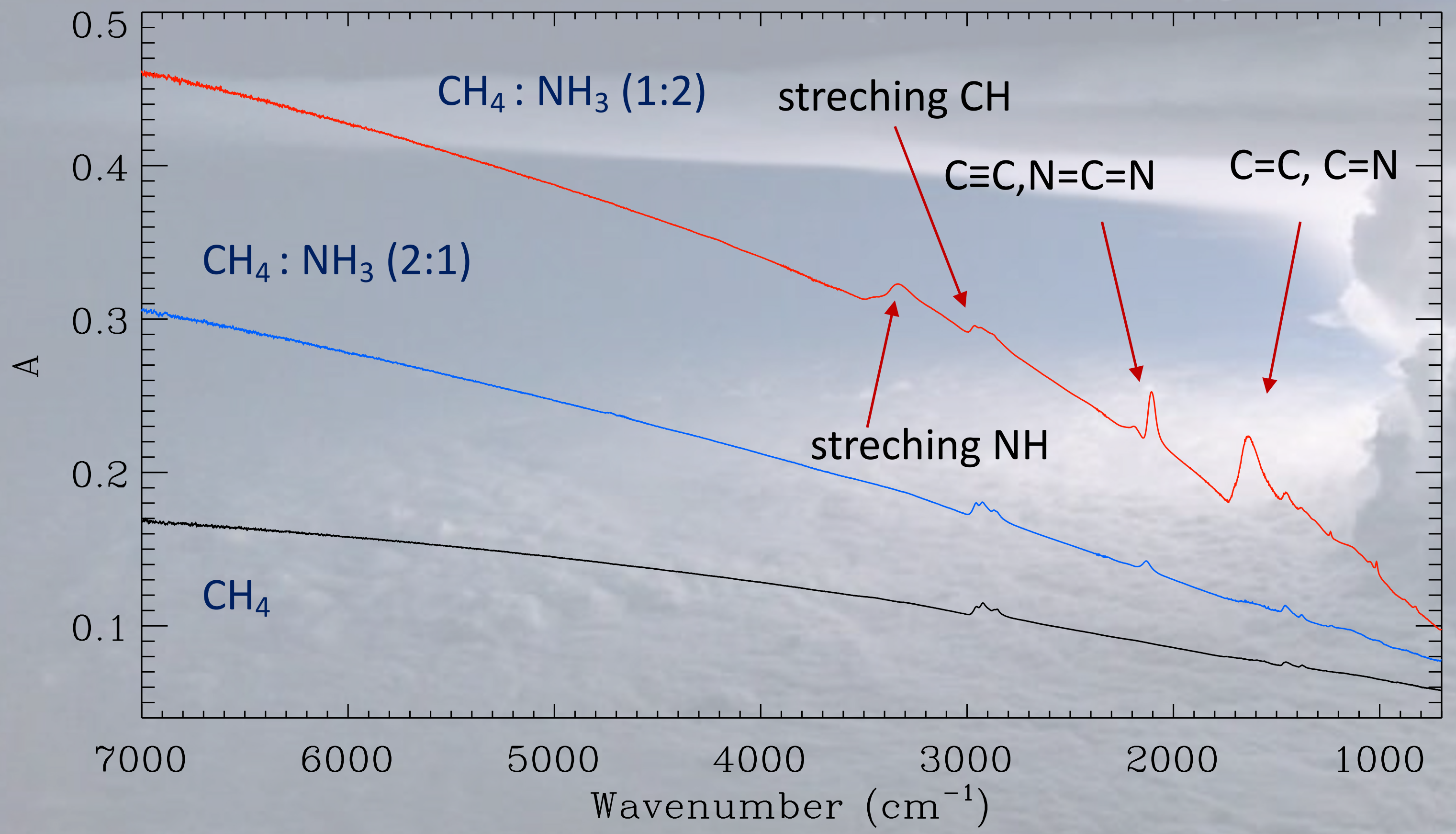


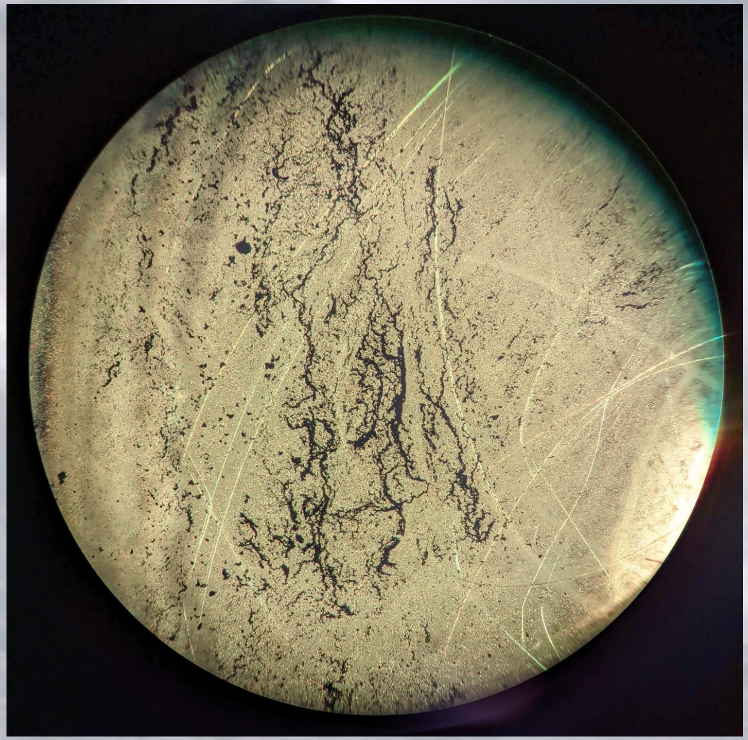
$CH_4 : NH_3$ (1:2)

CH_4 + spark → $CH_4 + CH_4$ → $C_2H_6 + H_2$ no!, CH_4 + spark → fragmentation + reformation → C_2H_4, C_2H_2,
perhaps diacetylene $CH_2 + CH_2 \rightarrow H-C\equiv C\setminus H \rightarrow H-C\equiv C-C\equiv C-H$, C_4H_2

SPLASCH@OAPa (prototype)

