Quantum chemical and atomistic modelling of dust

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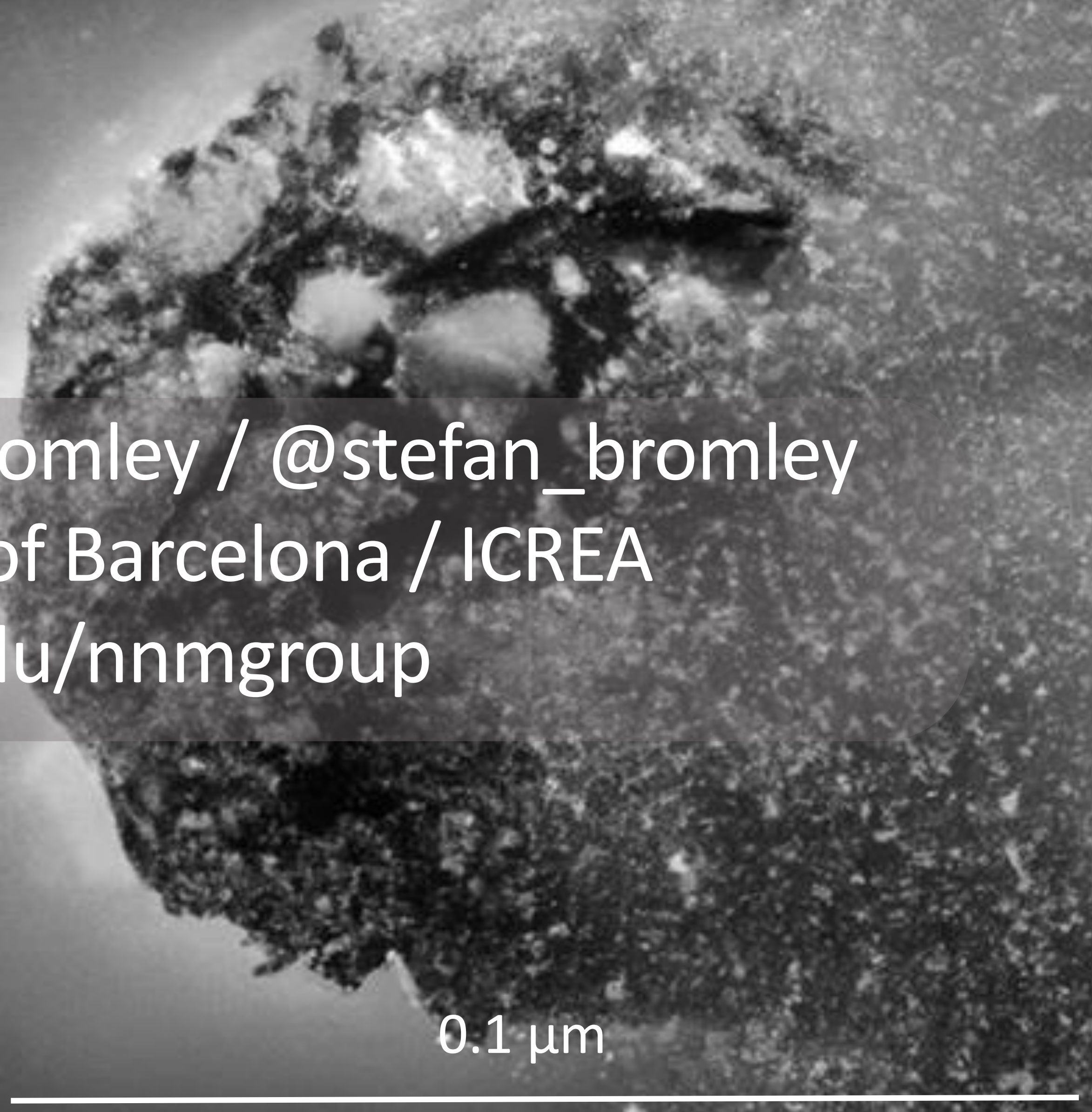
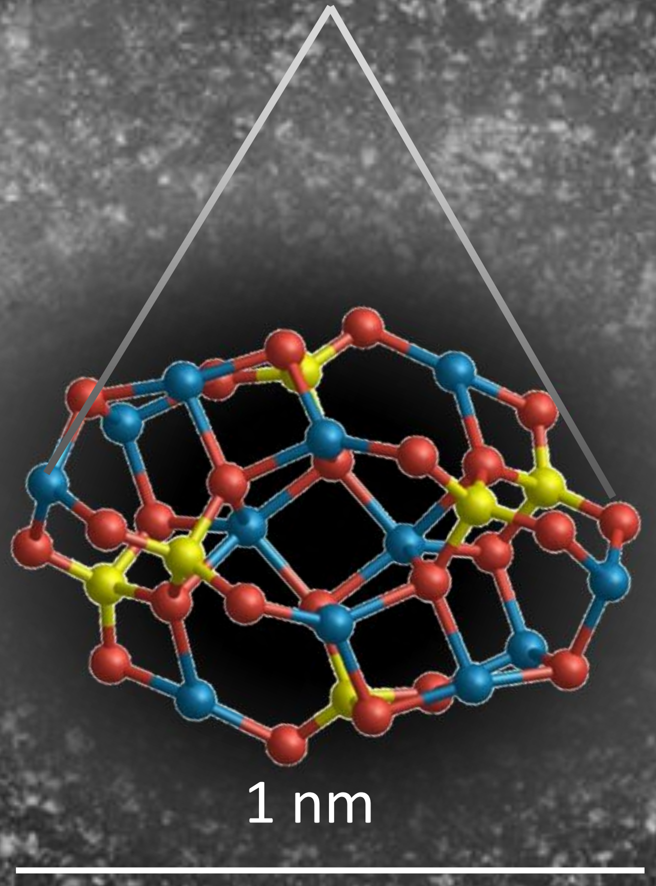
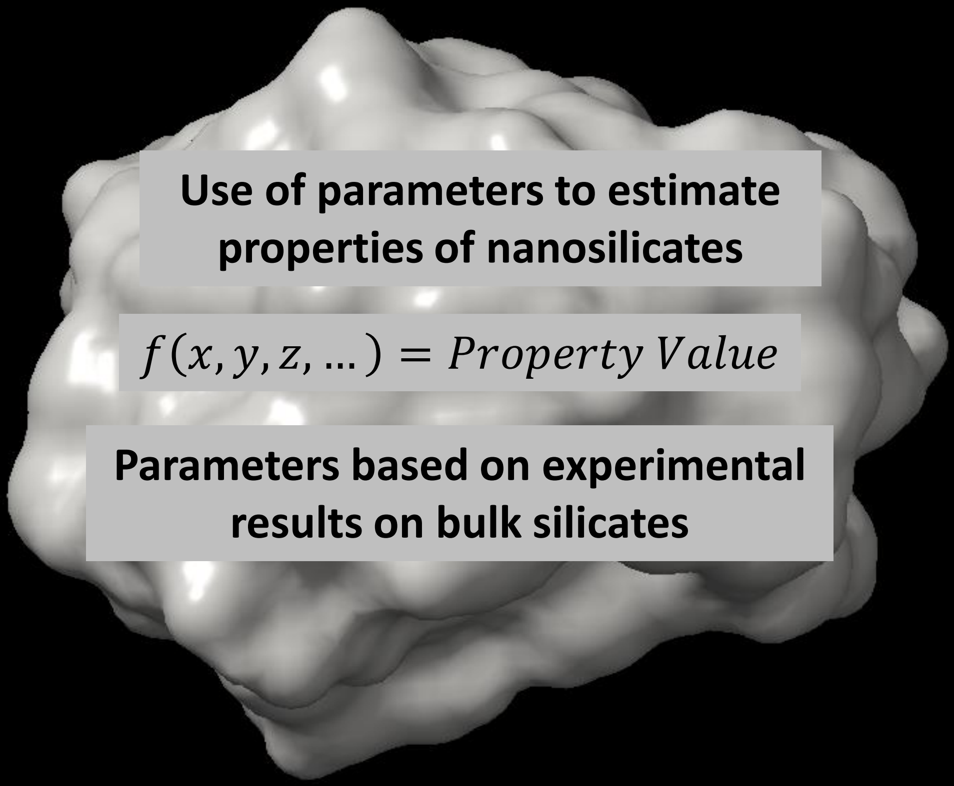




Top-down *vs* bottom-up grain models

TYPICAL ASTRONOMICAL DUST GRAIN MODEL



Use of parameters to estimate properties of nanosilicates

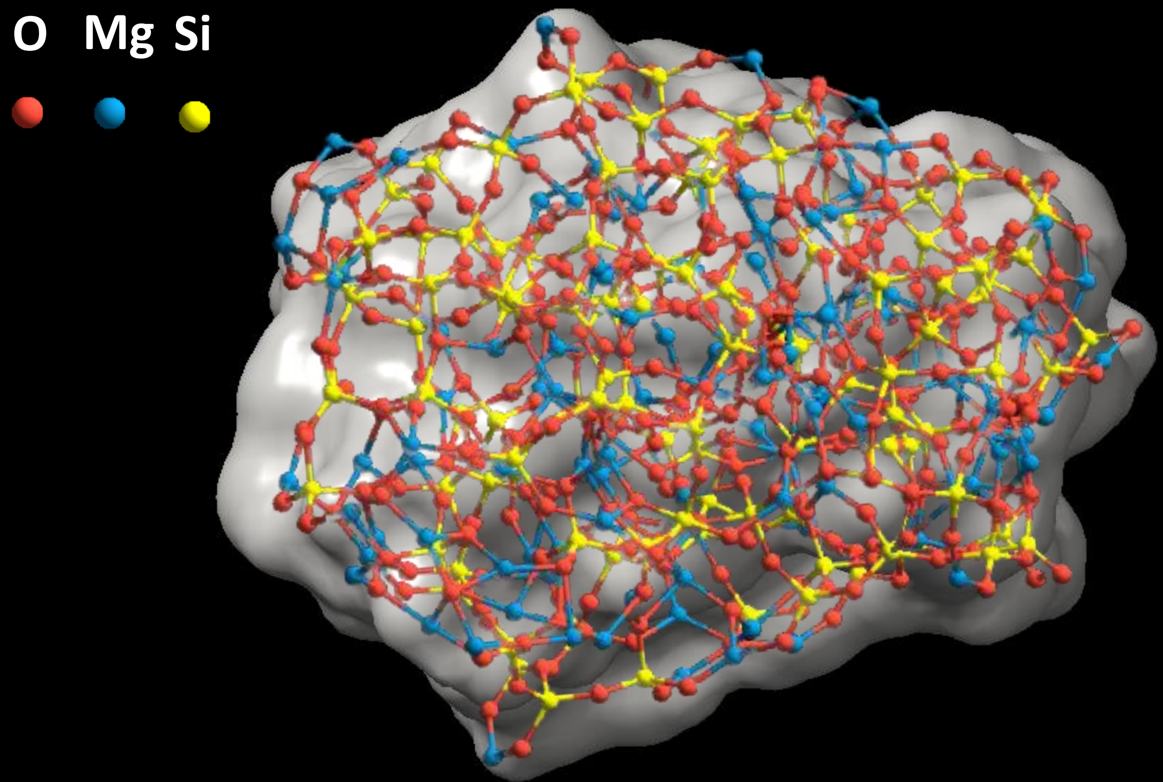
$$f(x, y, z, \ldots) = Property\ Value$$

Parameters based on experimental results on bulk silicates

TOP-DOWN APPROACH

Top-down *vs* bottom-up grain models

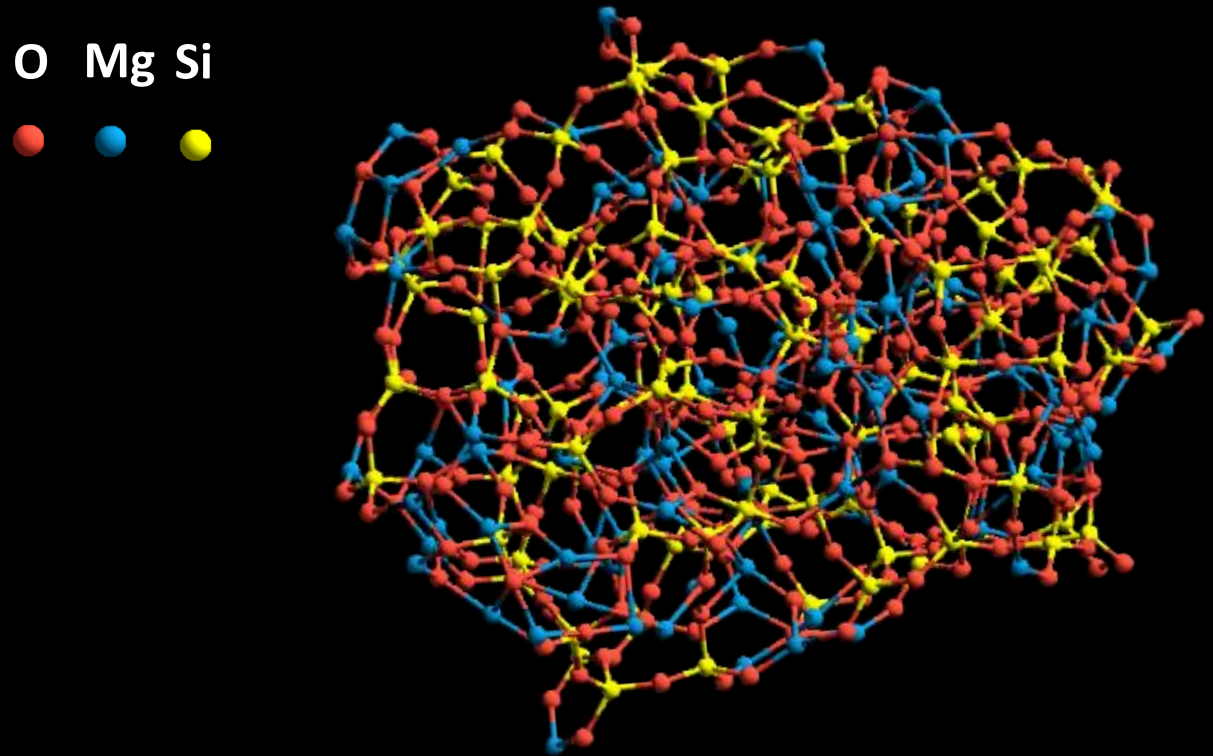
INTERNAL STRUCTURAL DETAIL



BOTTOM-UP APPROACH

Top-down *vs* bottom-up grain models

ATOMISTIC STRUCTURE + DYNAMICS



BOTTOM-UP APPROACH

DIRECTLY OBTAIN ACCURATE NANOSILICATE PROPERTIES

- Chemical structure
- Morphology
- Chemical Composition
- **Vibrational frequencies**

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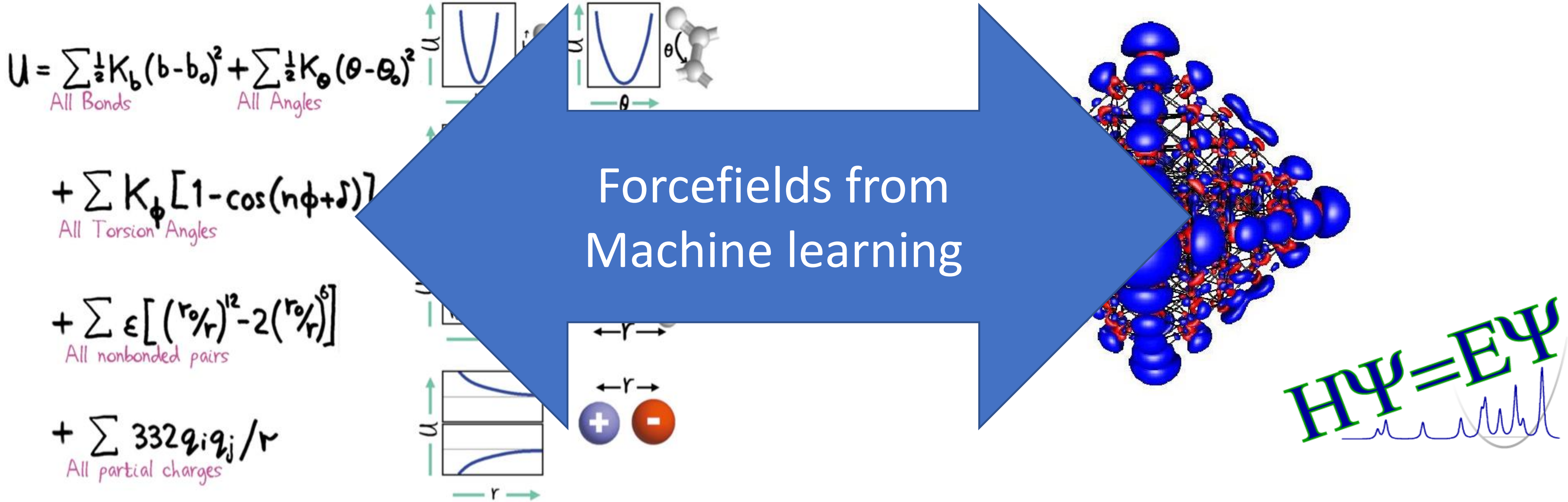
Bottom-up atomistic modelling methods

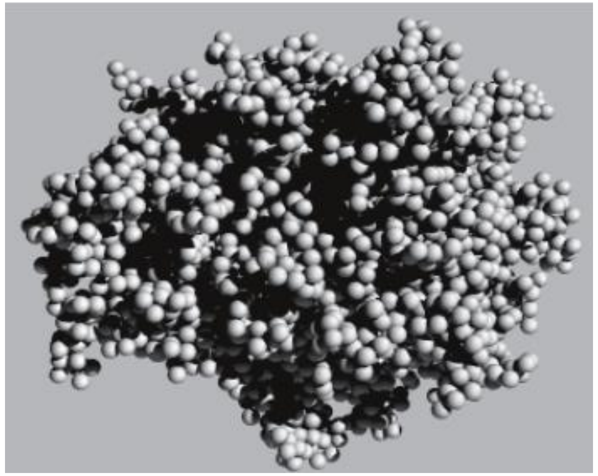
Computationally cheap / less accurate	***Computationally costly / more accurate***
Empirically fitted force field methods – atomistic structure, molecular dynamics, **global optimisation**	*"Ab initio"* quantum mechanical electronic structure methods (e.g. density functional theory - DFT)



10000's of atoms and nanoseconds

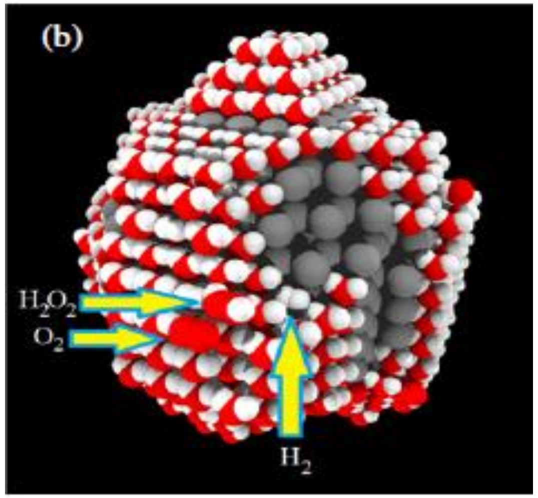
100's of atoms and picoseconds

Other bottom-up approaches to dust grain modelling



"Coarse grained" approaches
(e.g. Wada et al. ApJ 2011)

1000s of **identical elastic sphere monomers** (typically ~100 nm / 0.01 μm diameter). Positions and dynamics consider all local mechanical interparticle interactions



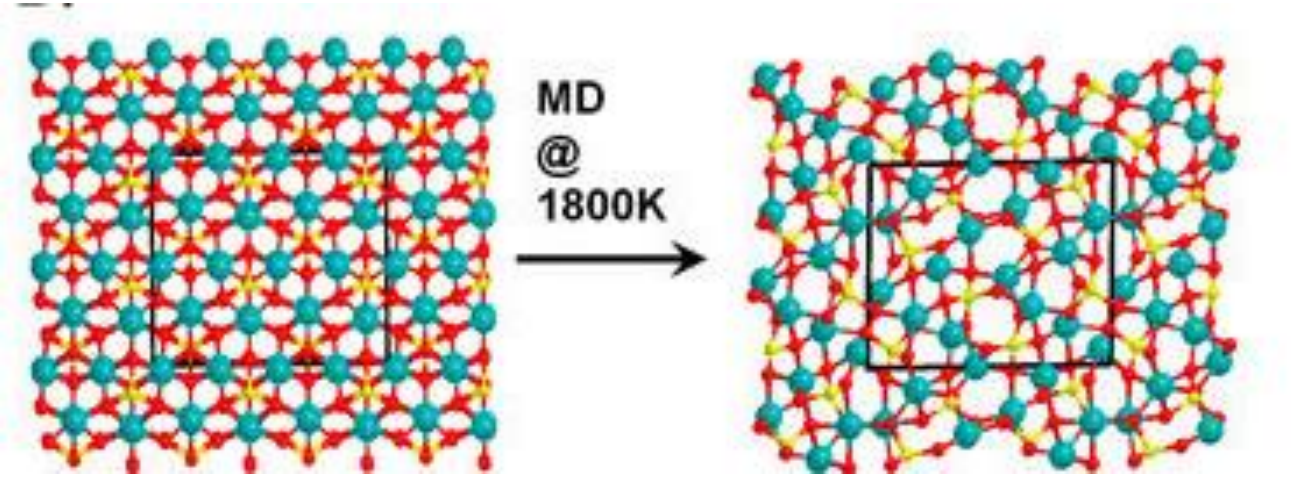
Off-lattice Monte Carlo kinetic model
(e.g. Jarrod ApJ 2013)

Icy mantles with 10000s of atoms/molecules
Fixed positions determined by local interactions with nearest surface atoms.

Realistic morphologies but no atomistic dynamical degrees of freedom…IR spectra?