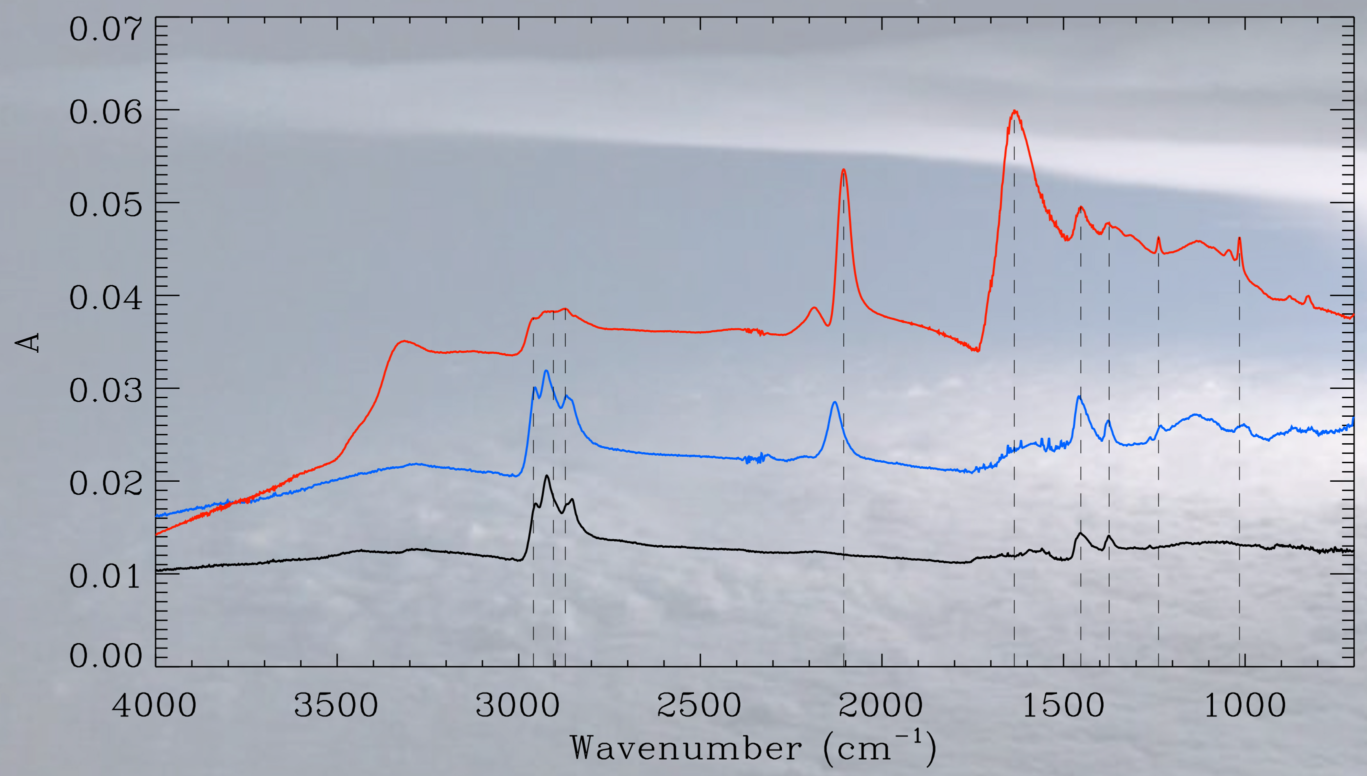
- room (sparks & plasma), IR spectroscopy post processing residue (= particles)





SPLASCH@OAPa (prototype)

- room (sparks & plasma), from amorphous carbon to organic chemistry



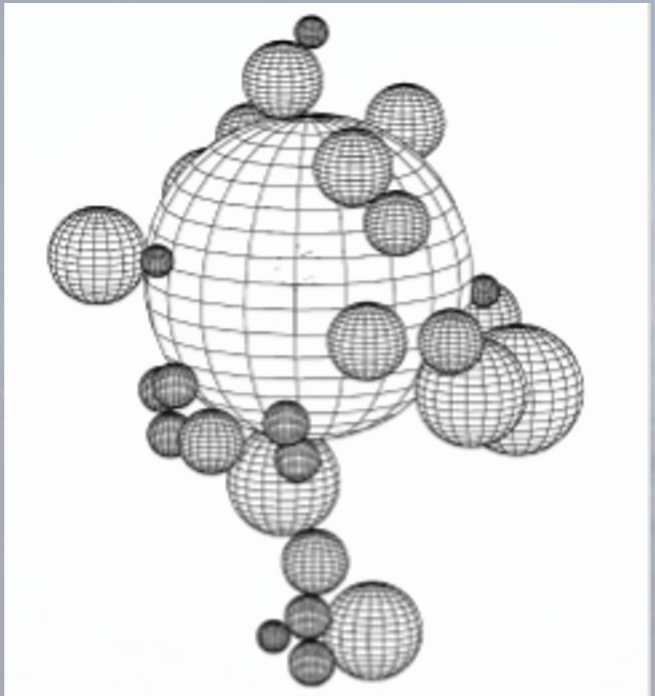
2260-2222	weak	C≡N stretching	nitrile	
2260-2190	weak	C≡C stretching	alkyne	disubstituted
2140-2100	weak	C≡C stretching	alkyne	monosubstituted
1650-1600	medium	C=C stretching	conjugated alkene	
1650-1580	medium	N-H bending	amine	
1650-1566	medium	C=C stretching	cyclic alkene	
1648-1638	strong	C=C stretching	alkene	monosubstituted
1620-1610	strong	C=C stretching	α,β-unsaturated ketone	
1465	medium	C-H bending	alkane	methylene group
1450	medium	C-H bending	alkane	methyl group
1342-1266	strong	C-N stretching	aromatic amine	
2145-2120	strong	N=C=N stretching	carbodiimide	

Optics of complex classic particles

- unlike haze, cloud particulates do go through cycles of evaporation and condensation
- «inpure» morphology and composition

coagulation of liquid particles results in larger spheroidal droplets
solids collisions lead to their aggregation

aggregation can result in a significant enhancement of absorption relative to that computed for idealized spherically-shaped aerosols using the Lorenz–Mie theory



frequently used (brutal) approximation

step 1: effective medium theory, material interfaces and shapes are smeared out in a homogeneous mixture;

step 2: mass evaluation, and construction of the equivalent sphere;

step 3: optical properties computed using Lorenz–Mie theory.

Optics of complex classic particles

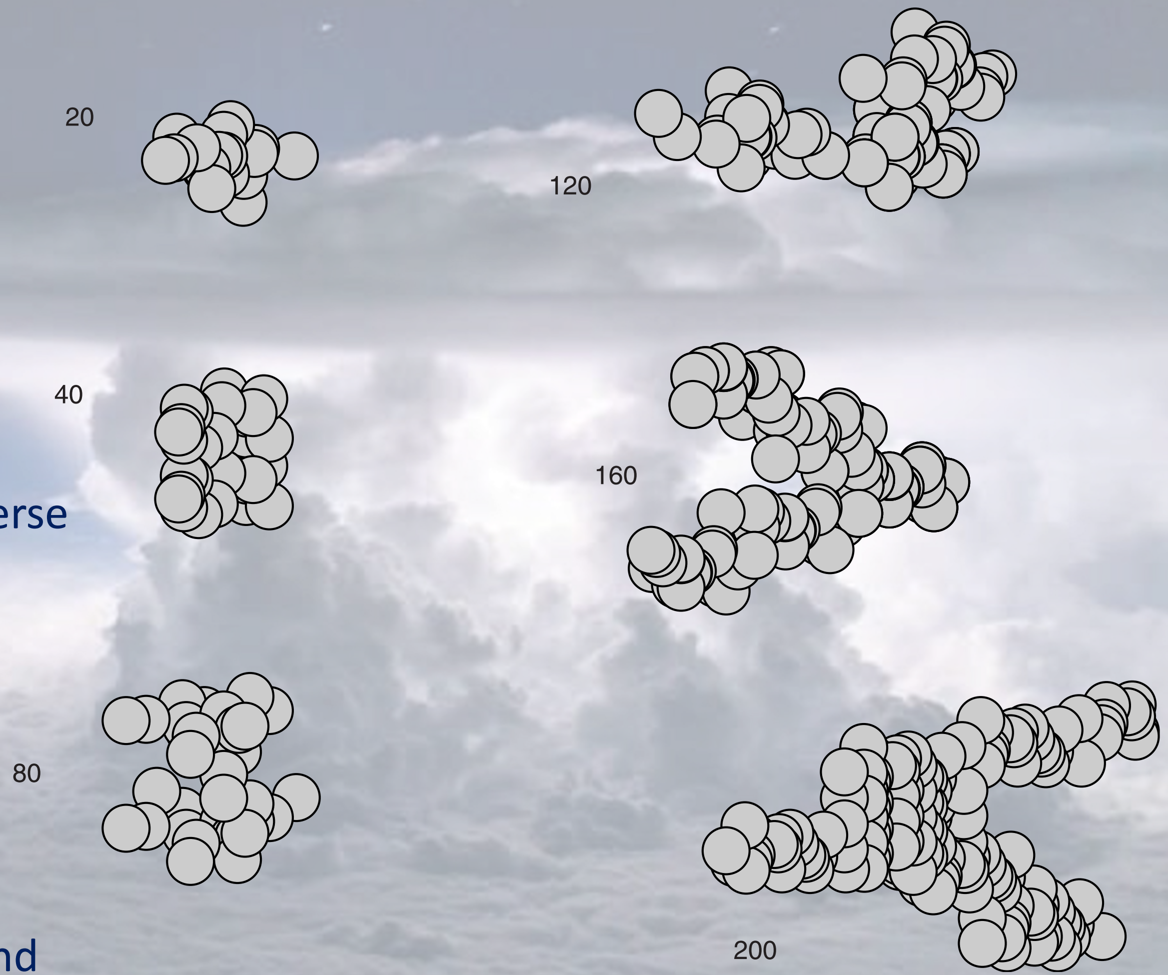
- T-matrix technique (TMT): direct solutions of the macroscopic Maxwell equations;