Bottom-up atomistic modelling approaches

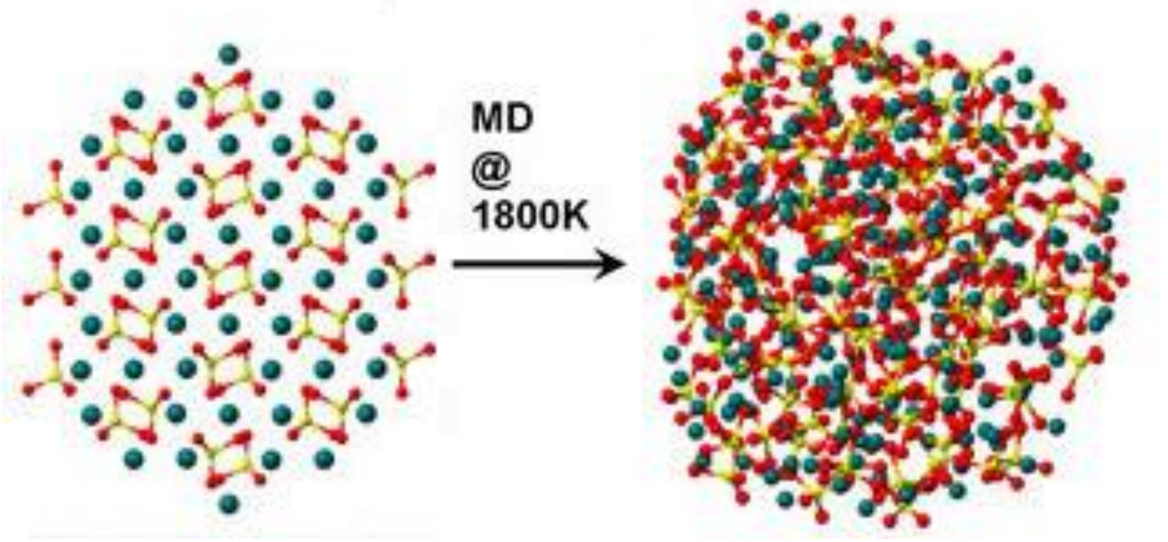
Periodic models



Crystalline Amorphous

- Assumes infinitely repeated unit cell structure.
- Bulk crystalline systems
- Amorphous/discrete systems

Cluster models



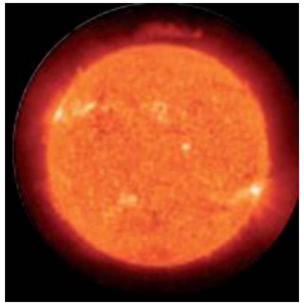
Crystalline Amorphous

- Complex discrete models
- Bulk crystalline systems
- Amorphous/discrete systems

From stars to dust grains

÷ 1000000000000000000

÷ 10^{18}

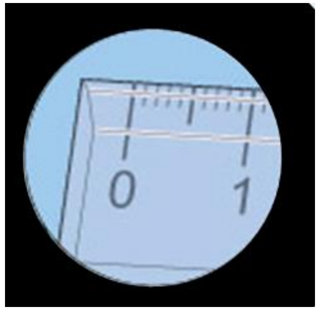


1 Gm
(x1000)

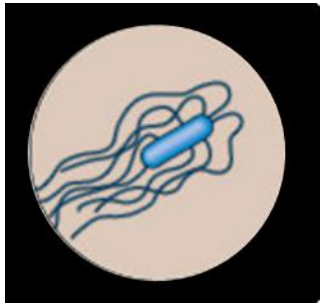
1000 km
(x1000)

1 km
(x1000)

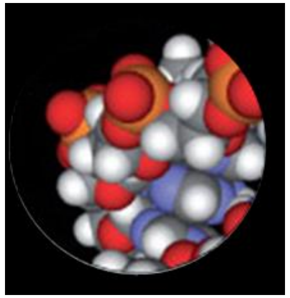
1 metre



1 mm
(/1000)



1 µm
(/1000)

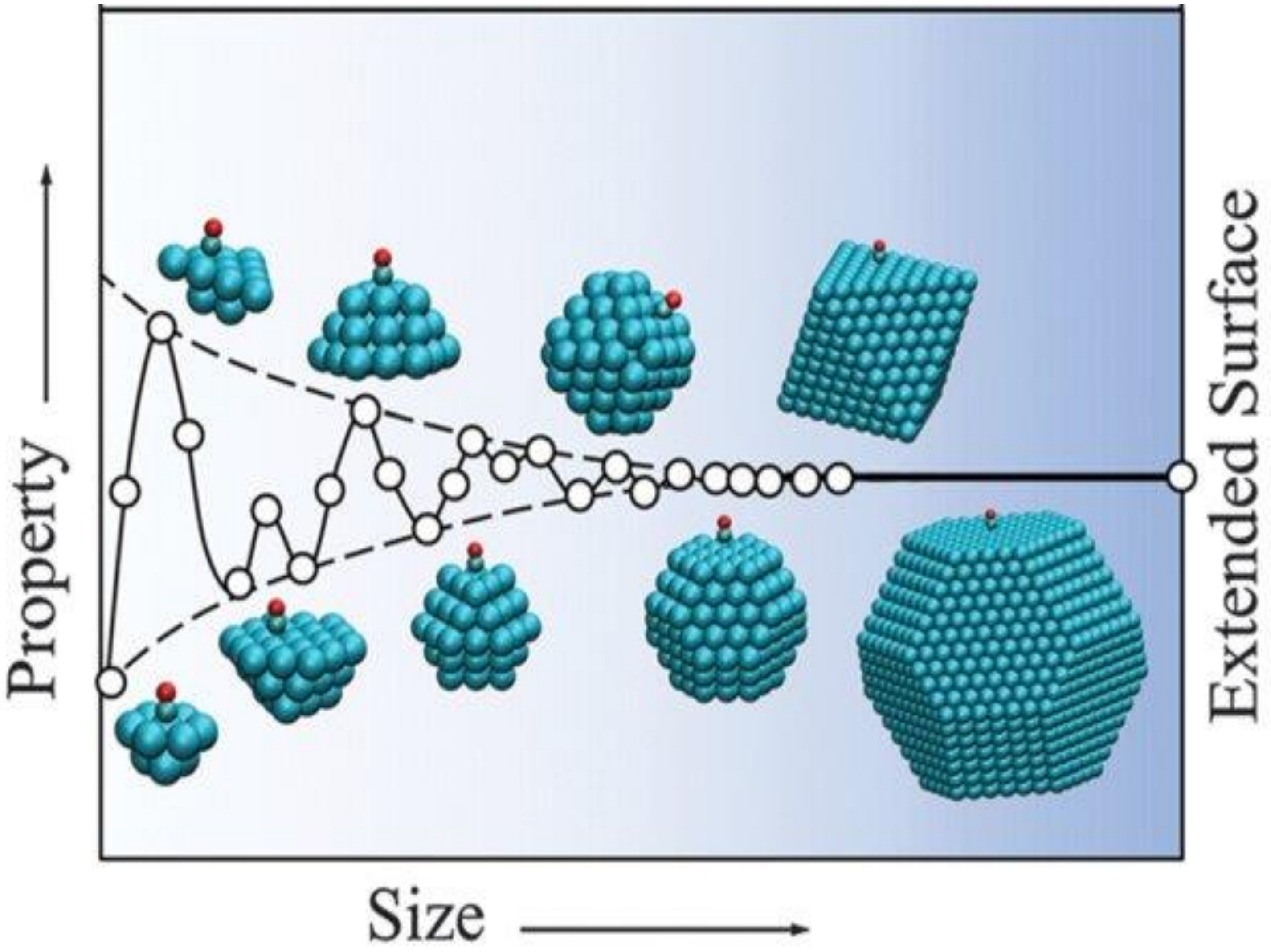


1 nm
(/1000)

Dust grains

Atomistic models

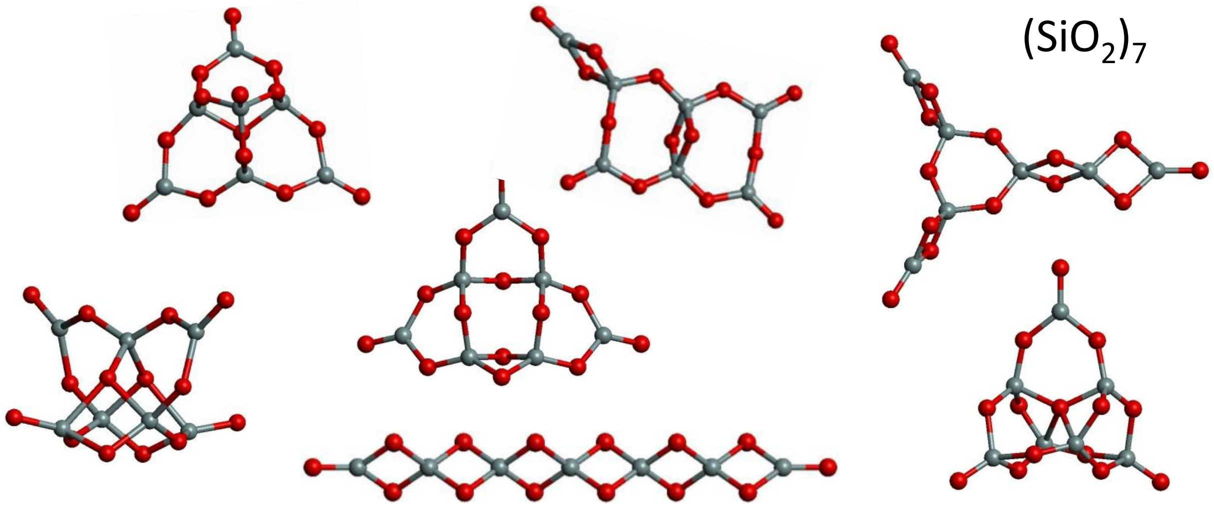
Size-dependency of grain properties



- Large surface area/volume ratios
- Non crystalline structures
- Specific surface sites
  (e.g. low coordination)
- Quantum effects
  (e.g. quantum confinement)

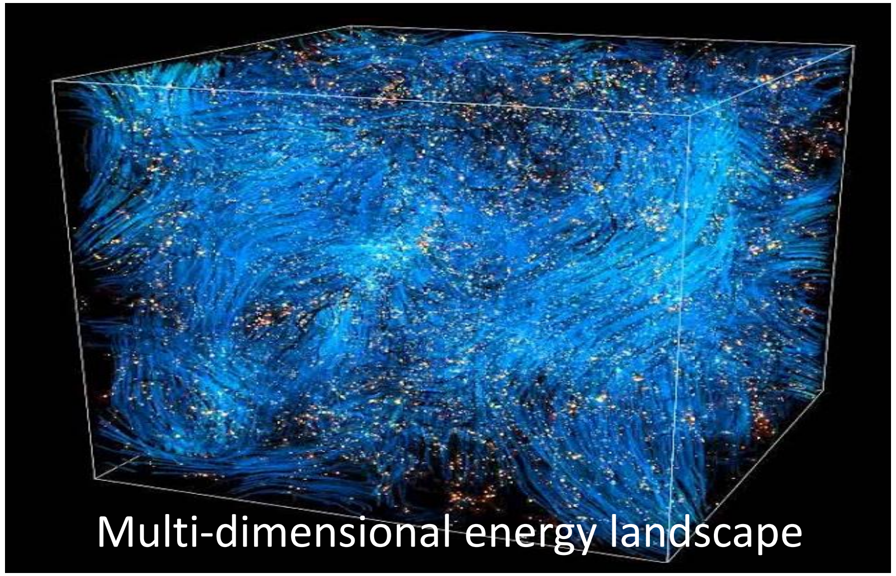
Special astro-chemical/physical properties for nanograins?

Structure of low energy nanoclusters



Size: the number of cluster isomers grows exponentially with increasing system size

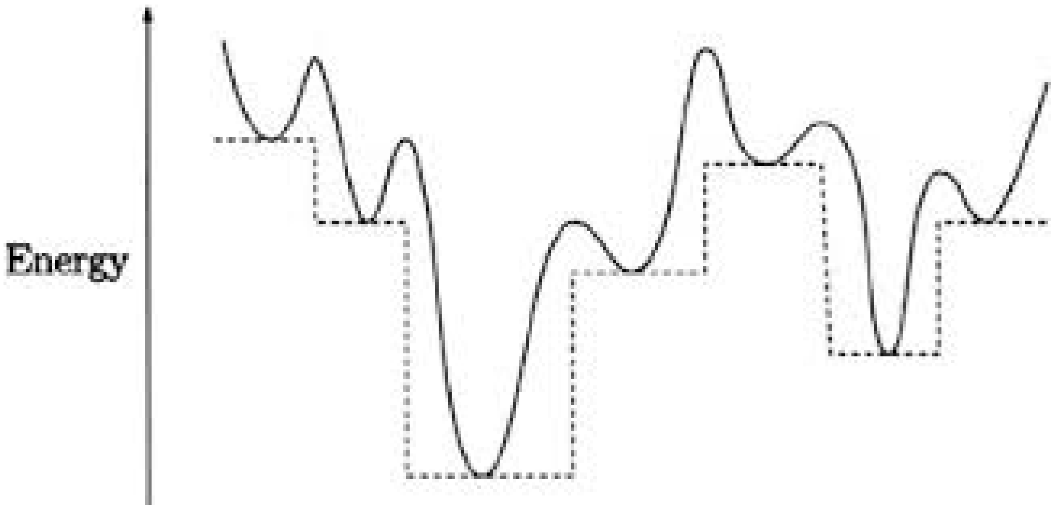
Complexity: isomer energy depends on coordinates of all atoms $E(r_1, r_2, r_3 \ldots\ldots\ldots r_N)$ leads to a multi-dimensional “energy landscape”

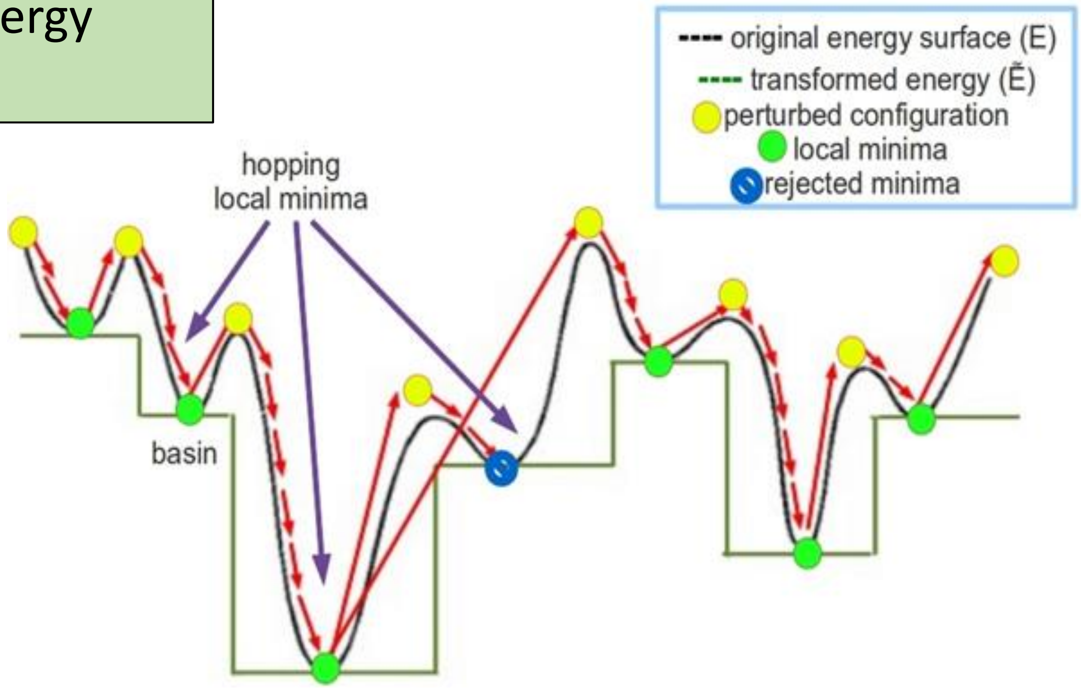


Need **global optimisation** methods to search energy landscapes (e.g. Basin Hopping, Evolutionary Algorithms)

Basin Hopping global optimisation

Basic Idea
- Transform energy landscape into a step-wise function of energy
- Energy within a basin (minimum) becomes constant





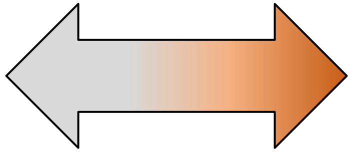
Why
- Maintain all minima but remove all barriers
- Easier landscape to explore

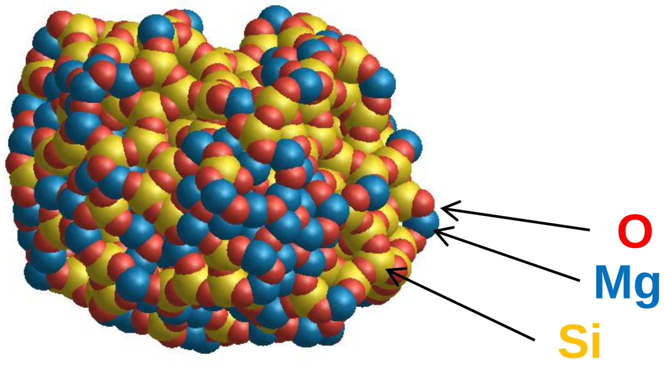
Basin Hopping
Stochastic Monte-Carlo based exploration of the transformed energy landscape

Bottom-up models of nanosilicate dust grains

Observational / laboratory data + physical assumptions

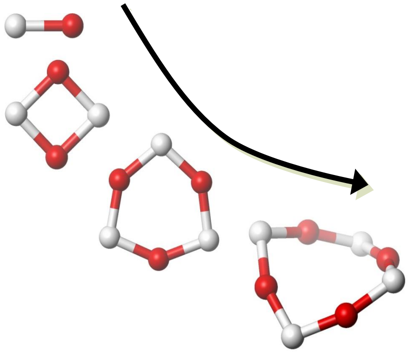
Astronomical Grain Models



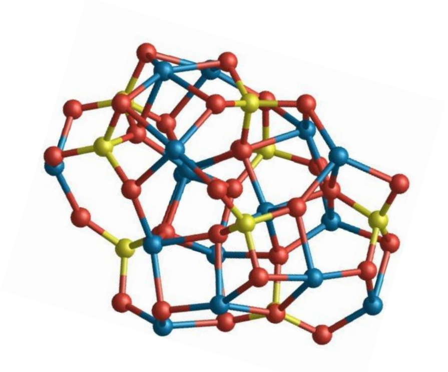


Atomistic Grain Models

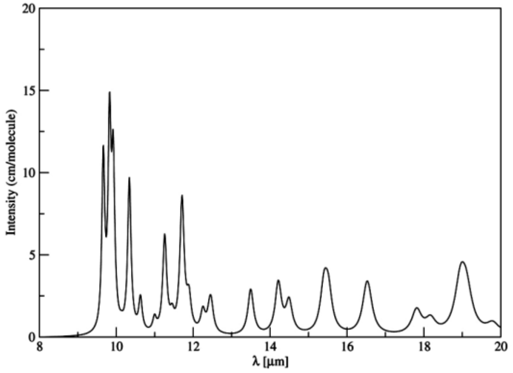
Bottom-up grain models allow for detailed understanding of:



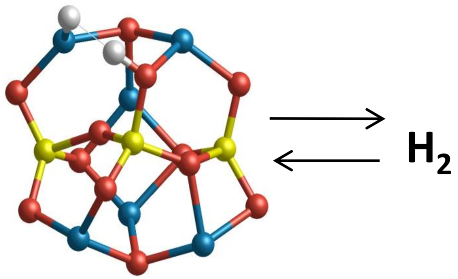
Dust nucleation



Structure & crystallinity

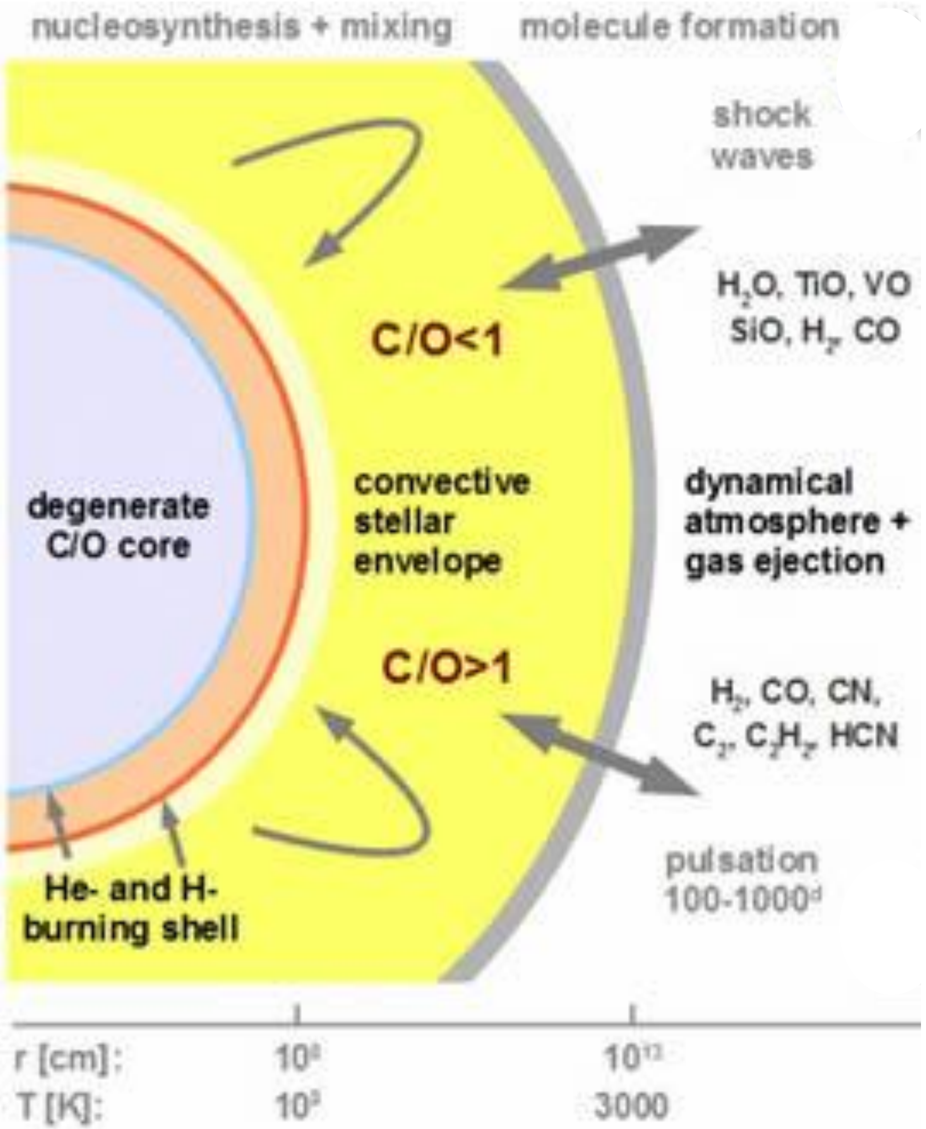


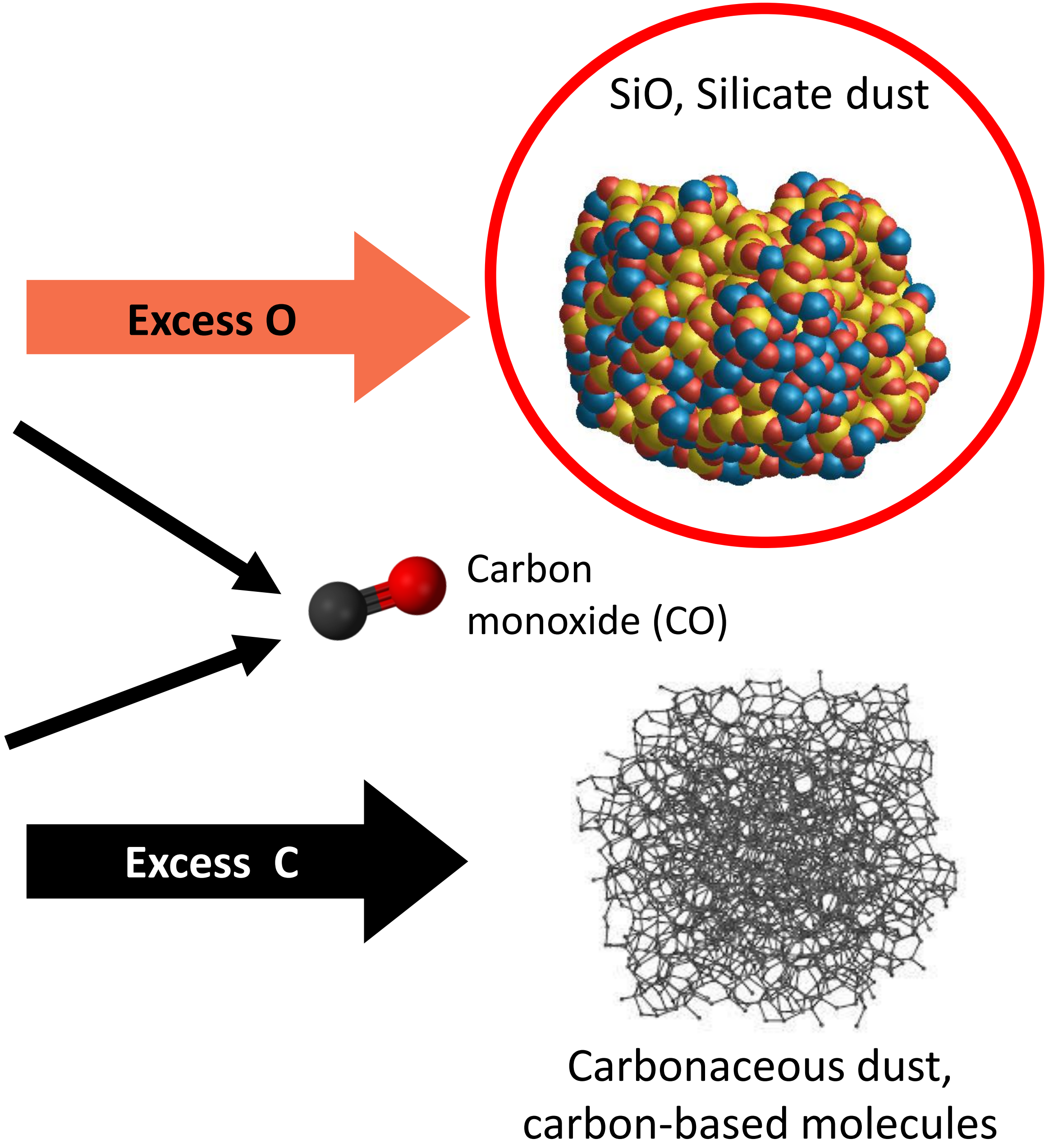
Interpreting observed spectra



Grain catalysed astrochemistry

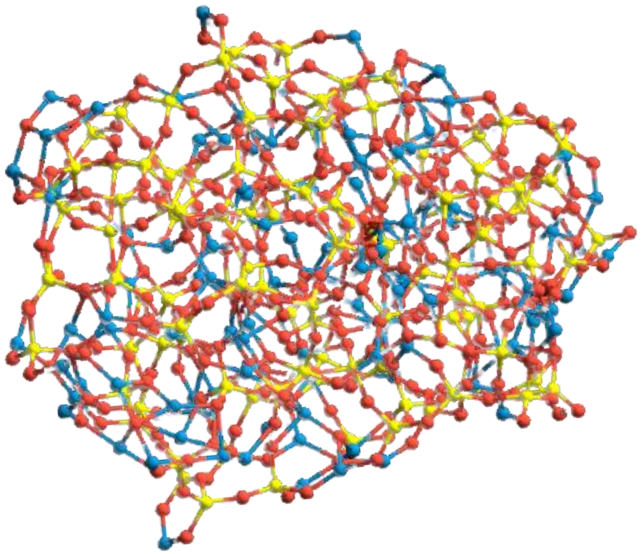
C/O ratio and dust formation





Dust grain size and structure

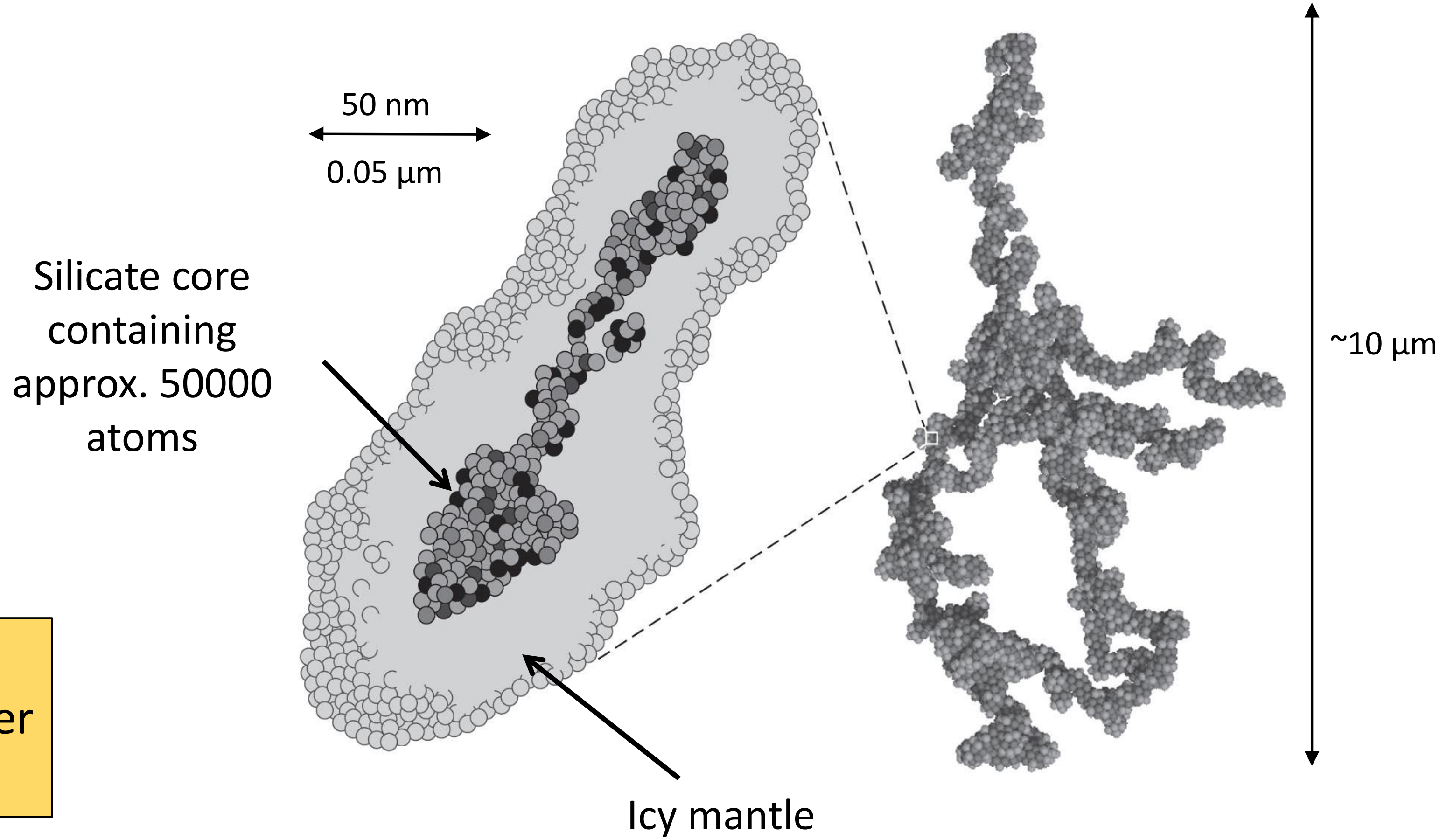
Bare silicate grains



Found in regions with higher energetic processing (e.g. diffuse ISM) and/or higher temperatures (e.g. protoplanetary disks)