the field scattered by the whole aggregate is written as the superposition of the fields scattered by the single spheres.

$$E_S = T \times E_i$$

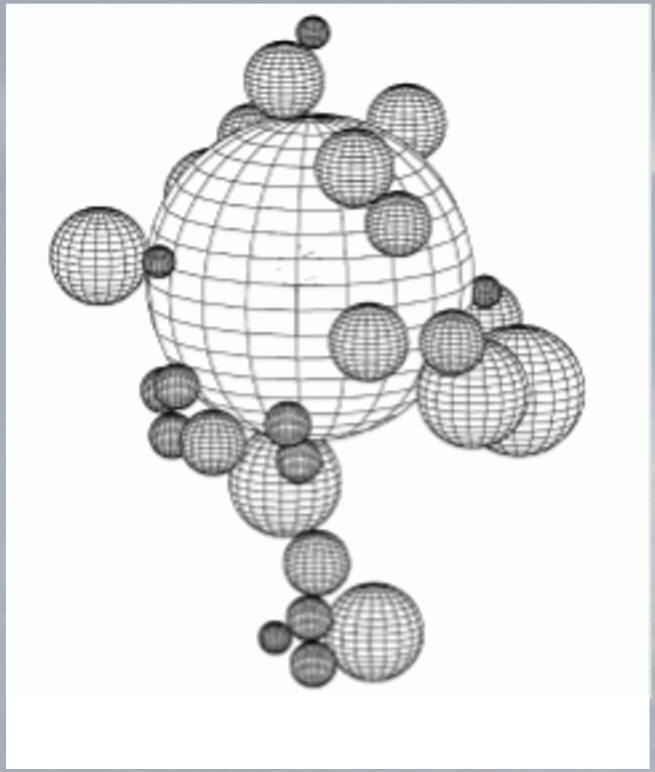
- optimal combination of accuracy, computational speed, and versatility;
- non-spherical particles modelled as a collection of polydisperse spheres (sub-units);
- sub-units may be all different, and they don't need to be homogenous (e.g., radial density);
- analytic orientational averages of the optical quantities;

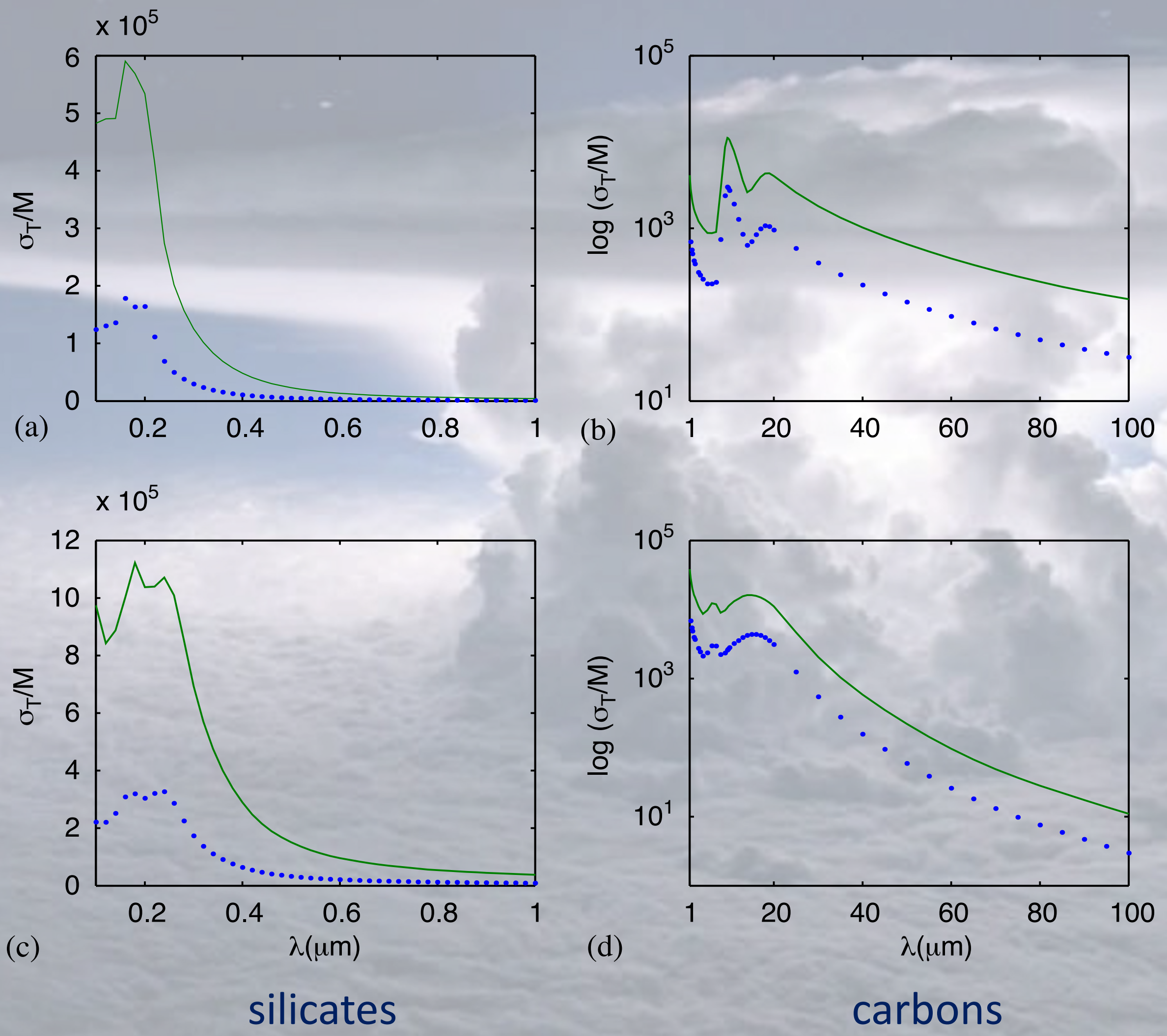
TMT involves building a matrix of order 2 N × L (L + 2), where
N is the number of monomers that constitute the aggregate, and
L is the truncation index of the series expansion of electromagnetic fields (i.e. the accuracy).



Optics of complex classic particles

extinction cross-sections for a true particle and its equivalent sphere





Wishlist (> statement of intent)

- multiscale, coordinated theoretical and laboratory work;
- creation of a database of absorption and scattering properties of particles sampling all the relevant properties, i.e. composition, size, morphology;
- theoretical toolbox: from methods based on the Bethe-Salpeter equation for small molecules, through various flavours of the DFT for larger molecules and nano-sized clusters, to the TMT for complex macroscopic particles;
- laboratory data will serve as the “golden standard” against which to validate the more systematic theoretical results
- for selected cases, laboratory measurements, where possible, will be directly used to populate the database;
- radiative transfer models of exoplanetary atmospheres will be updated to make use of these newly available data to properly account for dust, haze, and clouds;
- incorporation in the parallel database (under construction) of chemical atmospheric profiles and spectral synthesis;
- testing the impact on the capability of forward models to accurately reconstruct the actual properties of exo-atmospheres.