Monomeric dust grain

Dust grain aggregate

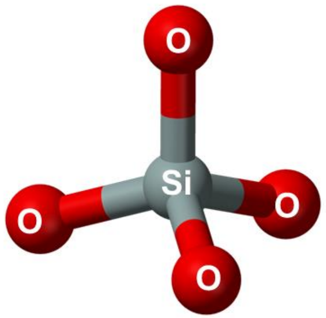


Astronomical relevance of nanosilicates

- Silicates: most abundant solids in space
- Silicate dust is found in interstellar clouds, circumstellar disks, interplanetary space, comets, exoplanet atmopheres…
- Silicate dust grains grow to a size ~0.1 µm before entering the ISM
- Dust in the ISM is "processed" (e.g. supernovae shocks)

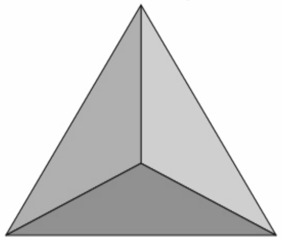
- **~10% of interstellar Si could be in nanosilicate grains (<3 nm diameter)**
- **×10000 more nanosilicates than ~0.1 µm grains**

Bulk silicate structure

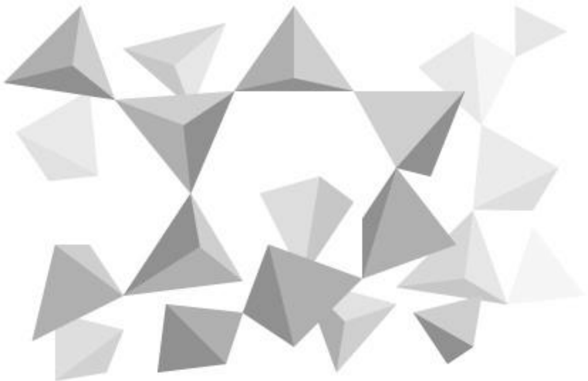


Silica tetrahedron

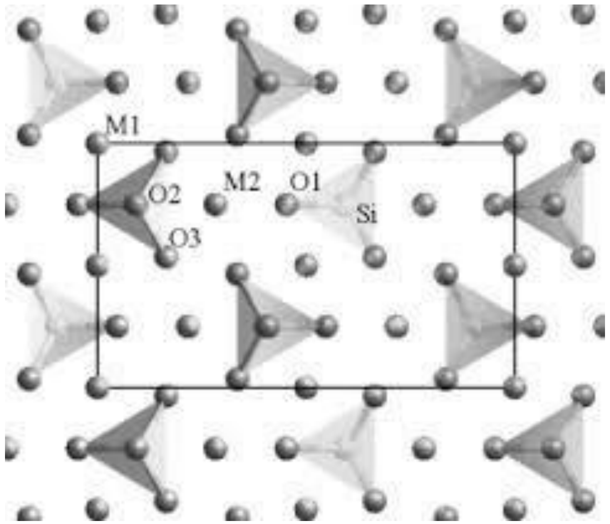
-4e charge



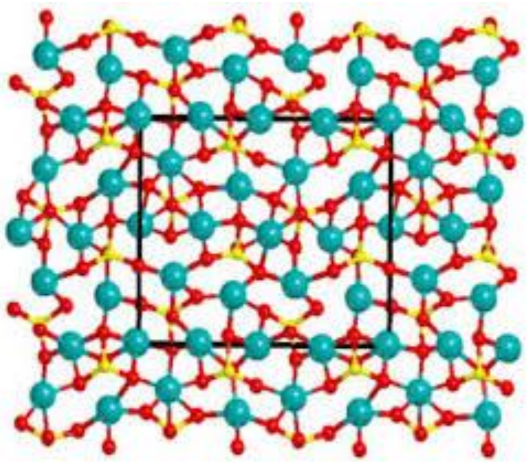
No dipole



Silica (SiO_2) - O-sharing



Silicates: SiO_2 + Mg/Fe cations

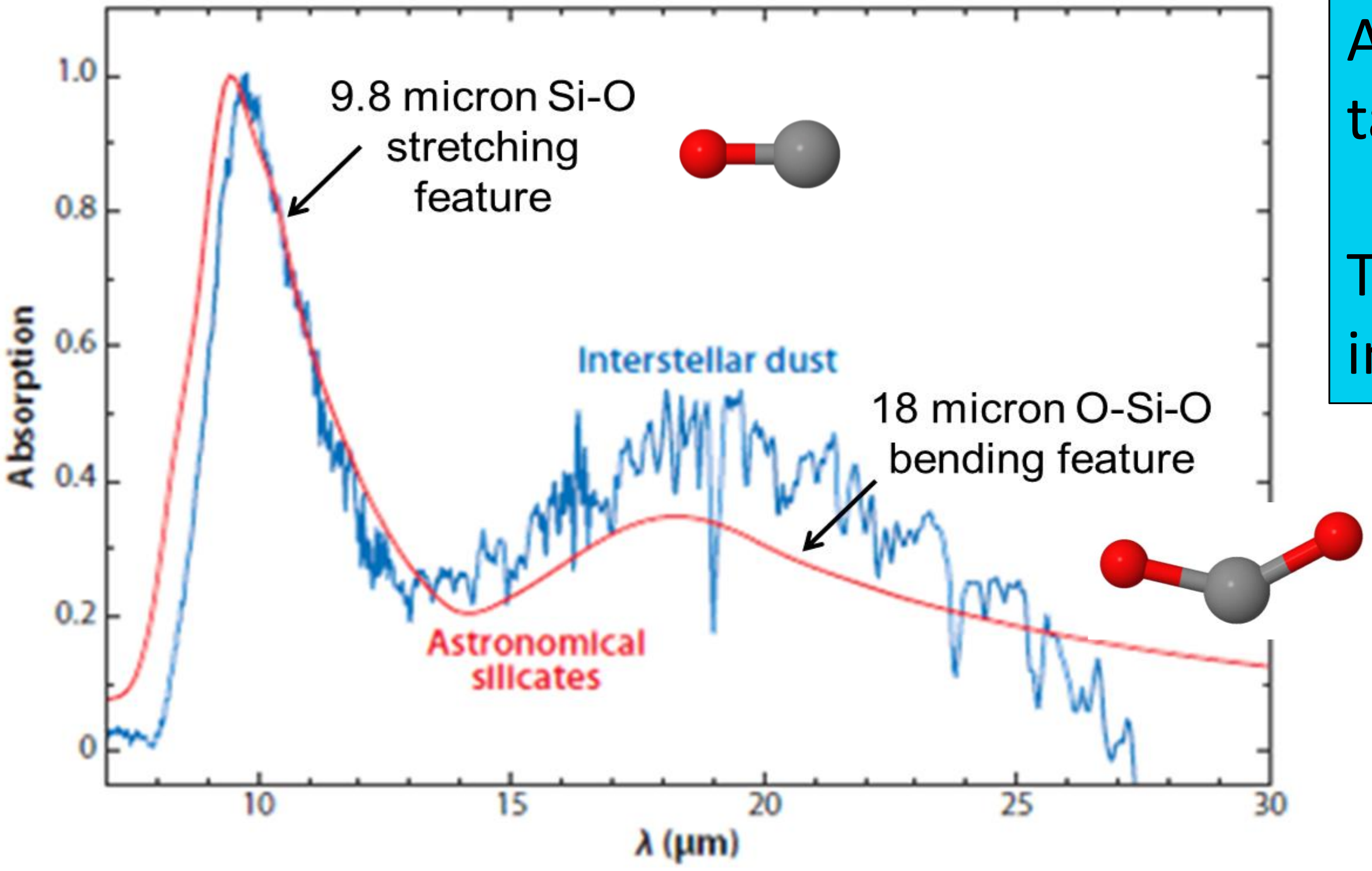


Astronomical silicates are Mg-rich:

Mg-rich olivines: $Mg_2Si_2O_4$

Mg-rich pyroxenes: $MgSiO_3$

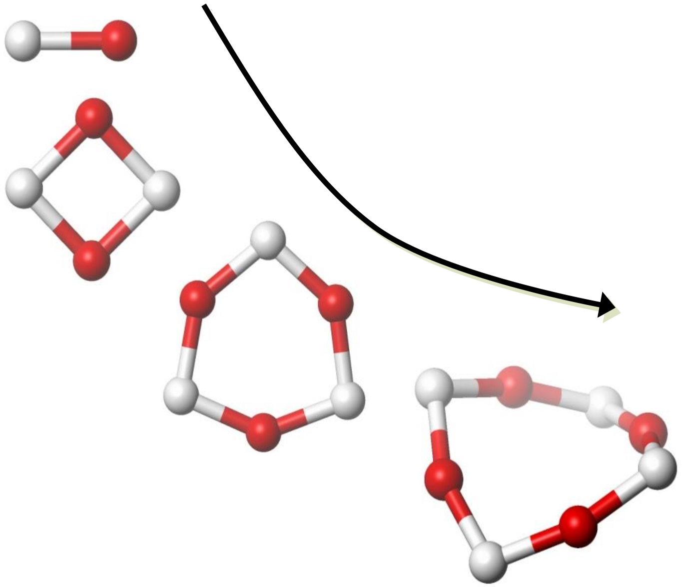
Infrared spectra of silicate dust grains



Average silicate grain size taken to be approx. 0.1 μm.

Two main broad features indicates lack of crystallinity

How does silicate dust form?



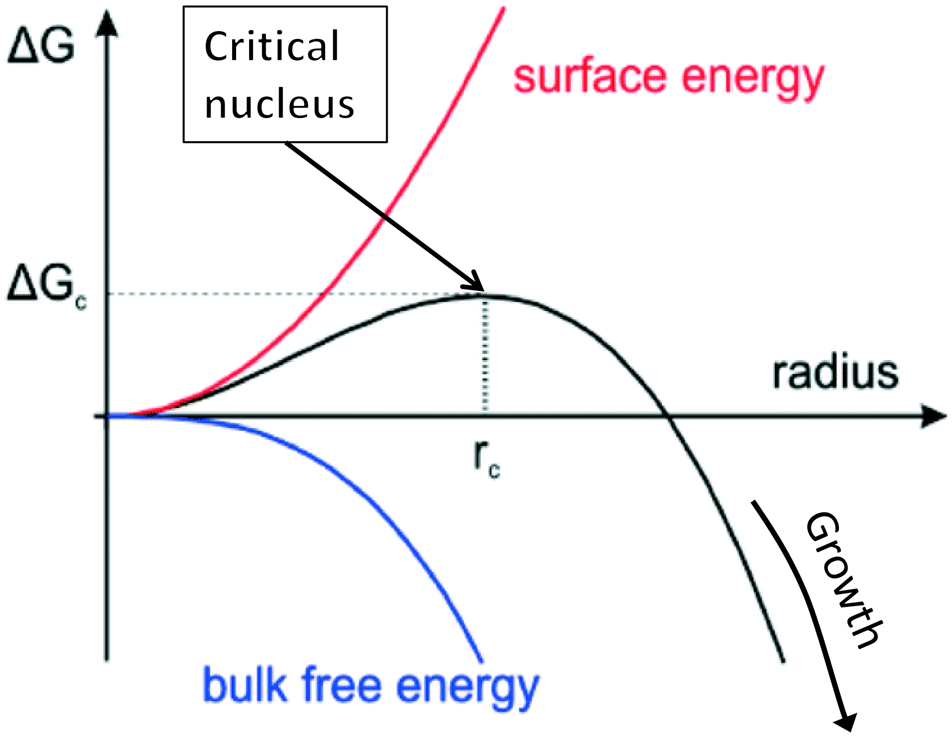
Circumstellar nucleation conditions:

- Temperature: 800 – 1200 K
- Pressure: 0.1 Pa
- Chemical species: SiO, H_2O, Mg

Initial attempts to understand silicate dust formation used classical nucleation theory (CNT) to model the condensation of SiO molecules…

Classical Nucleation theory (CNT)

Homogeneous (i.e. not on a surface) nucleation of a spherical particle

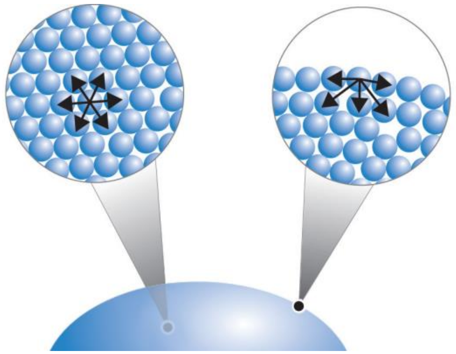


Total change in free energy

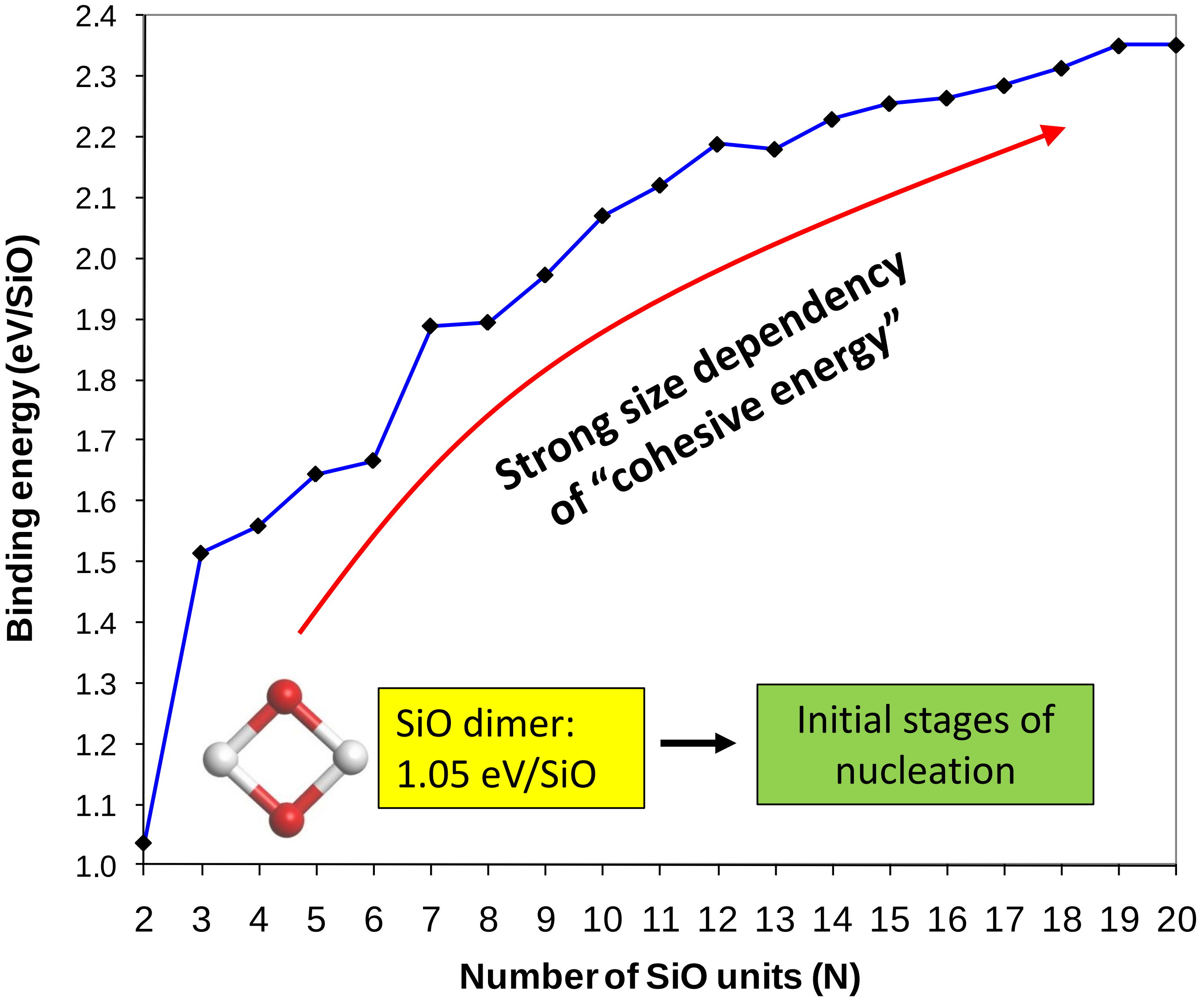
$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma$$

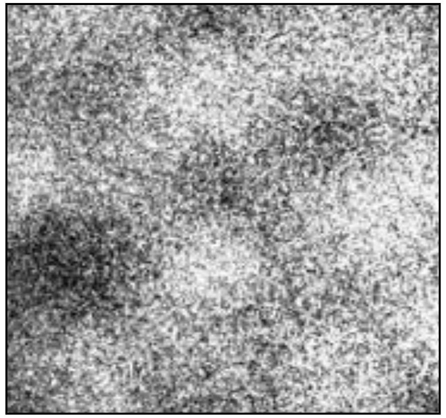
Free energy gain per unit volume

Free energy consumed per unit surface



Problems for CNT: cohesive energy of clusters





Bulk SiO: >2.35 eV/SiO

Input parameter for classical nucleation theory

Problems for CNT: nanostructure *vs* bulk structure

TEM investigation into the structure of amorphous SiO, Schulmeister & Mader J. Non-Cryst. Solids 320, 143 (2003)

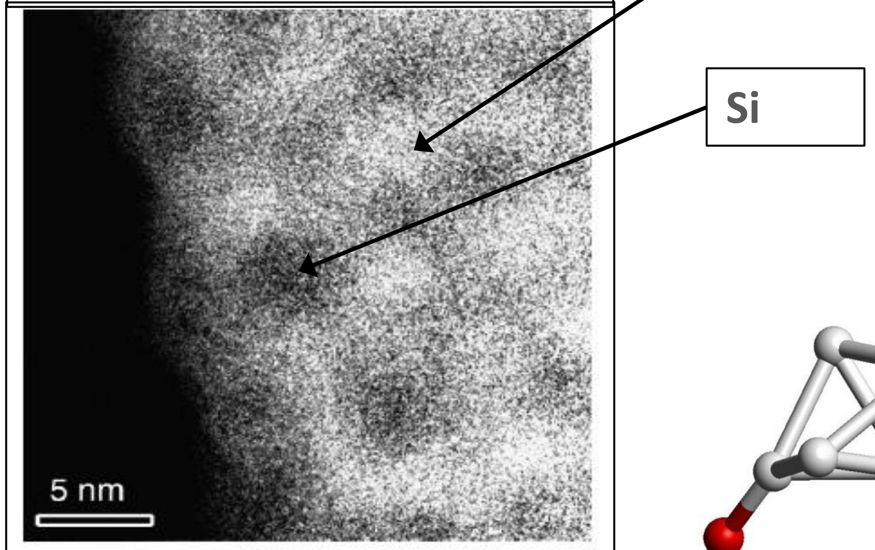
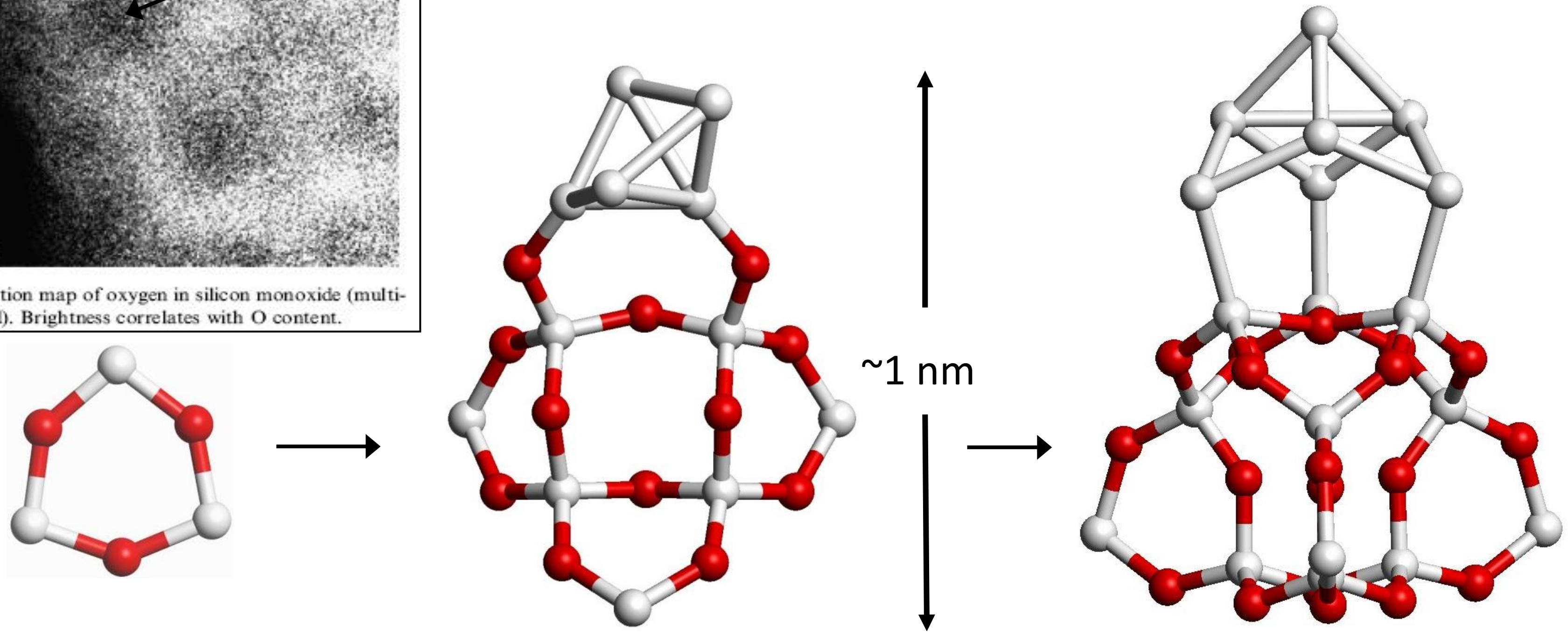


Fig. 8. Distribution map of oxygen in silicon monoxide (multi-window method). Brightness correlates with O content.

SiO_2–Si segregation occurs rapidly with $(SiO)_n$ cluster size increase
→
Problems for defining a surface energy



$(SiO)_3$ $(SiO)_{12}$ $(SiO)_{19}$

Classical Nucleation Theory for Silicates? The case of $(SiO)_x$

Donn and Nuth, *ApJ.* 288, 187 (1985)

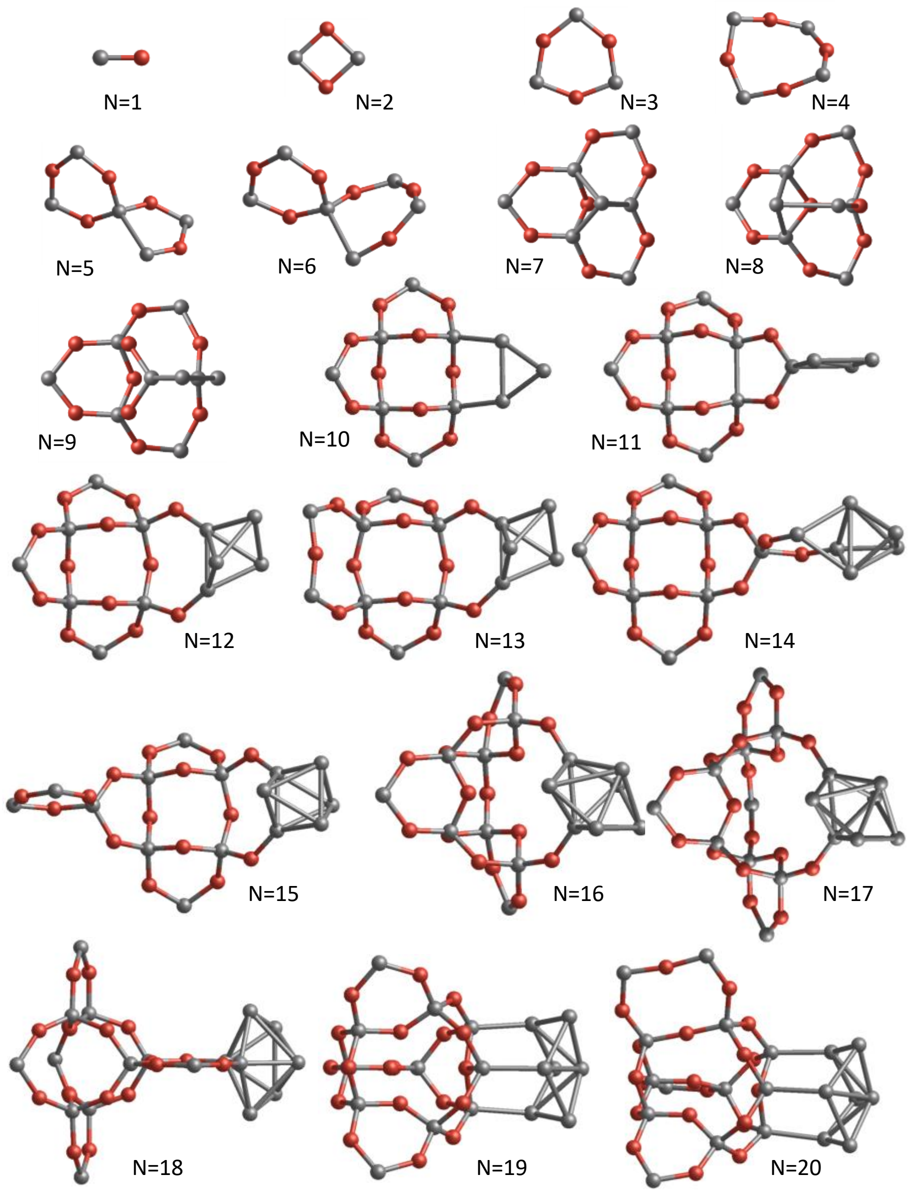
"…experimental evidence now suggests that nucleation theory is not applicable to the condensation of refractory species….

…determine the relative stability of a series of $(SiO)_x$ clusters…via experimental techniques or modern quantum mechanical calculations.

A kinetic route…could then be postulated and the rate of formation of circumstellar grains via this reaction network calculated."

Bromley, Gomez and Plane, *PCCP* 18, 26913 (2016)

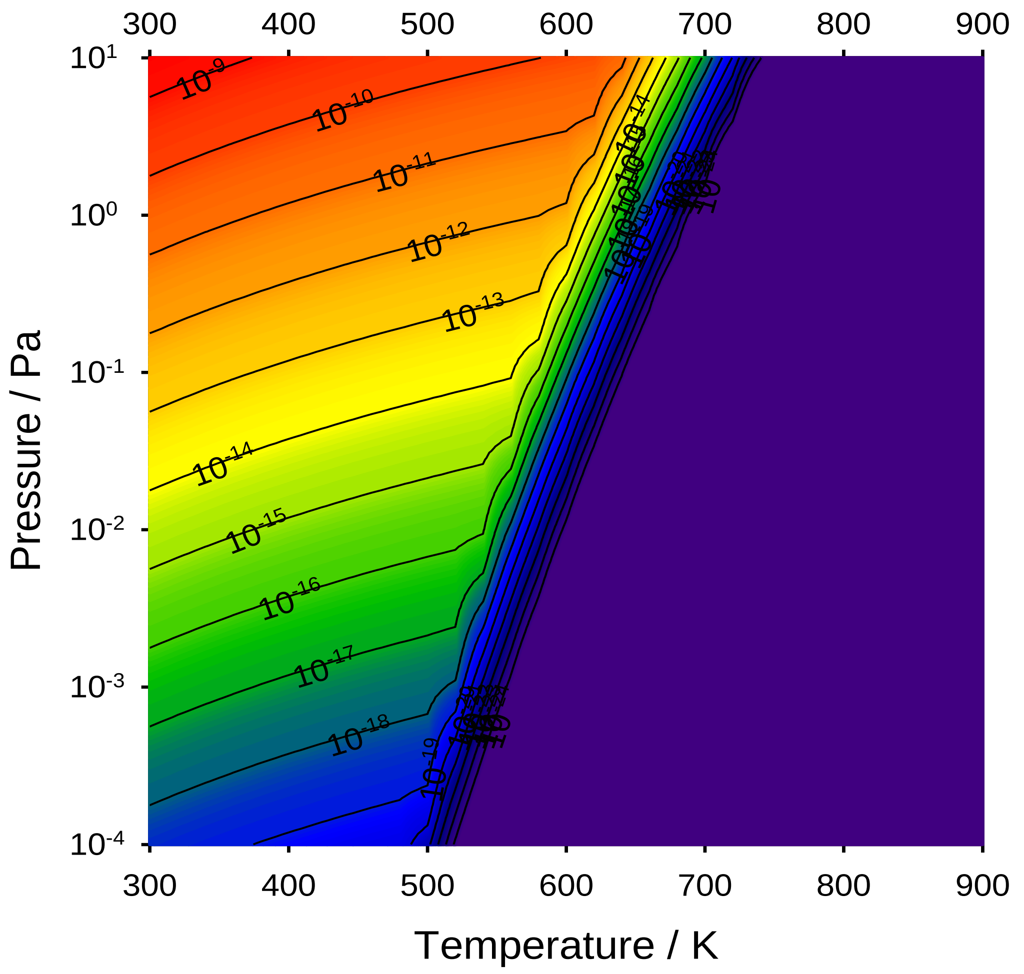
Using classical global optimisation + *ab initio* quantum chemical calculations + kinetic modelling…



Nucleation of $(SiO)_x$ from Kinetic Nucleation Theory (KNT)

- $(SiO)_x$ isomer structures from global optimisation
- Free energies from quantum chemical calculations
- Apply chemical kinetic rate equations

$$J = k_{1\to2}[\mathrm{SiO}]^2 \left(1 + \sum_{n=2}^{20} \frac{k_{2\to1}\, k_{3\to2} \ldots k_{n\to n-1}}{(k_{2\to3}[\mathrm{SiO}])(k_{3\to4}[\mathrm{SiO}])\ldots(k_{n-1\to n}[\mathrm{SiO}])}\right)^{-1}$$



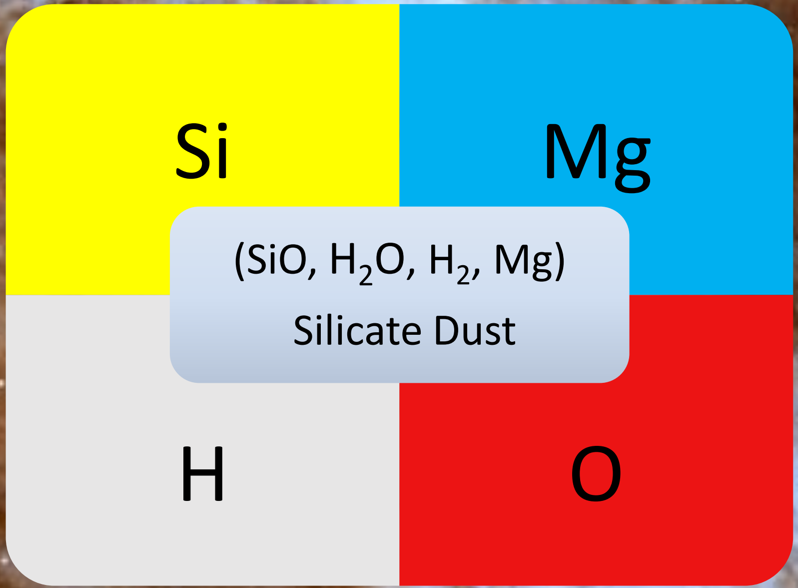
Predictions from KNT:

- $(SiO)_x$ particles will <u>NOT</u> be produced in a stellar outflow (T > 900 K, P < 0.1 Pa)
- Significant nucleation below 10 Pa should only be observed for T < 700 K

Bromley, Gomez, Plane, *PCCP*, 18, 26913 (2016)

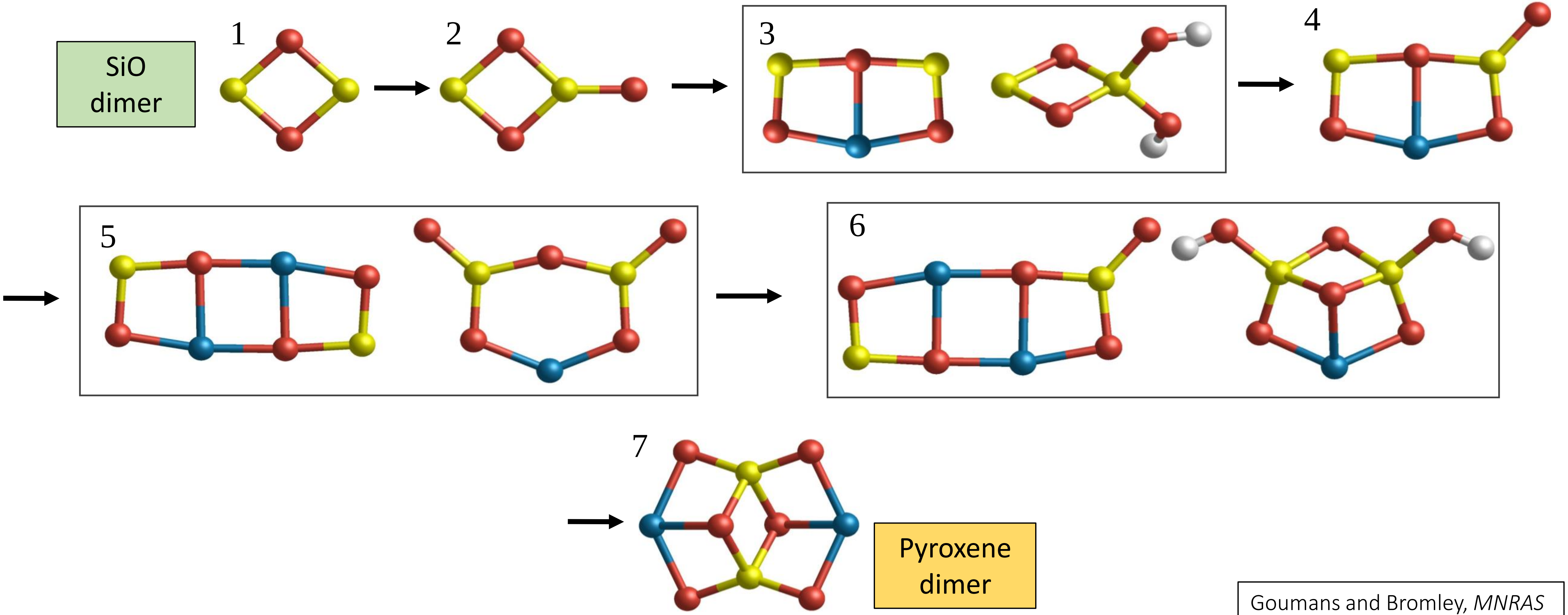
Need more than SiO…

Silicates detected via IR observations – most are assigned to be **amorphous** Mg-rich olivines ($Mg_2Si_2O_4$) or pyroxenes ($MgSiO_3$)



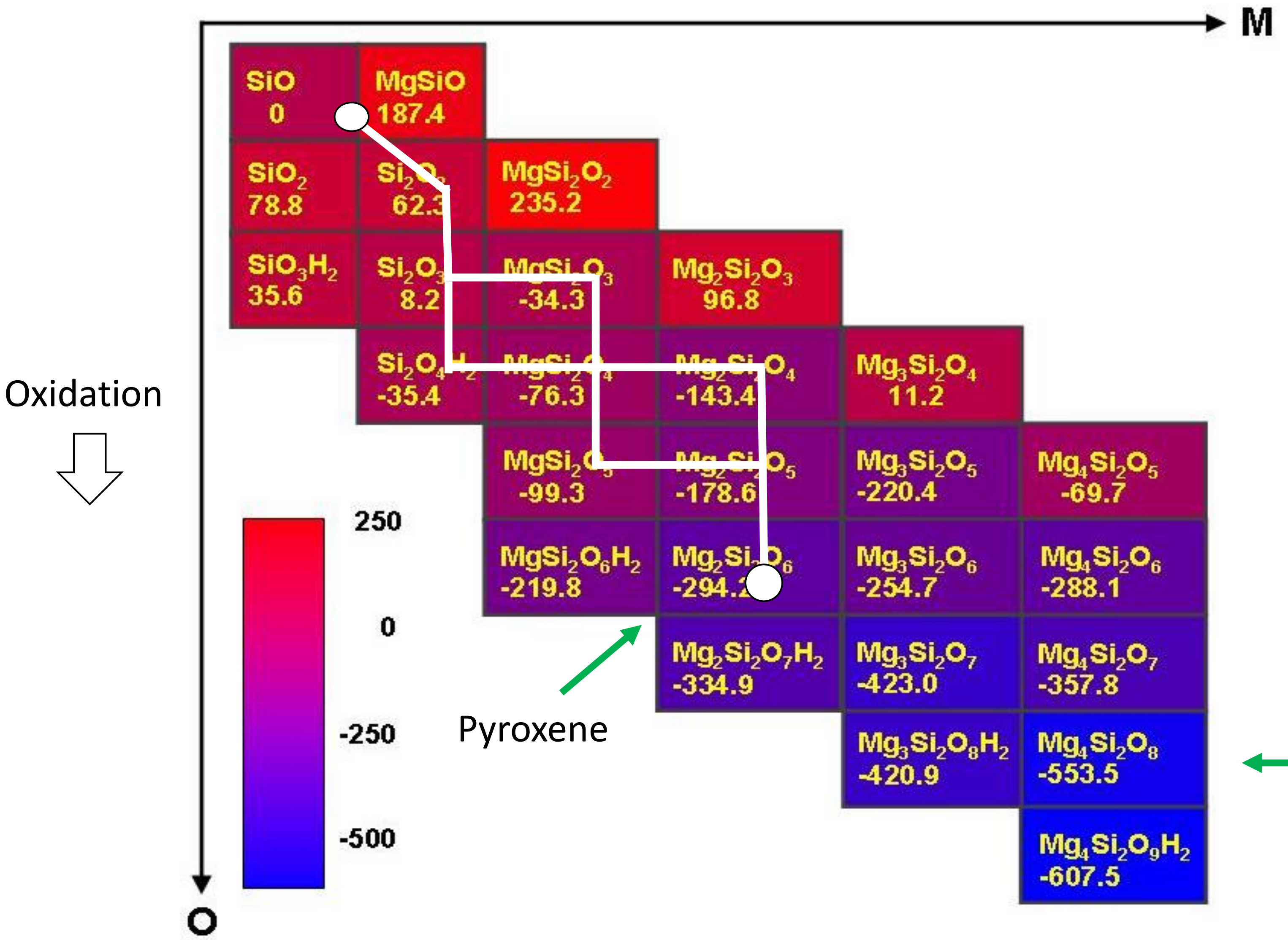
Less abundant Al, Ti, Fe, Ca could also be important…

Silicates from nucleation of SiO, H_2O/OH and Mg



Goumans and Bromley, *MNRAS* (2012) 420, 3344.

Free energies for addition reactions



Metal addition

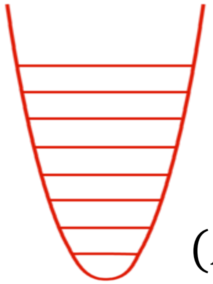
Olivine

Calculated Gibbs Free energies (kJ/mol) of the nucleation reactions at: T=1000K and p=0.1 Pa

Goumans and Bromley, MNRAS 2012

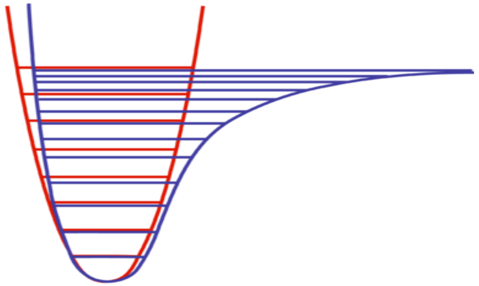
Calculating IR spectra using atomistic modelling

Harmonic vs Anharmonic:

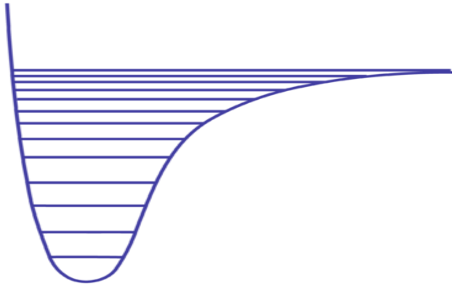


$$(R - R_e)^2 = \frac{1}{2}Kx^2$$

“Standard” 0K harmonic energy well



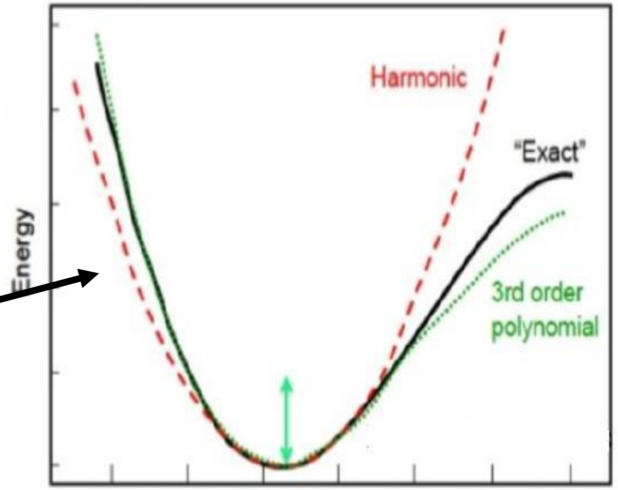
Harmonic *versus* anharmonic energy well



Anharmonicity leads to peak broadening and frequency dowshifting

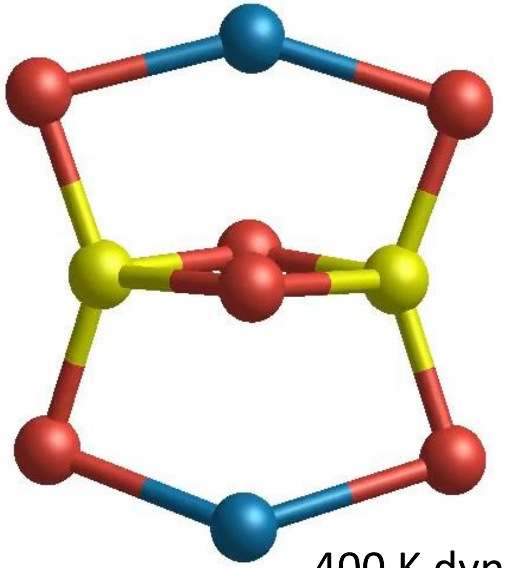
0K *vs* finite temperature:

- “Standard” IR spectra: distinct non-coupled normal harmonic modes from small 0K atomic displacements
- Molecular dynamics based IR spectra: coupled anharmonic vibrations of the system with temperature-dependent amplitudes

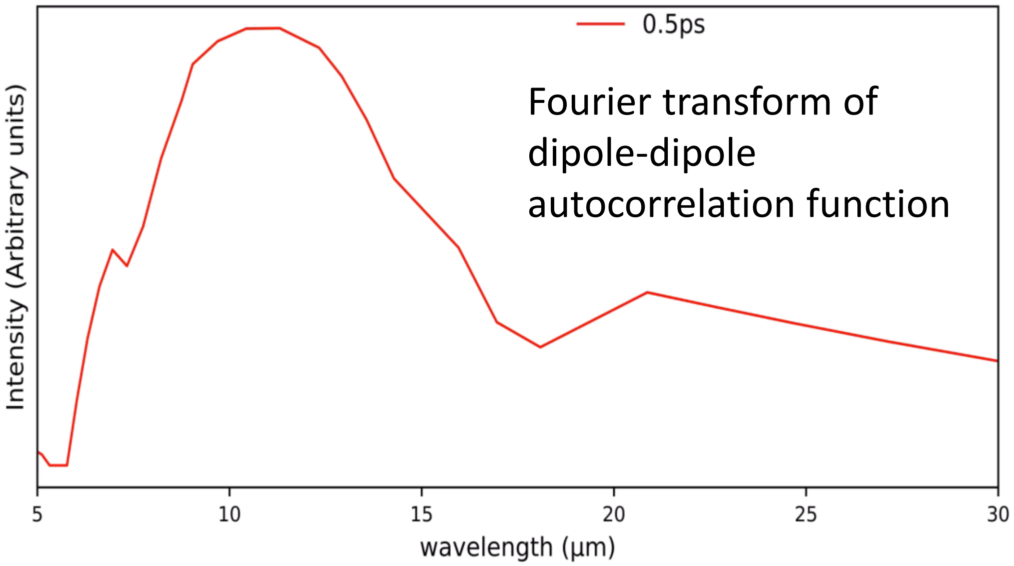


IR spectra of small nanosilicates

- Silicate dust in circumstellar environments is heated to between 100 -1000K
- Dynamics of nanoclusters modelled by ***ab initio* molecular dynamics (MD)**
- IR spectra can be calculated from recording periodic dipolar variations

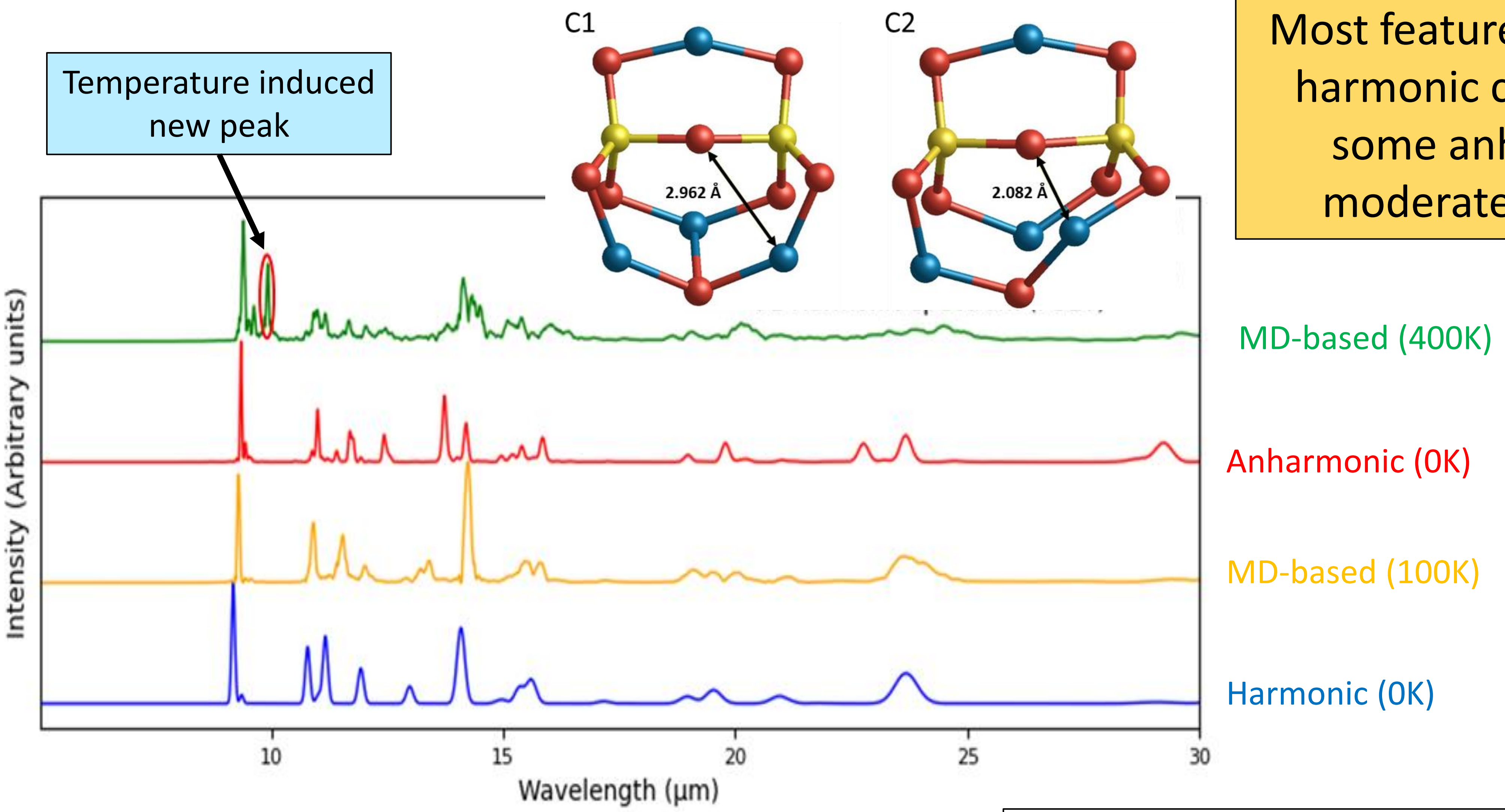


400 K dynamics



- MD-derived IR spectra describe anharmonicities, combination bands and overtones.

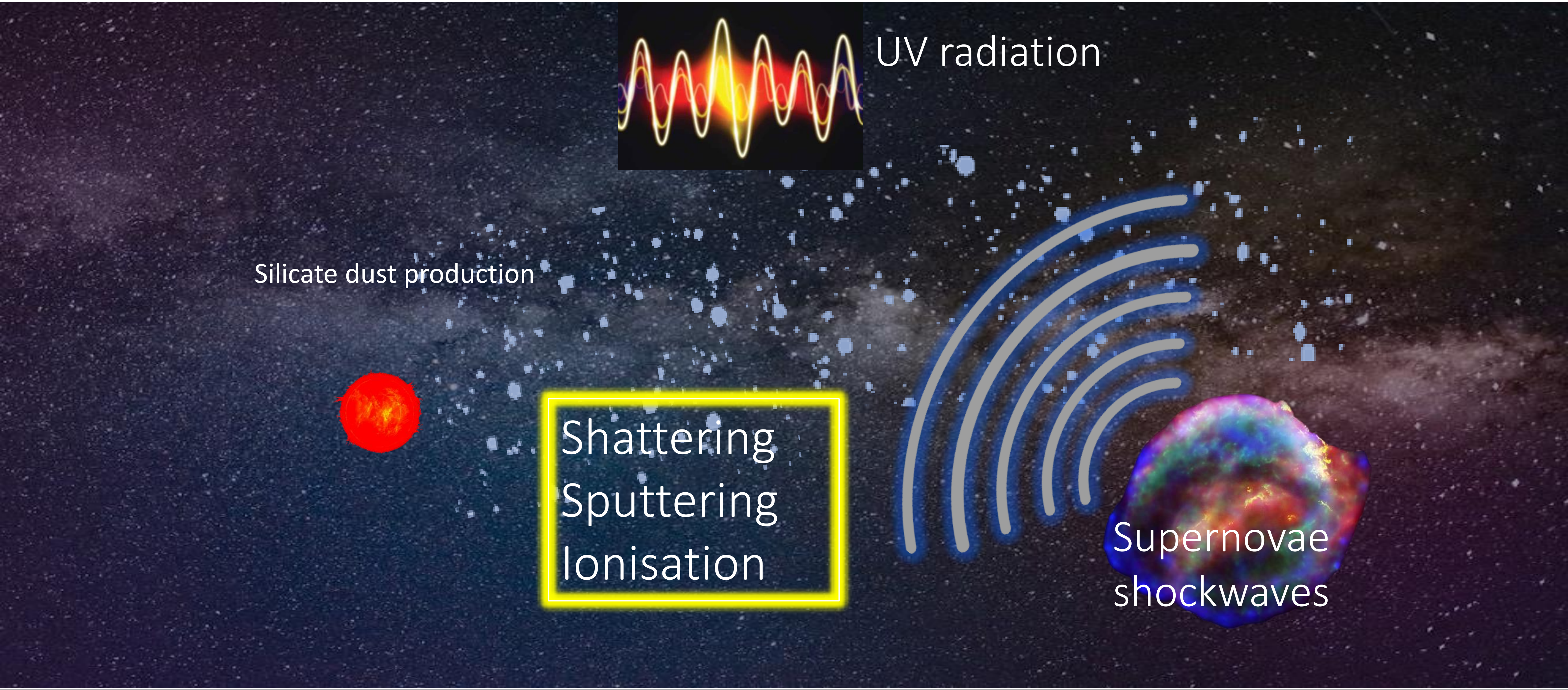
IR spectra of small nanosilicates



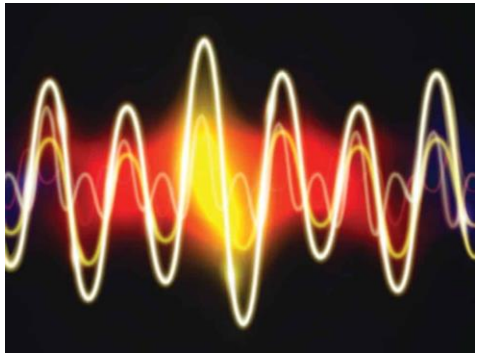
Most features captured by 0K harmonic calculations with some anharmonicity at moderate temperatures

Mariñoso, Macia, Bromley, *ACS Earth Space Chem.* (2021) 5, 812

Dust processing in the diffuse ISM

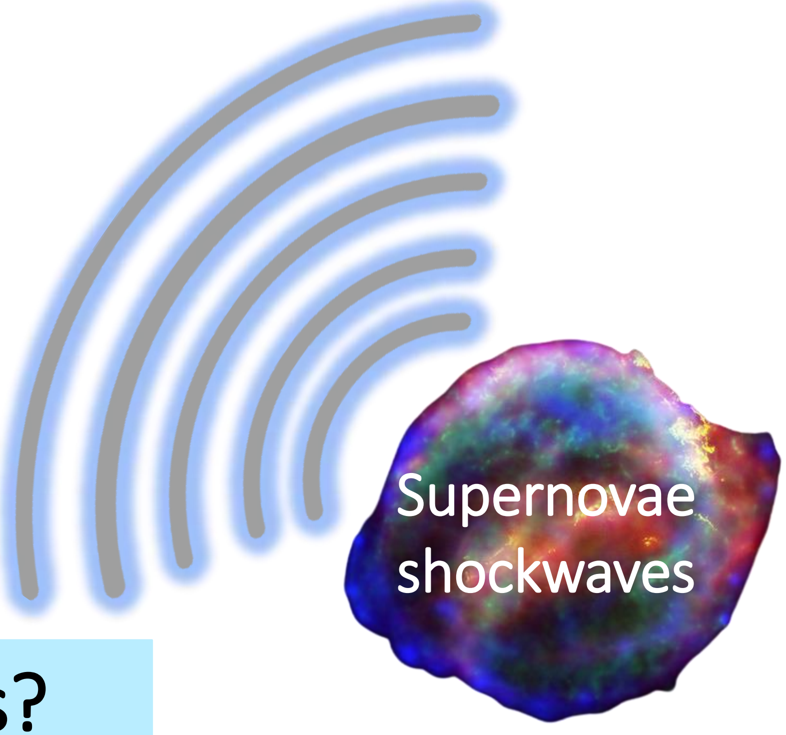


Dust processing in the diffuse ISM



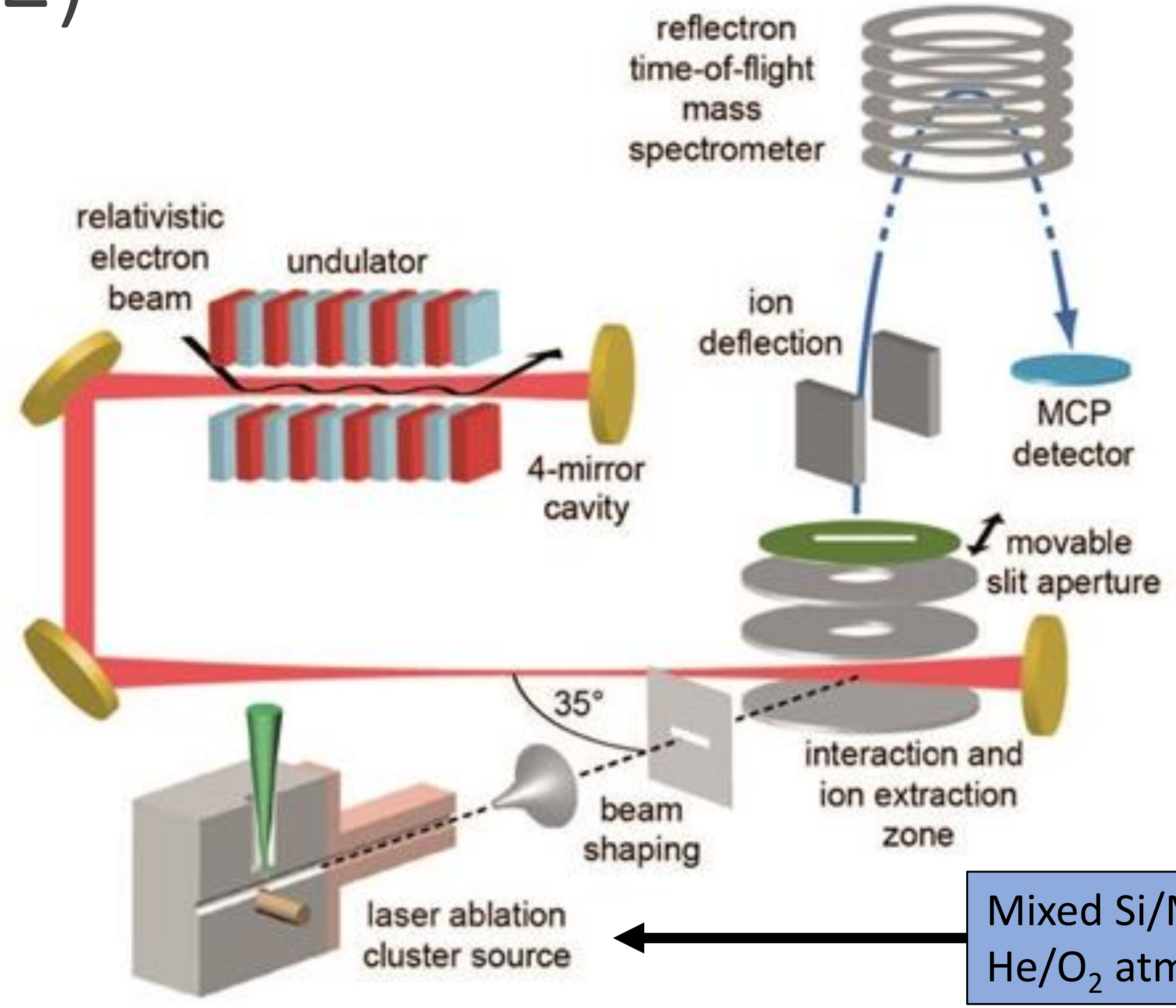
UV radiation

Shattering – smaller dust grains
Sputtering – reduced Mg (Olivine → Pyroxene)
Ionisation – cationic grains



ISM processing → Small cationic pyroxene species?

Free-Electron Laser for IntraCavity Experiments (FELICE)



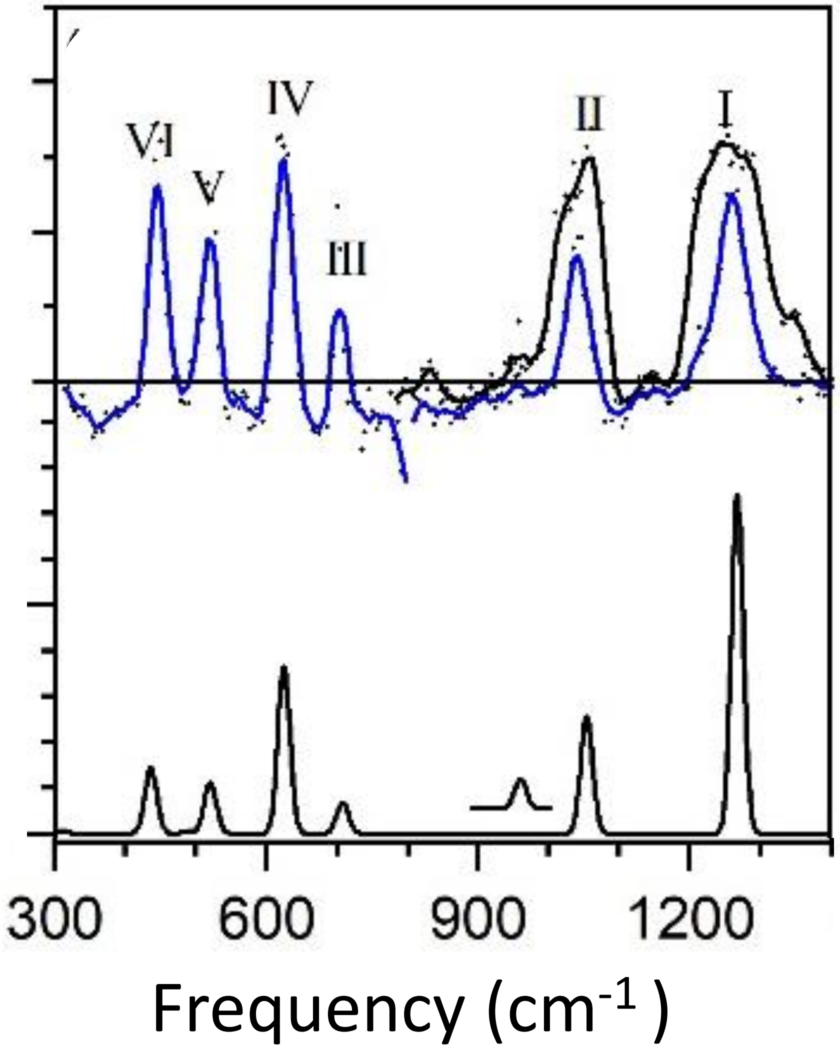
Can measure IR spectra of cluster ions in the range 5-100 μm / 2000 – 100 cm^{-1}

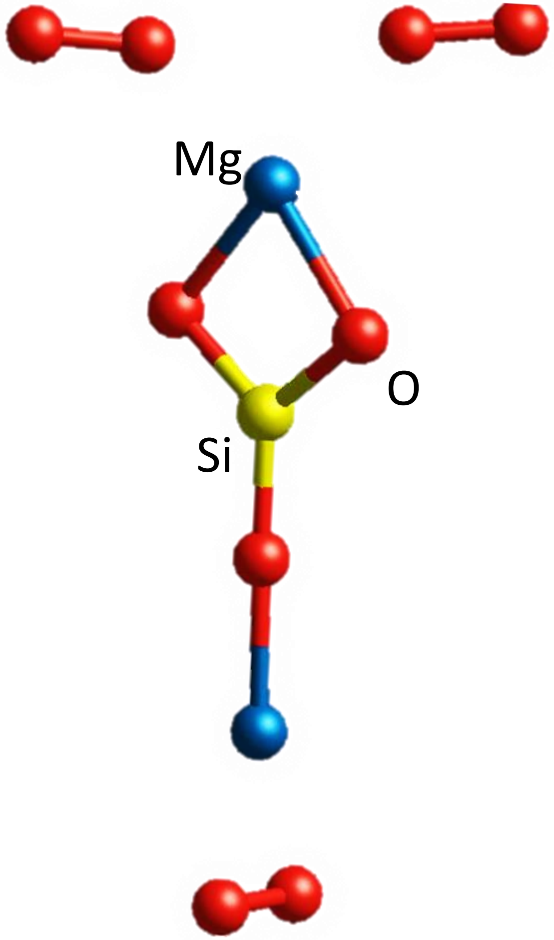
Mixed Si/Mg source with He/O_2 atmosphere

Experiment and theory for $(Mg_2SiO_9)^+$

Experiment (Free-Electron Laser for IntraCavity Experiments - FELICE)

Theory (Harmonic /DFT PBE0)





J. Mariñoso Guiu, B-A. Ghejan, T. M. Bernhardt, J. M. Bakker, S. M. Lang, STB, *ACS Earth and Space Chemistry*, 6, 2465 (2022)

Experiment and theory for $(MgSiO_9)^+$

Experiment (Free-Electron Laser for IntraCavity Experiments - FELICE)

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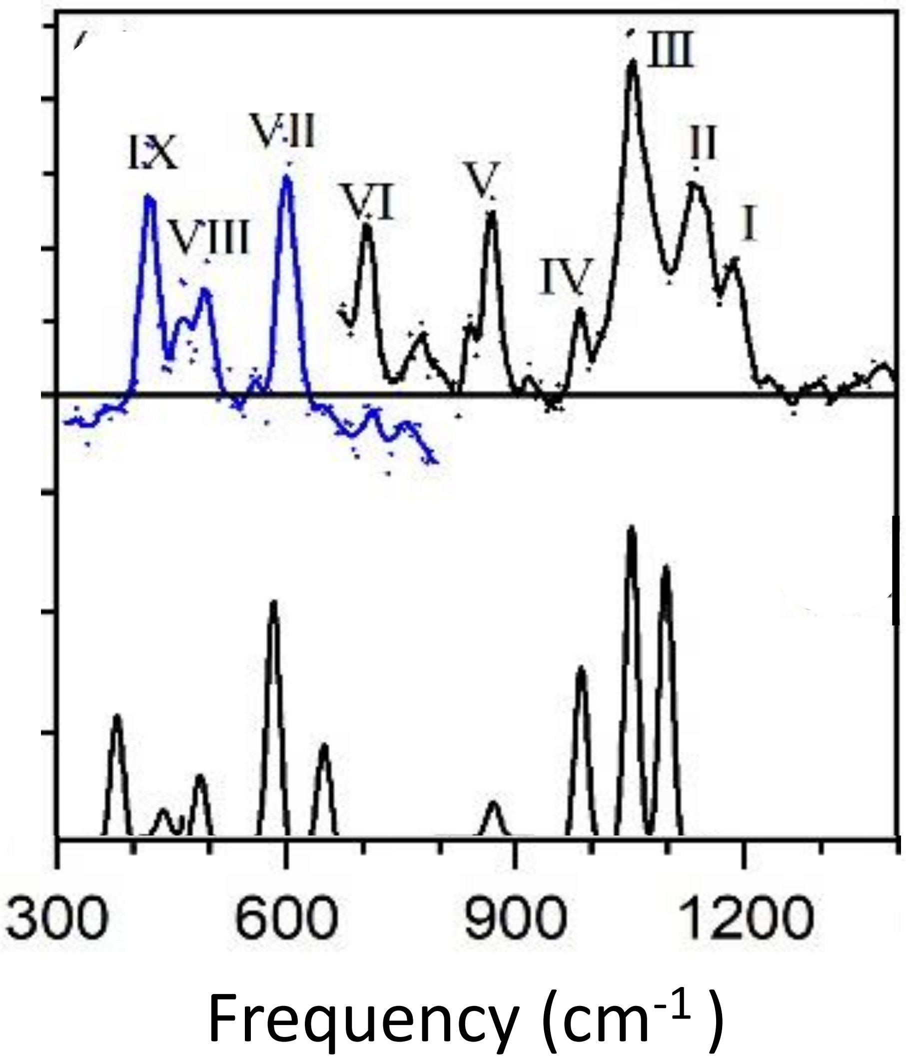
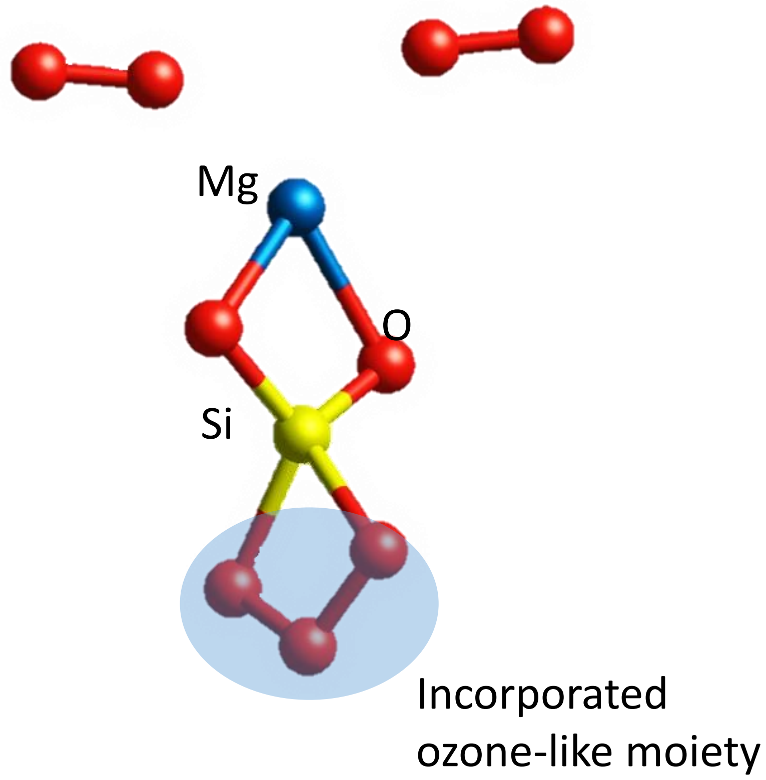
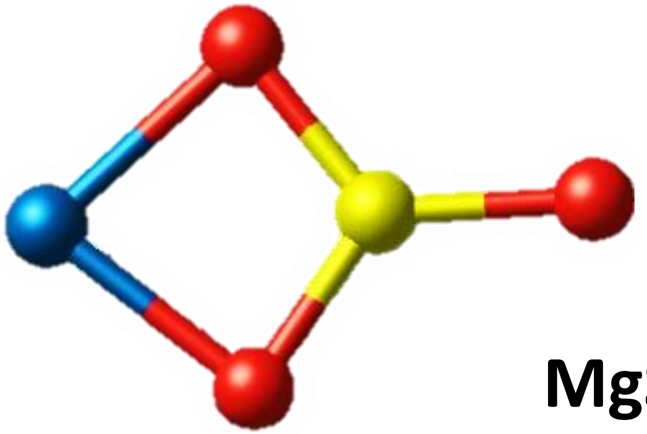




J. Mariñoso Guiu, B-A. Ghejan, T. M. Bernhardt, J. M. Bakker, S. M. Lang, S.TB, *ACS Earth and Space Chemistry*, 6, 2465 (2022)

Implications for silicates in the ISM



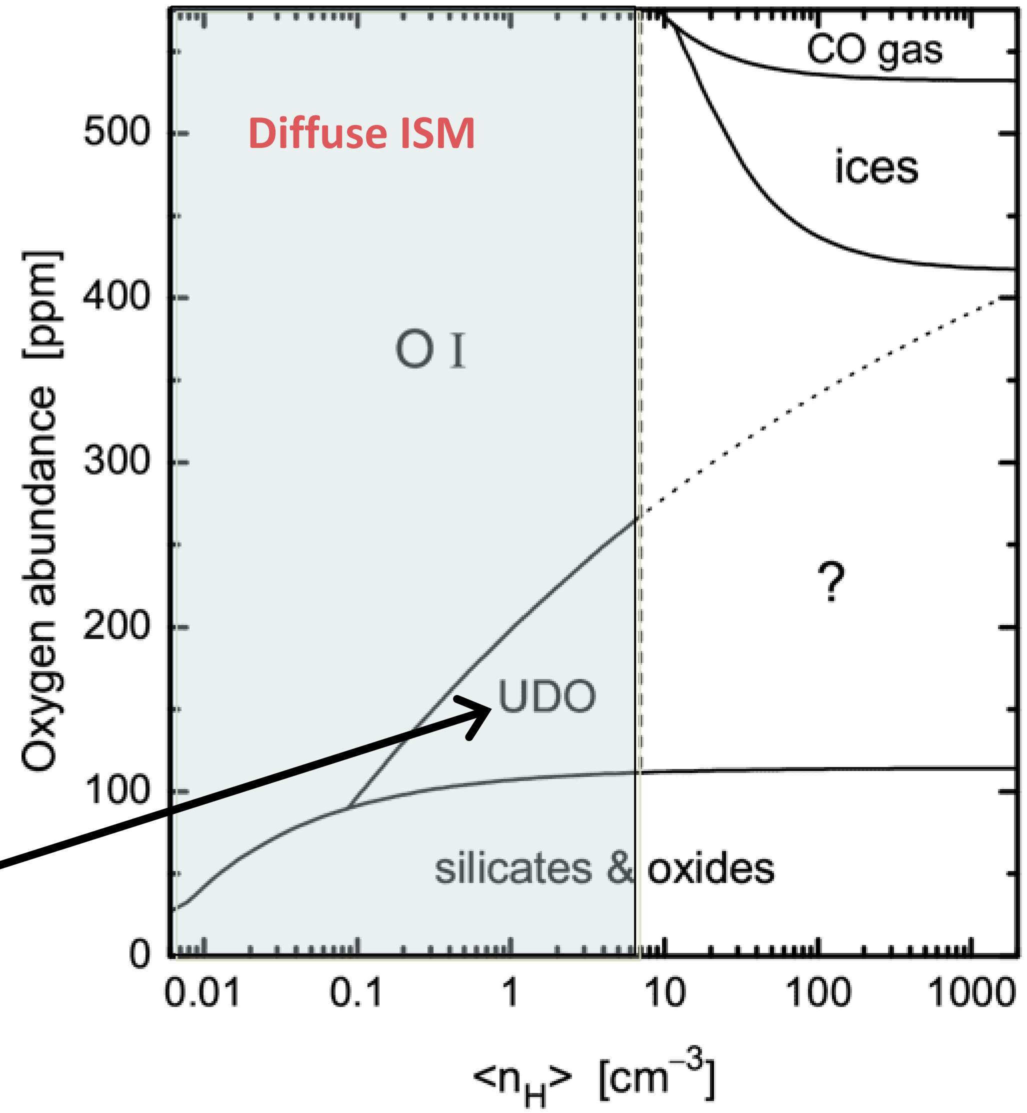
$MgSiO_3$ Pyroxene monomer

- All clusters found to be based on the $MgSiO_3$ monomer
- Previously assumed to be stable only part of bulk pyroxene solid
- Strongly interacts with oxygen molecules and Mg
- Highly dipolar species

Oxygen Depletion in the Diffuse ISM

- O_2 molecules predicted to be very common species in the ISM
- Only very rarely observed
- General depletion of oxygen in the ISM

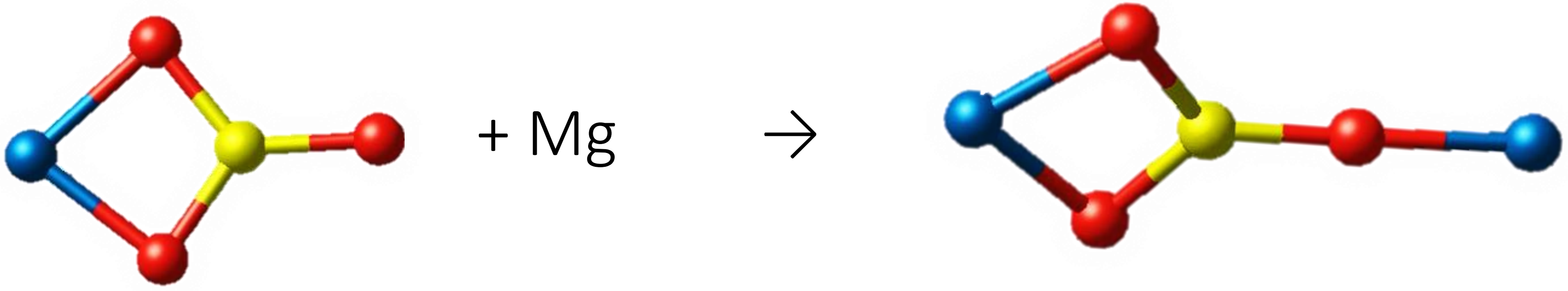
Need new oxygen sink – $(MgSiO_3)^+$?



Dust destruction and growth in the ISM?

Long-standing conundrum….

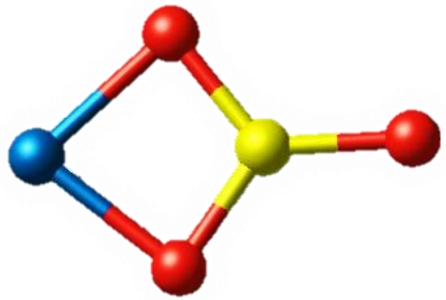
Time scale for dust formation from evolved stars	>	Time scale for dust destruction in the iSM

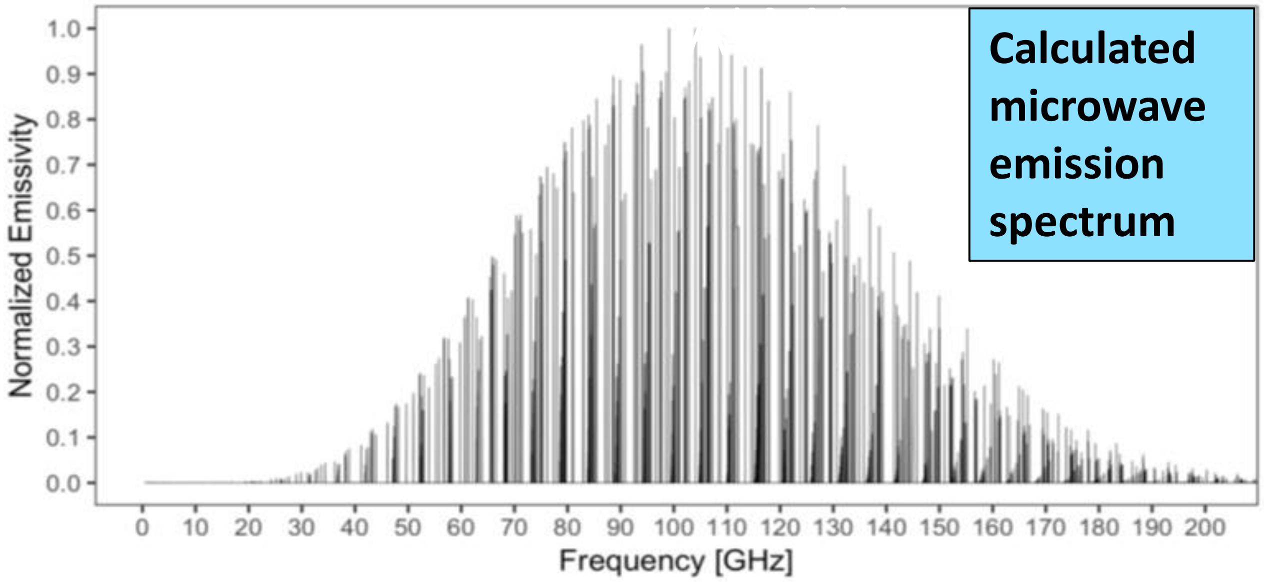


Seeds for dust (re)formation in the ISM?

Microwave signatures of pyroxene monomers?

$MgSiO_3$



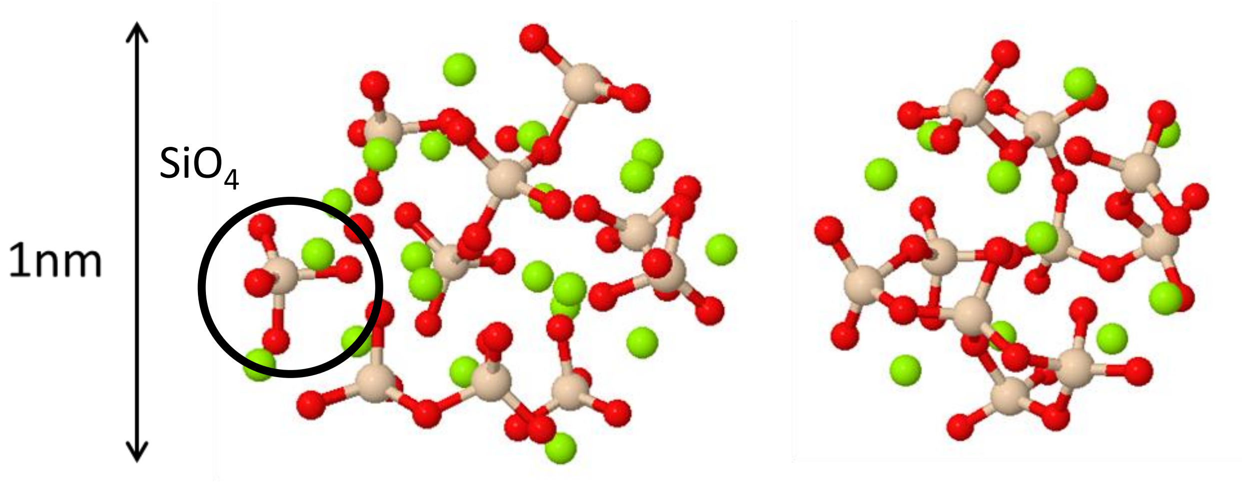


Calculated microwave emission spectrum

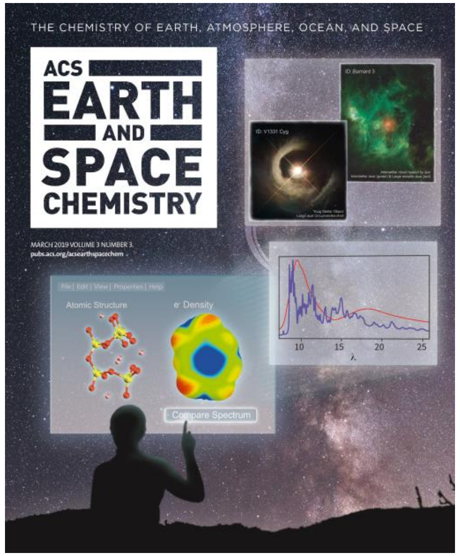
Macia & Bromley, A&A (2020) 634, A77

From the molecular scale to the nanoscale

- Global optimisation searches used to find the lowest energy structures for nanosilicates with diameters ≤ 1nm
- Structure and properties evaluated using accurate quantum chemical calculations



$(Mg_2SiO_4)_{10}$ $(MgSiO_3)_{10}$



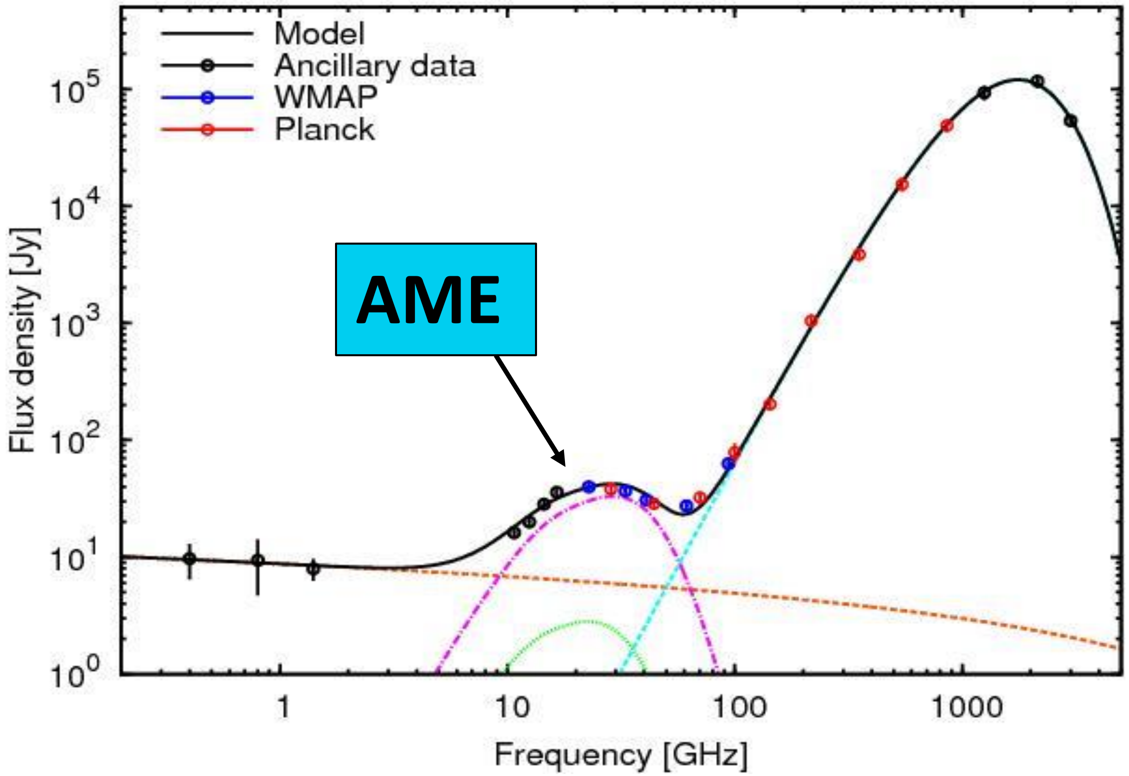
A. Macià Escatllar, T. Lazaukas, S. M. Woodley, STB, *ACS Earth and Space Chemistry*, 3, 2390 (2019)

Small nanosilicates have intrinsically non-crystalline structures and are highly dipolar

Nanosilicates and the Anomalous Microwave Emission (AME)

- **AME** observed as peak at ~30 GHz with 10 - 60 GHz range

- Observed in the interstellar medium (ISM), galactic clouds and circumstellar environments (*Dickinson+ New Astro Rev 2018*)

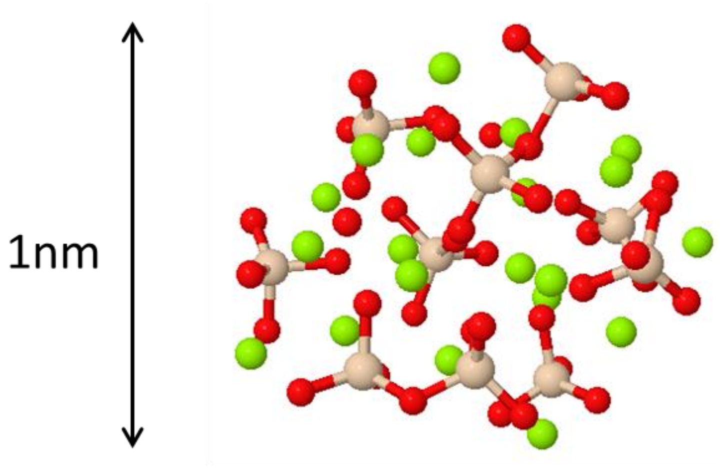


- Dust grains spin in the ISM due to collisions with gas atoms and other processes

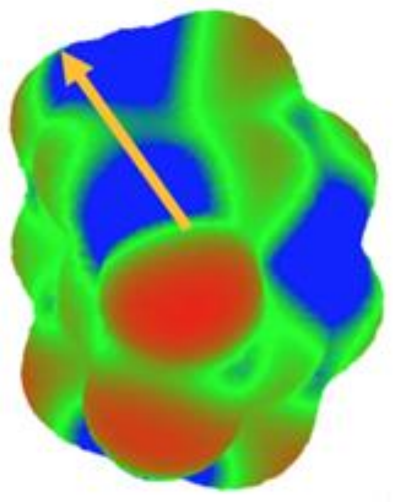
- 30 GHz emission constrains properties of spinning dust: **≤ 1 nm size, high dipoles**

- Spinning nanosilicates currently best candidate for AME carrier? (*Hoang+ ApJ 2016, Hensley & Draine ApJ 2017*)

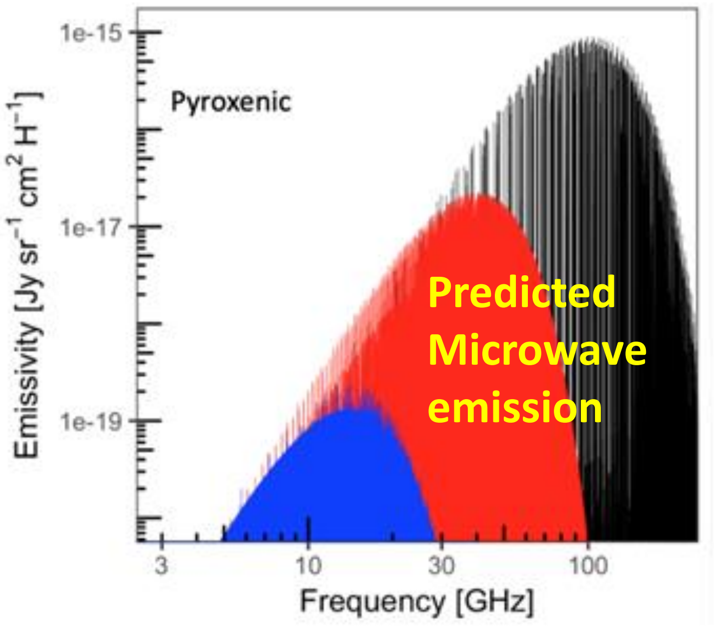
Bottom-up evaluation of microwave emission from nanosilicates



Dipole calculated from charge distribution



Spinning dipolar species generate microwave emission

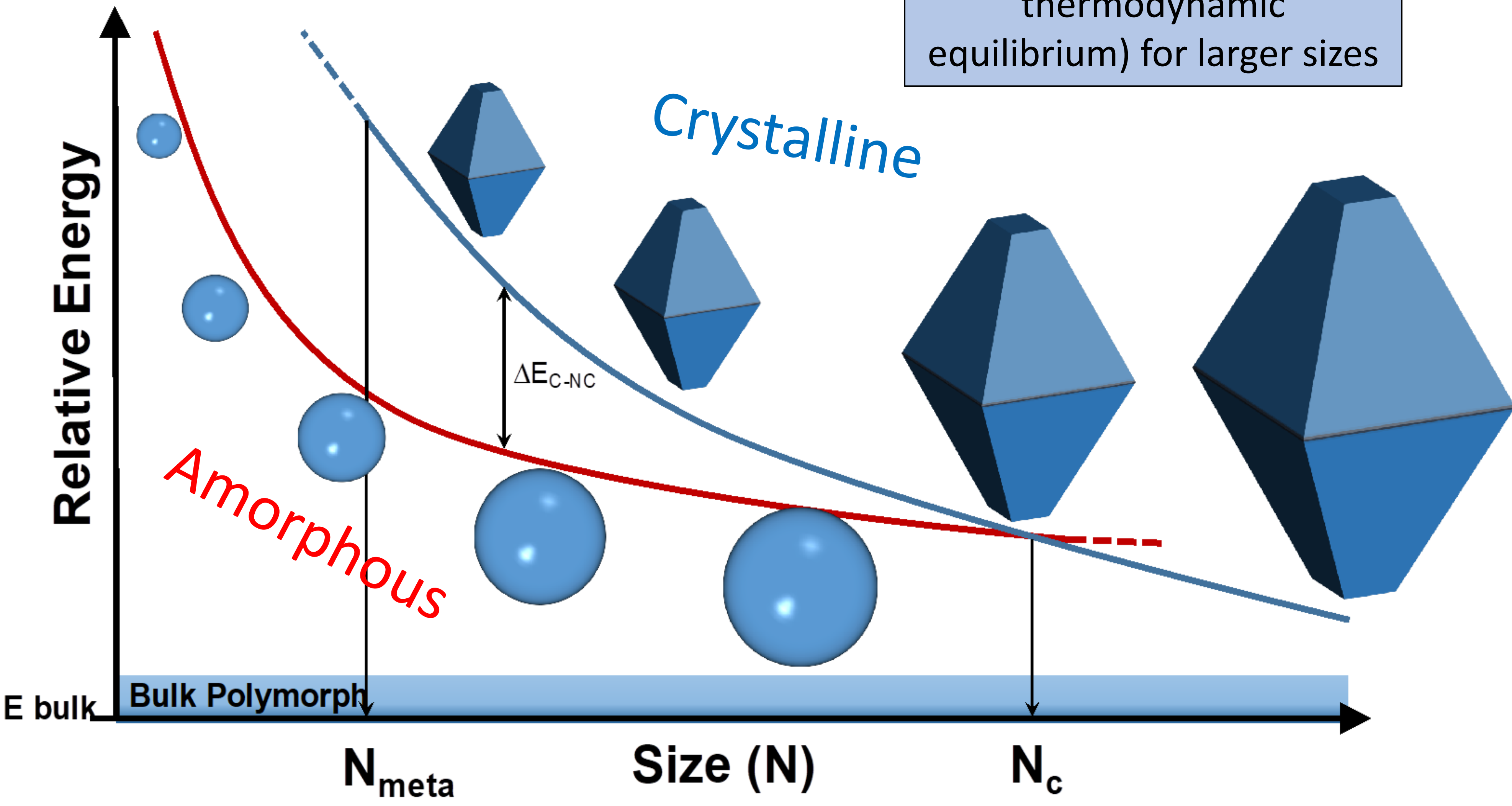


We predict that silicate nanoclusters containing only 1% of the total Si budget can reproduce the AME signal.

Macia & Bromley, *Astronomy & Astrophysics* (2020) 634, A77

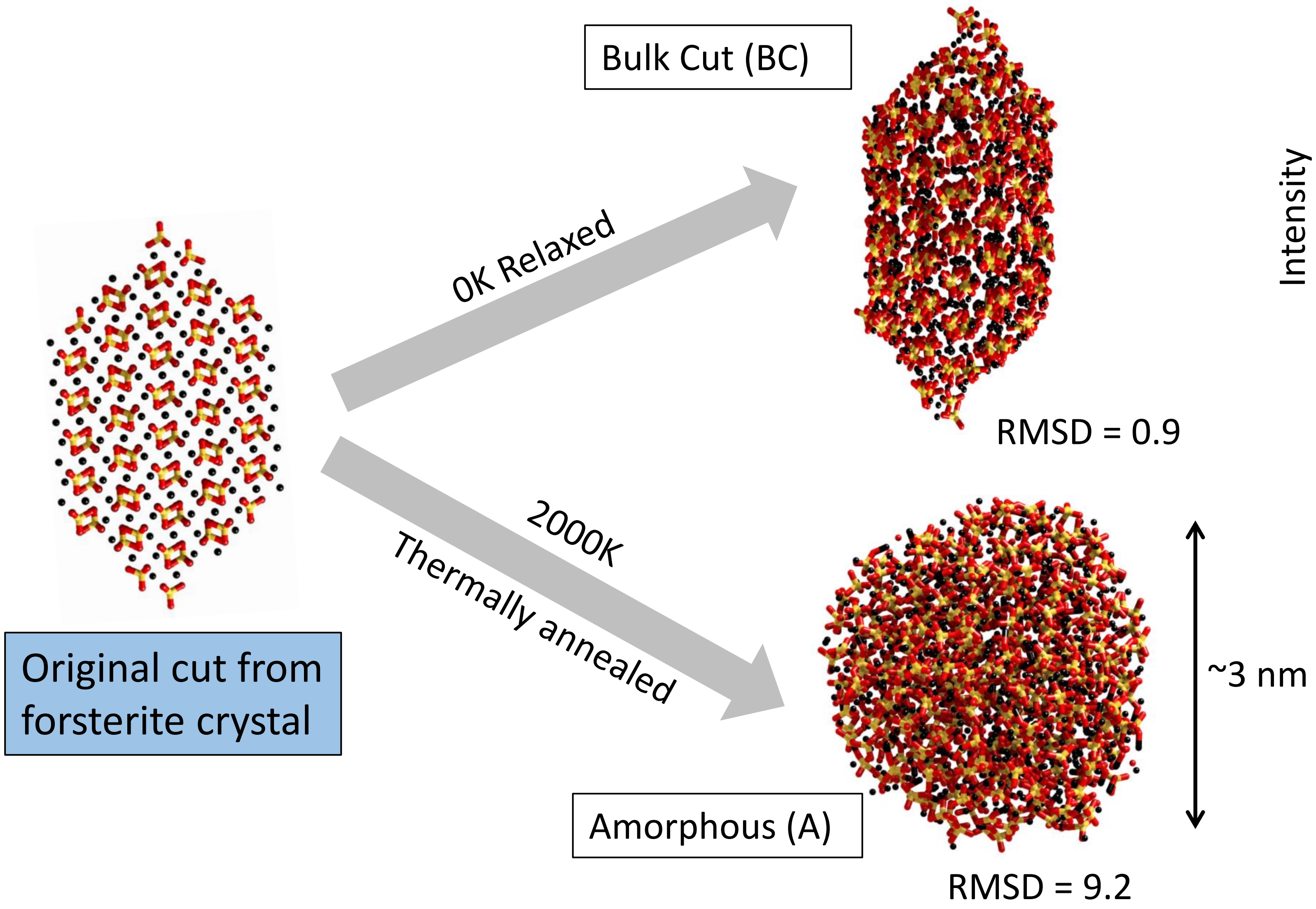
Size-dependency of crystallinity

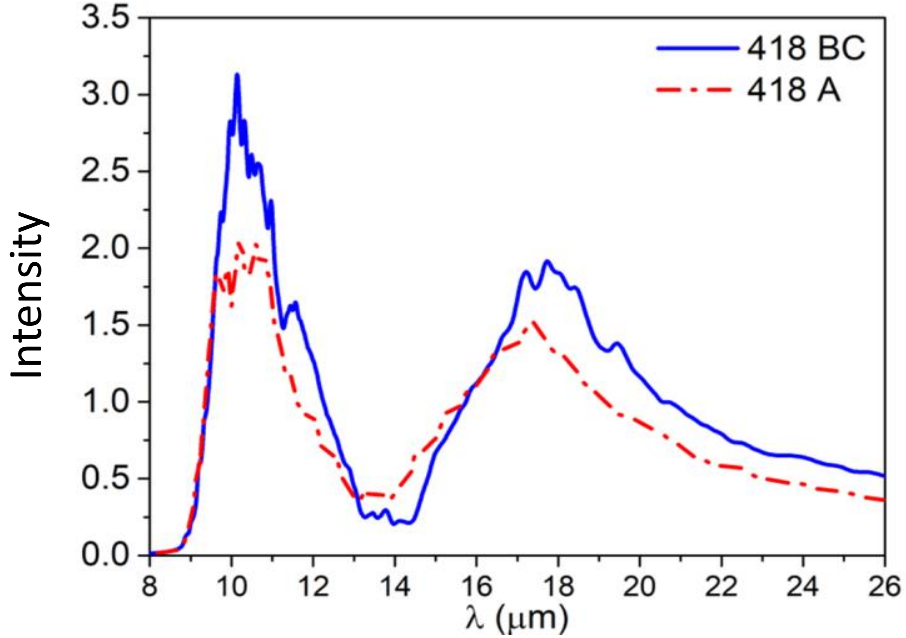
Crystalline grains are only energetically favoured (at thermodynamic equilibrium) for larger sizes



Non-crystalline grains are favoured for smaller grains and via energetic processing

Amorphicity and crystallinity at the nanoscale…

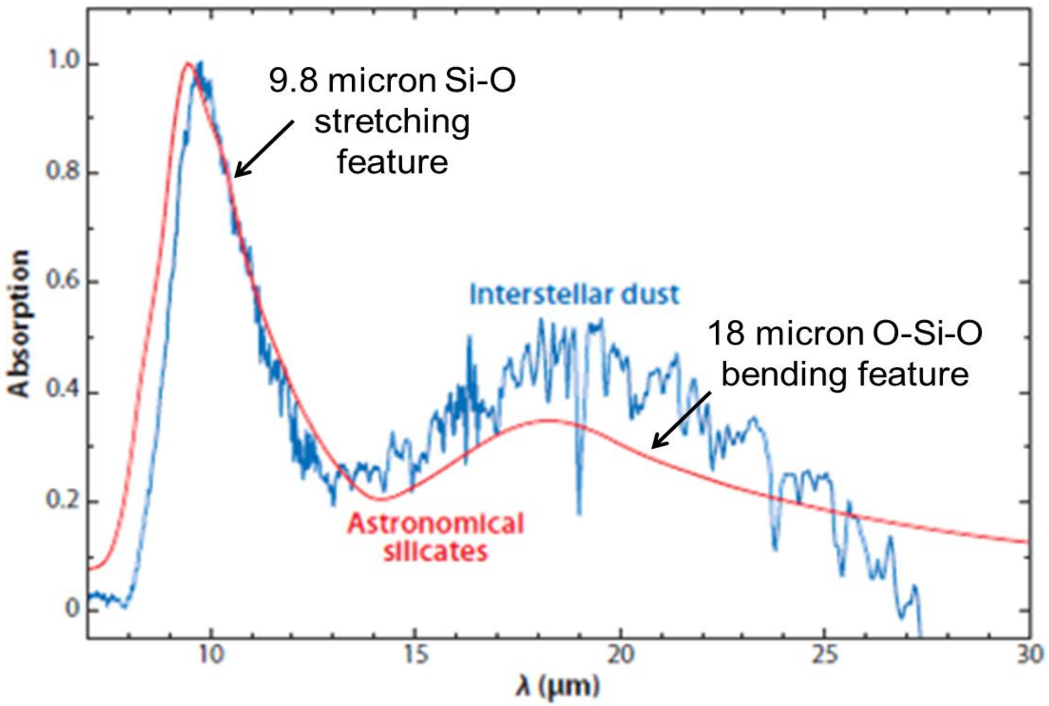




Little difference between amorphous and crystalline IR spectra for nanosilicates

Zamirri, Macia, Mariñoso, Ugliengo, Bromley, *ACS Earth Space Chem.* (2019) 3, 2323.

Size dependency of nanosilicate IR features



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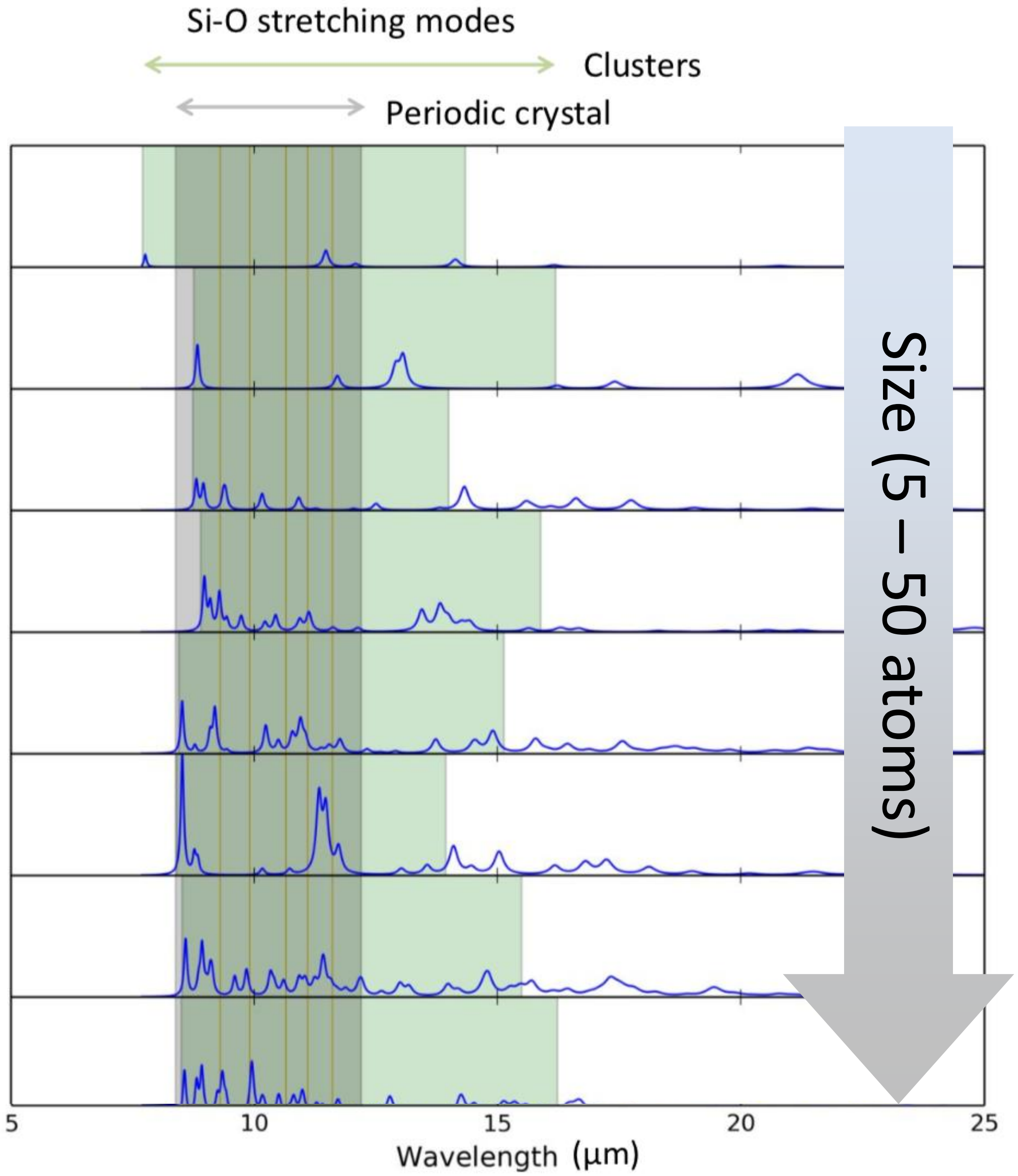
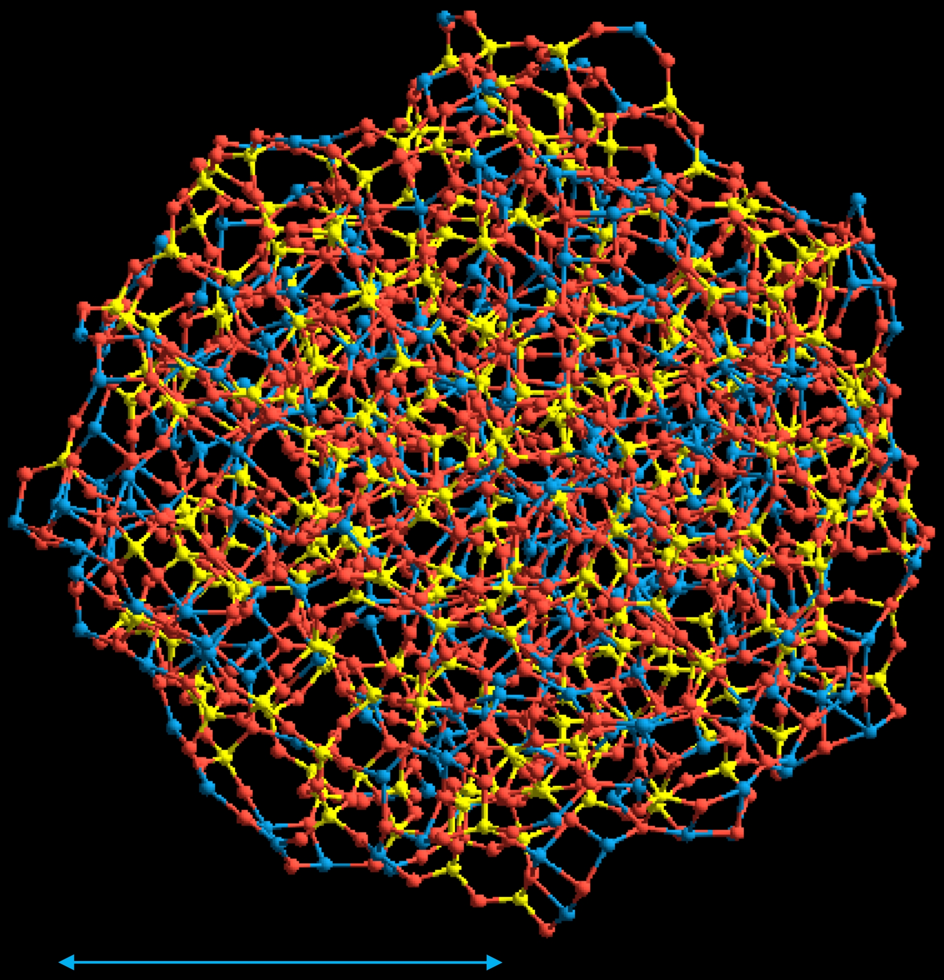


Size dependency of nanosilicate IR features

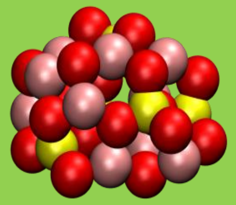
- Nanosilicates with up to ~1500 atoms
- Computationally very costly with DFT
- Use classical atomistic forcefield to model the grains
- Simulate circumstellar (~1000K) nucleation process



Radius ~ 1.7 nm

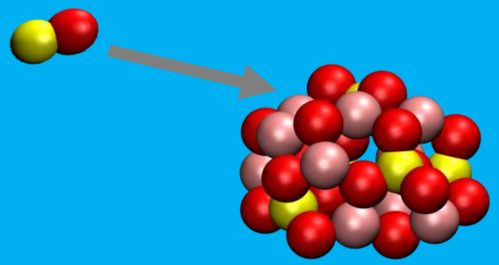
Atomistic modelling of dust grain growth

INITIALISE



Seed cluster with a desired temperature and stoichiometry

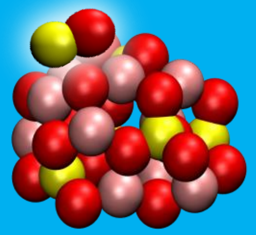
SELECTION



1. Monomer (e.g. SiO, Mg) with stoichiometry-related probability
2. Temperature-dependent velocity vector

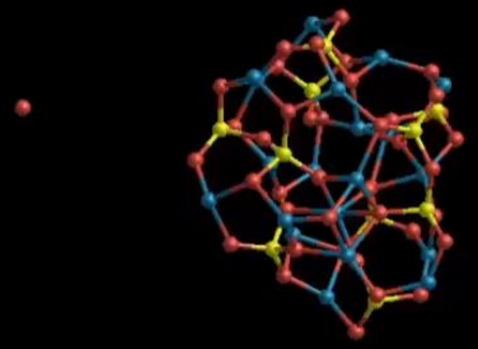
REPEAT

MOLECULAR DYNAMICS

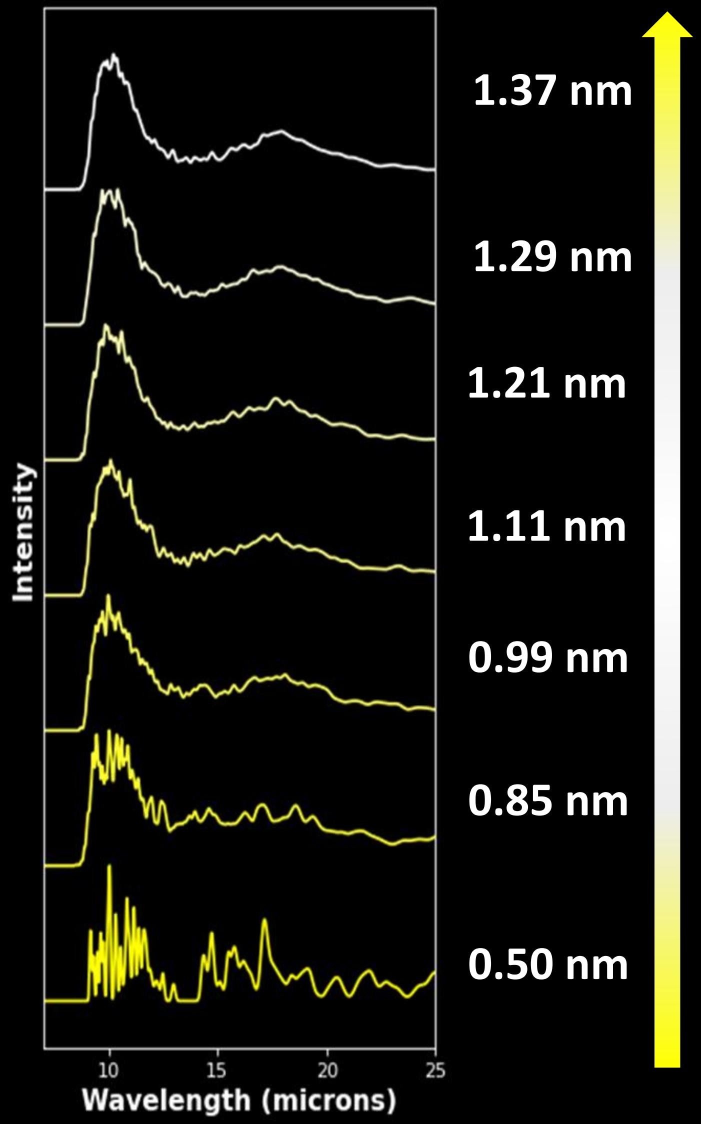


1) Collide monomer with grain
2) Cool the grain to the ambient temperature

Size dependency of nanosilicate IR features

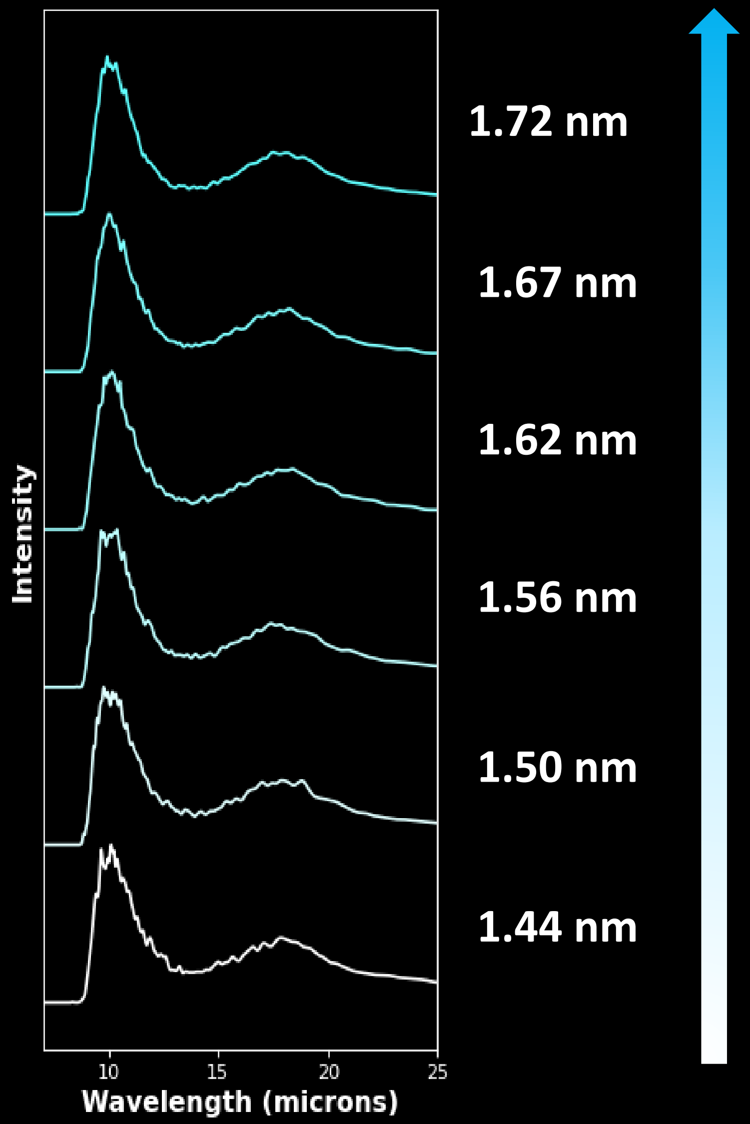


Size dependency of nanosilicate IR features

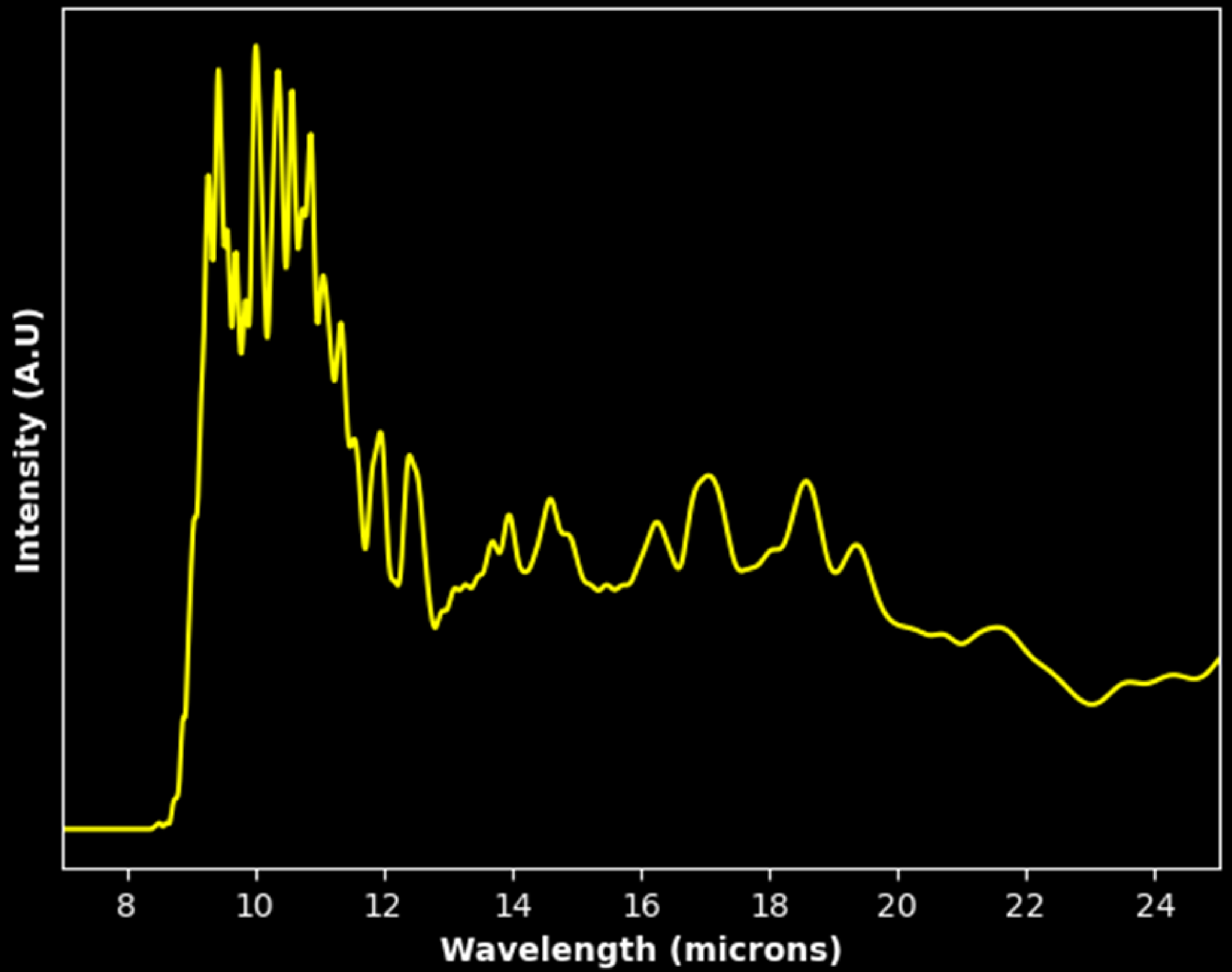


- Use forcefield that well-reproduces silicate IR spectra
- Nanosilicate features disappear slowly as the particle grows
- From ~1.5 nm radius spectra looks bulk-like

TYPICAL SILICATE SPECTRA APPEAR ~1.5nm

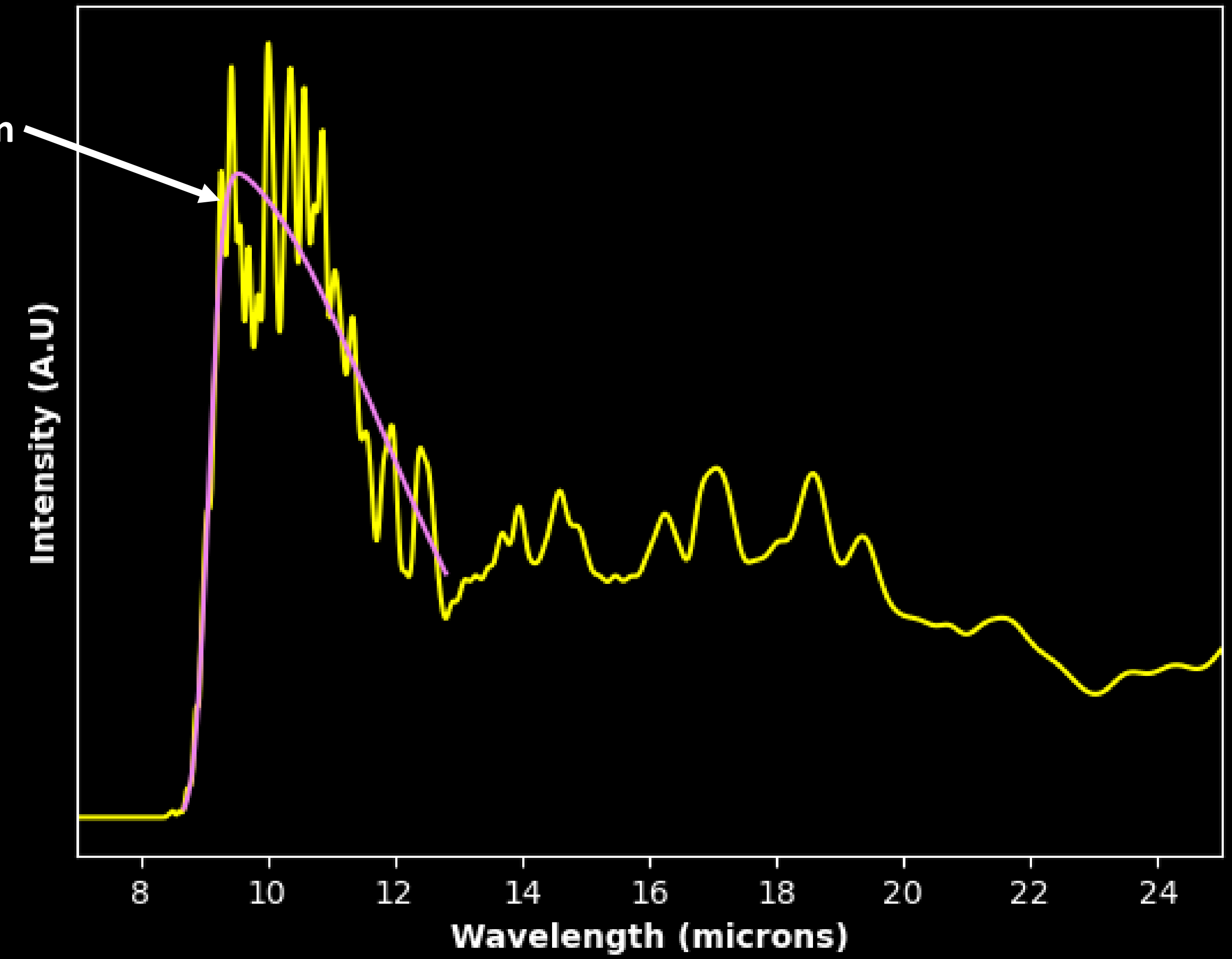


Size dependency of nanosilicate IR features

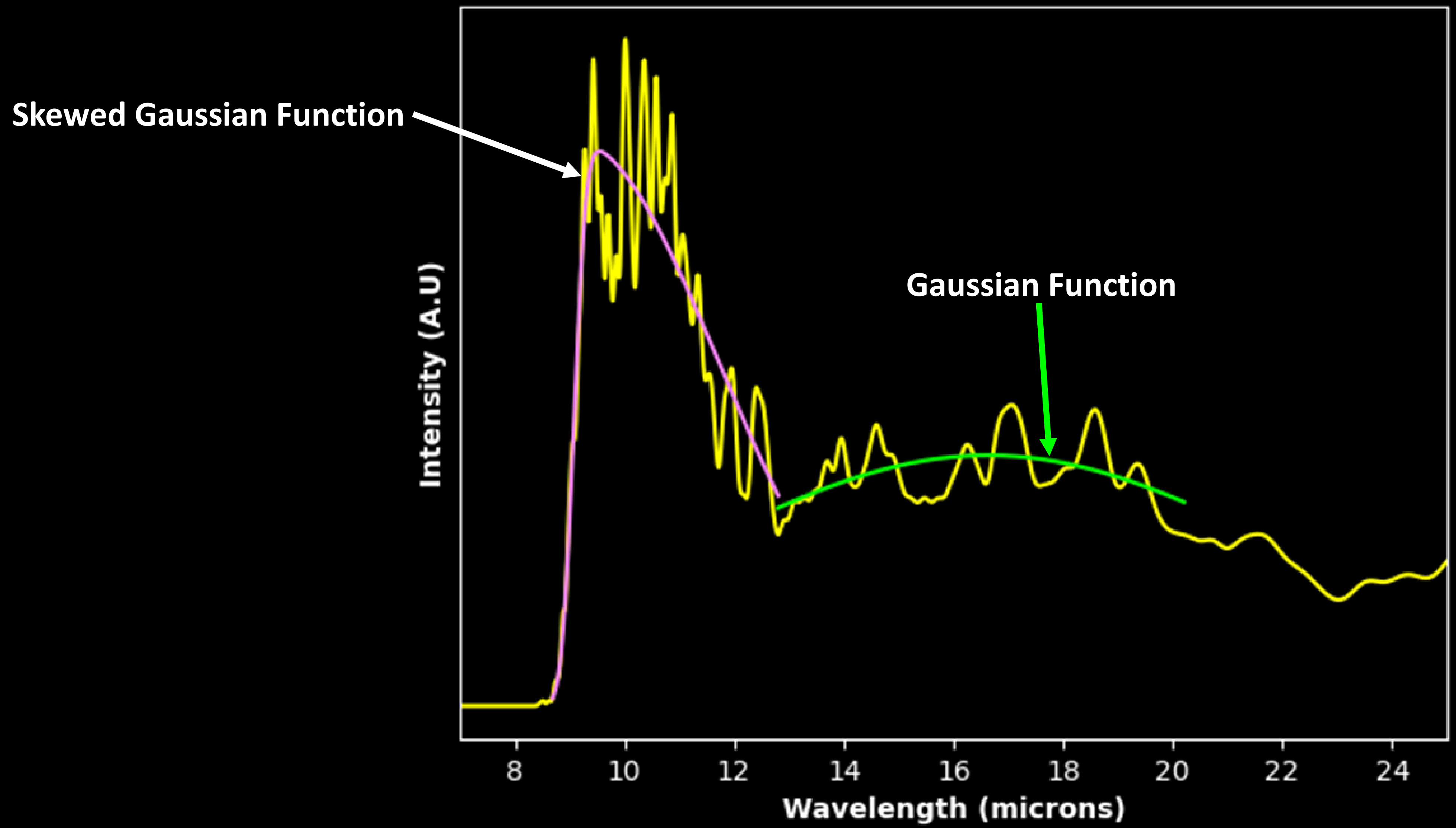


Size dependency of nanosilicate IR features

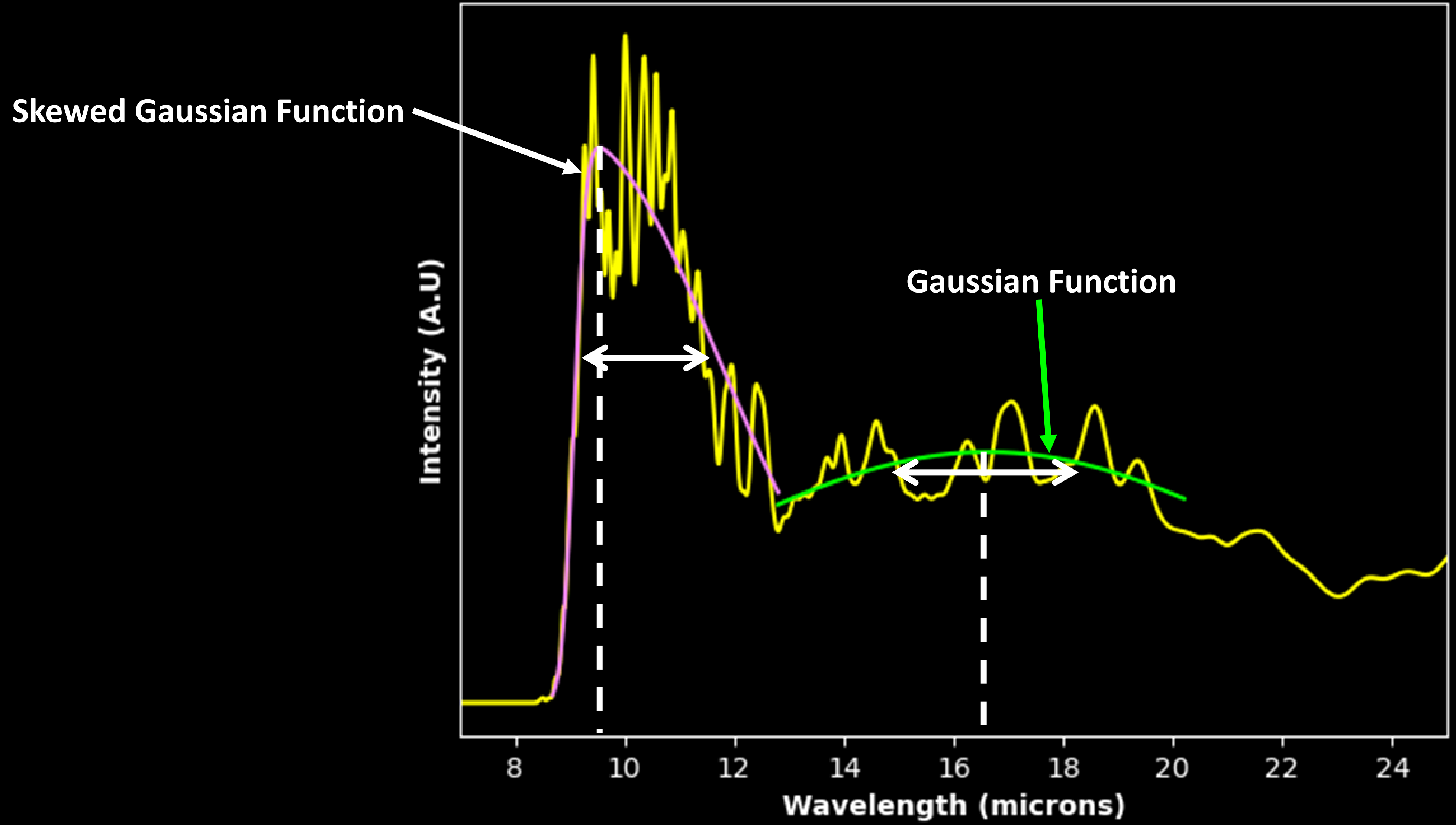
Skewed Gaussian Function



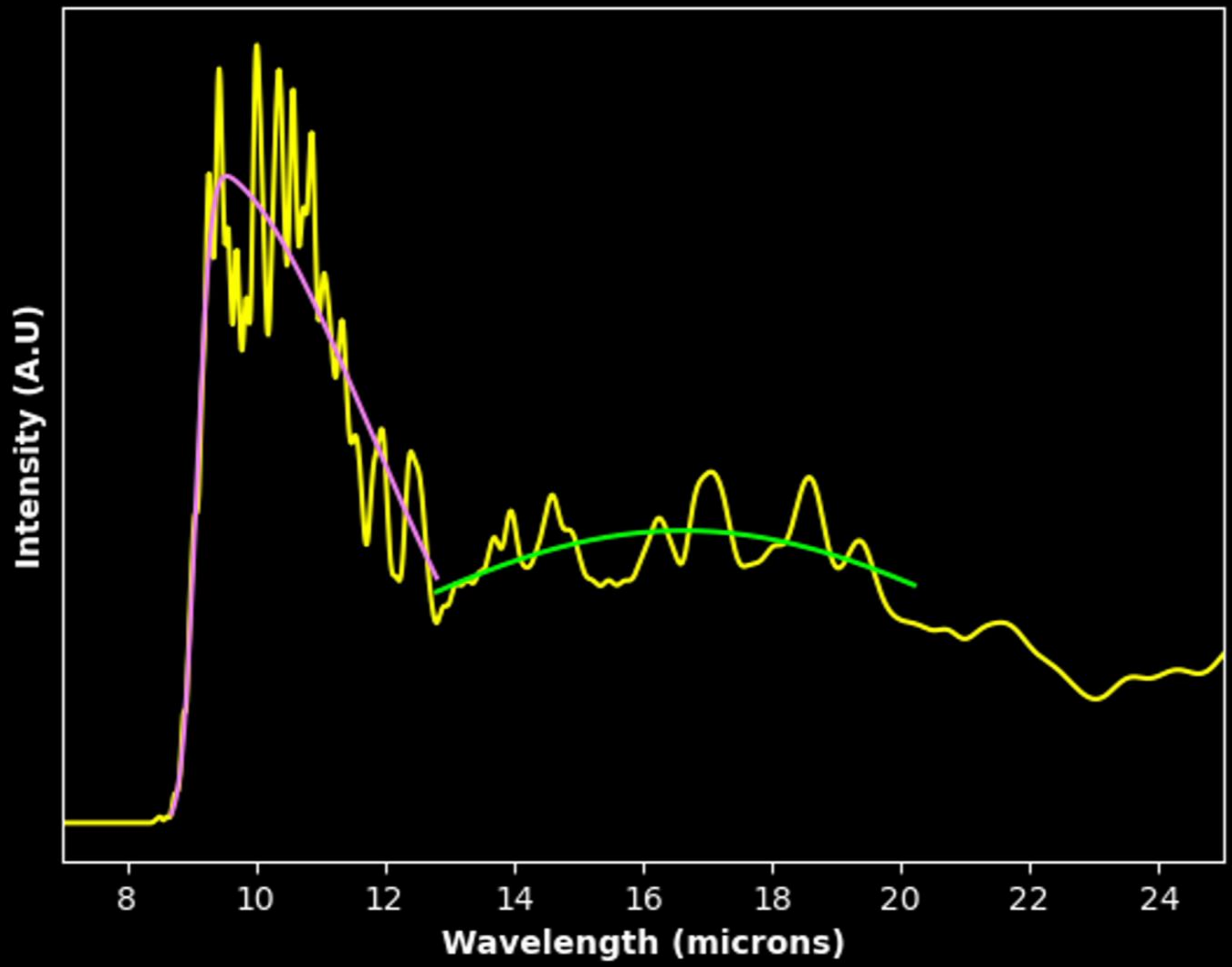
Size dependency of nanosilicate IR features

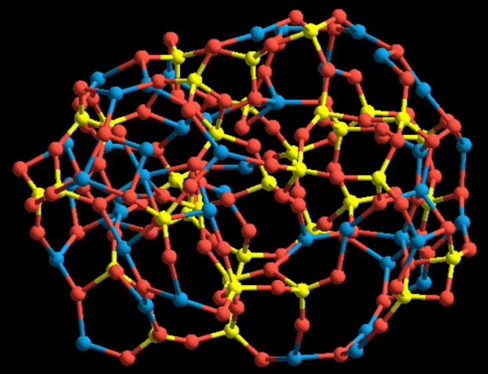


Size Dependency of Nanosilicate IR Features



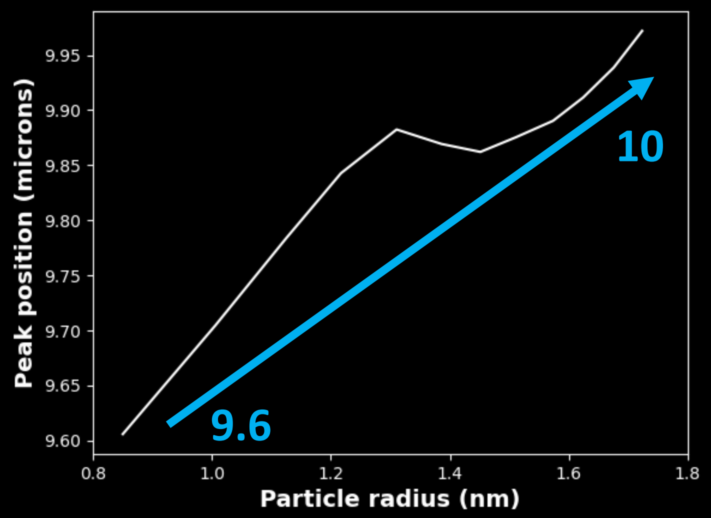
Size Dependency of Nanosilicate IR Features

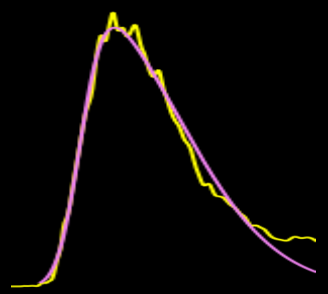




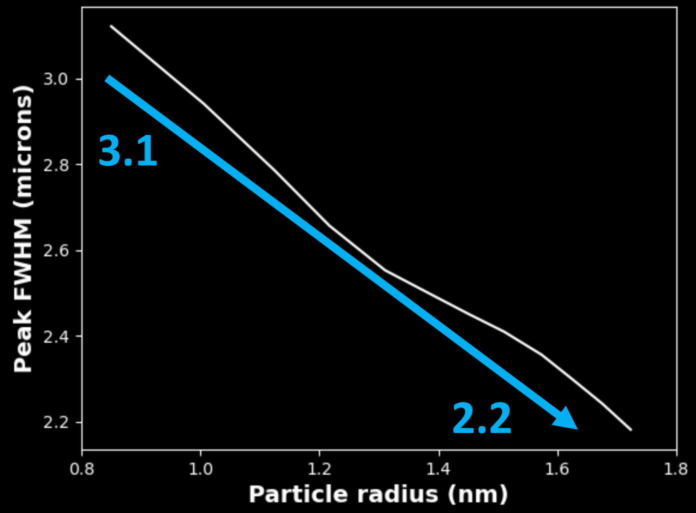
Radius = 0.85 nm

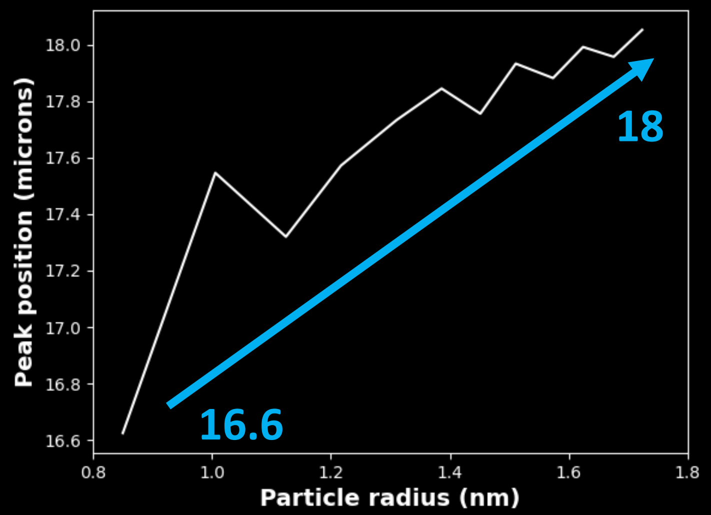
Size Dependency of Nanosilicate IR Features

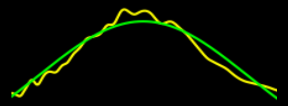




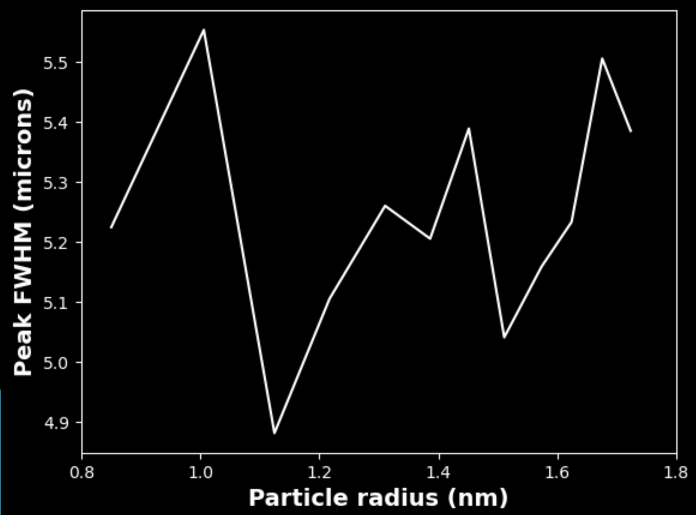
- Shifting towards 10 microns
  - Signal Narrows





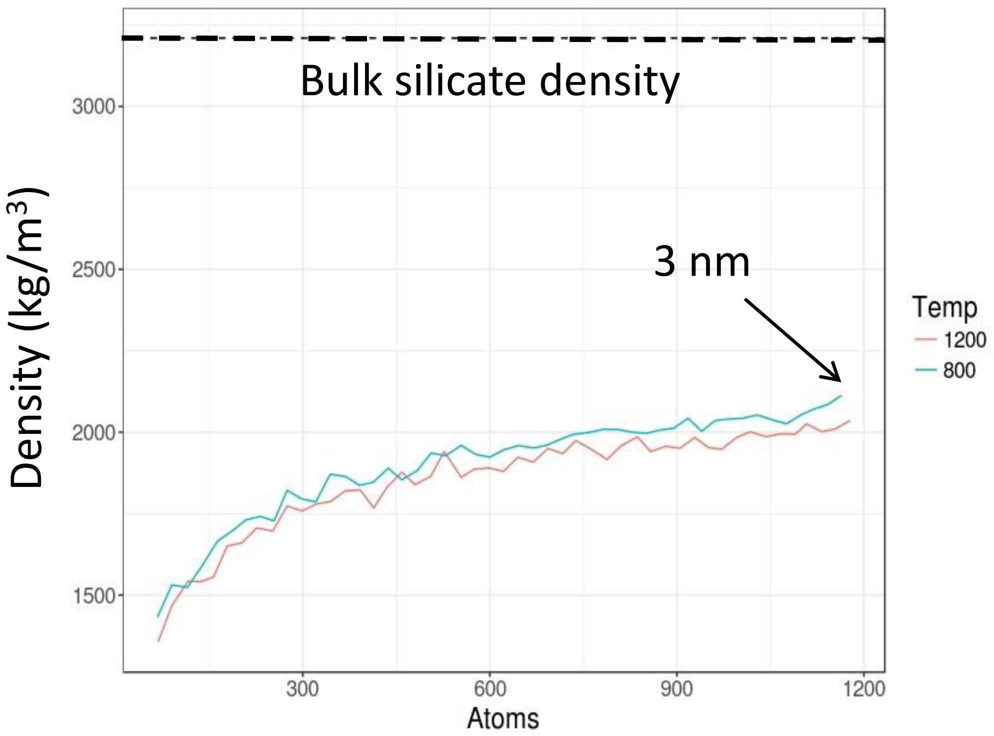


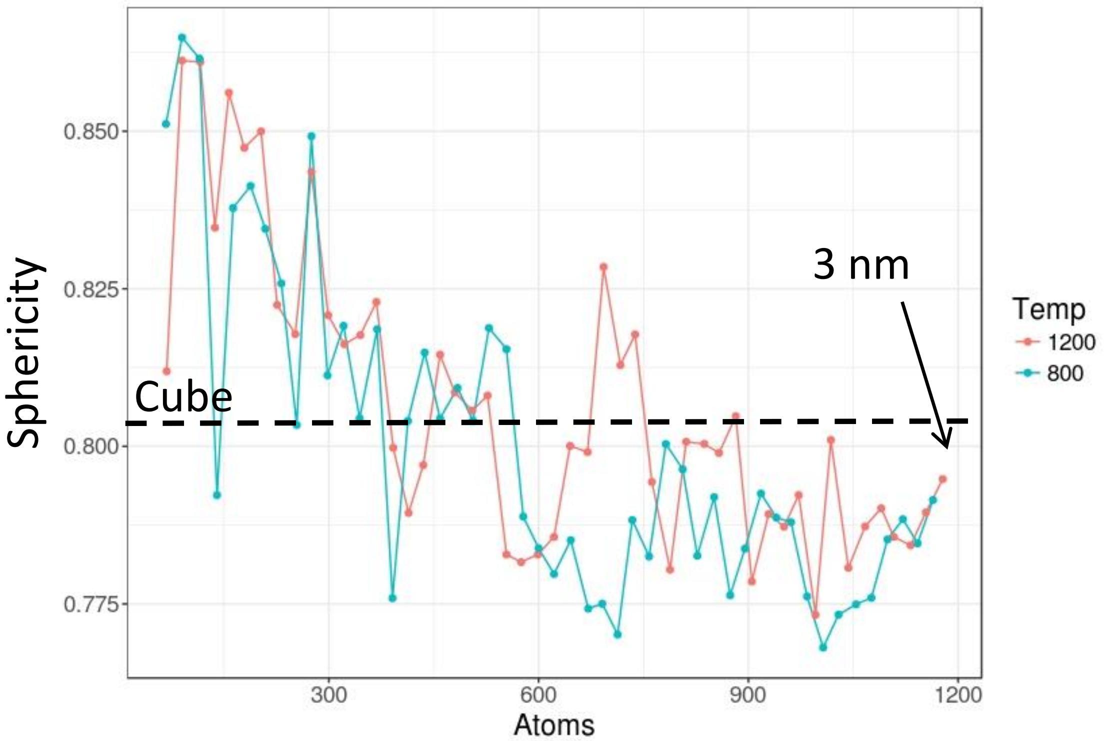
- Shifting towards 18 microns
  - Broadening ~constant

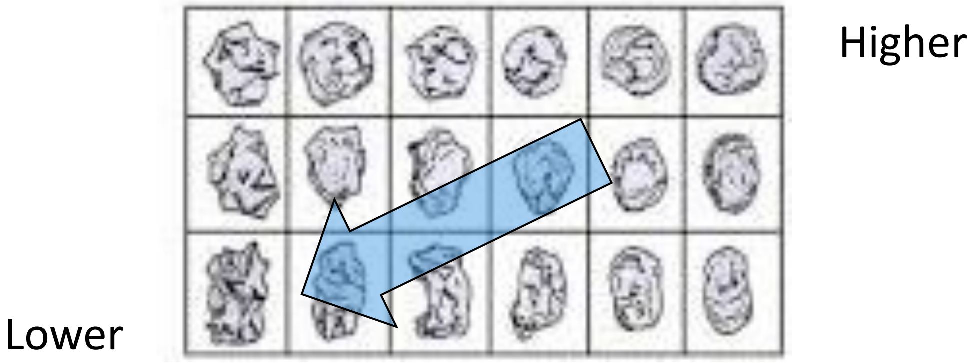


TYPICAL SILLICATE SIGNALS APPEAR FOR RADIUS ~1.5 nm

Density and sphericity of growing nanosilicate grains



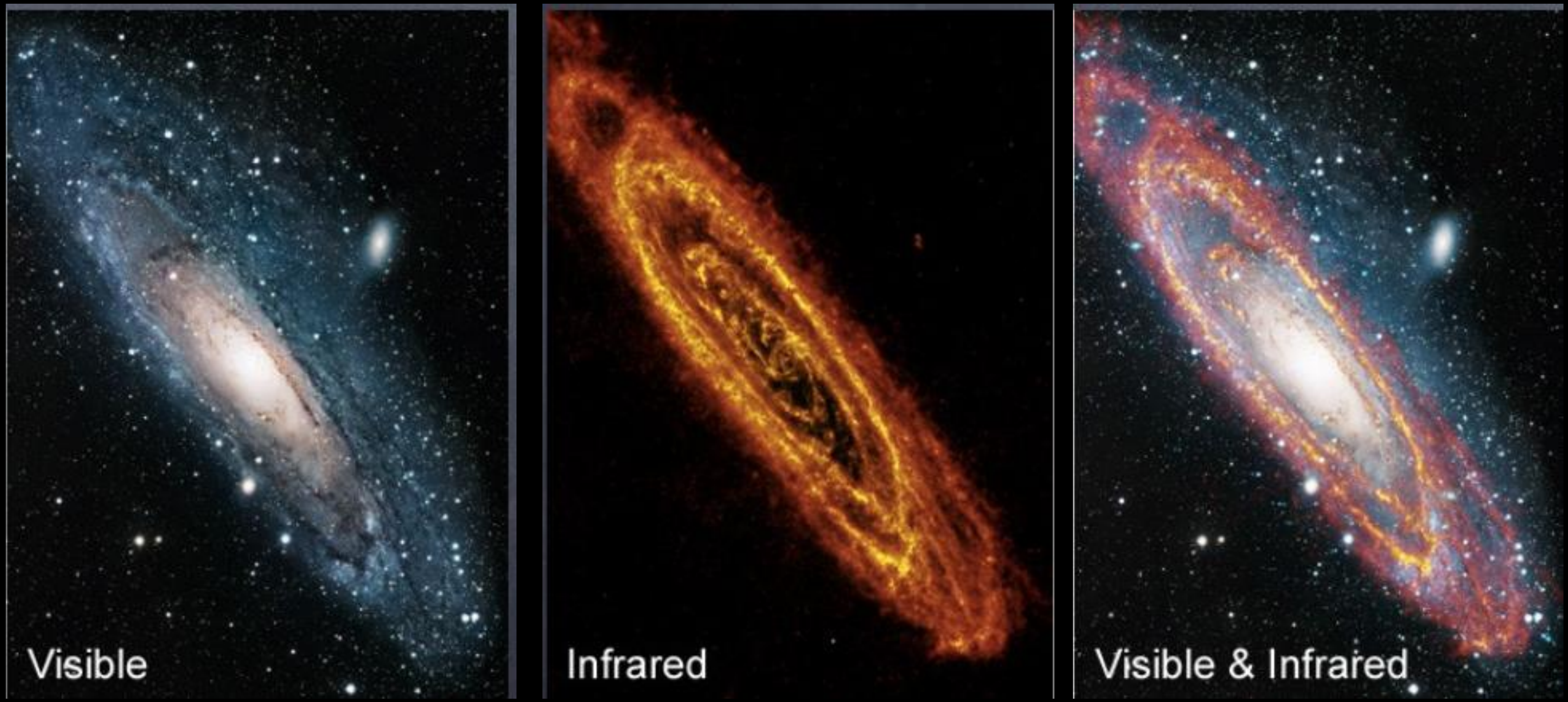




Density increases with increasing size to an apparent limiting value - independent of temperature

Limiting value appears to be approximately 70% of bulk crystalline silicate

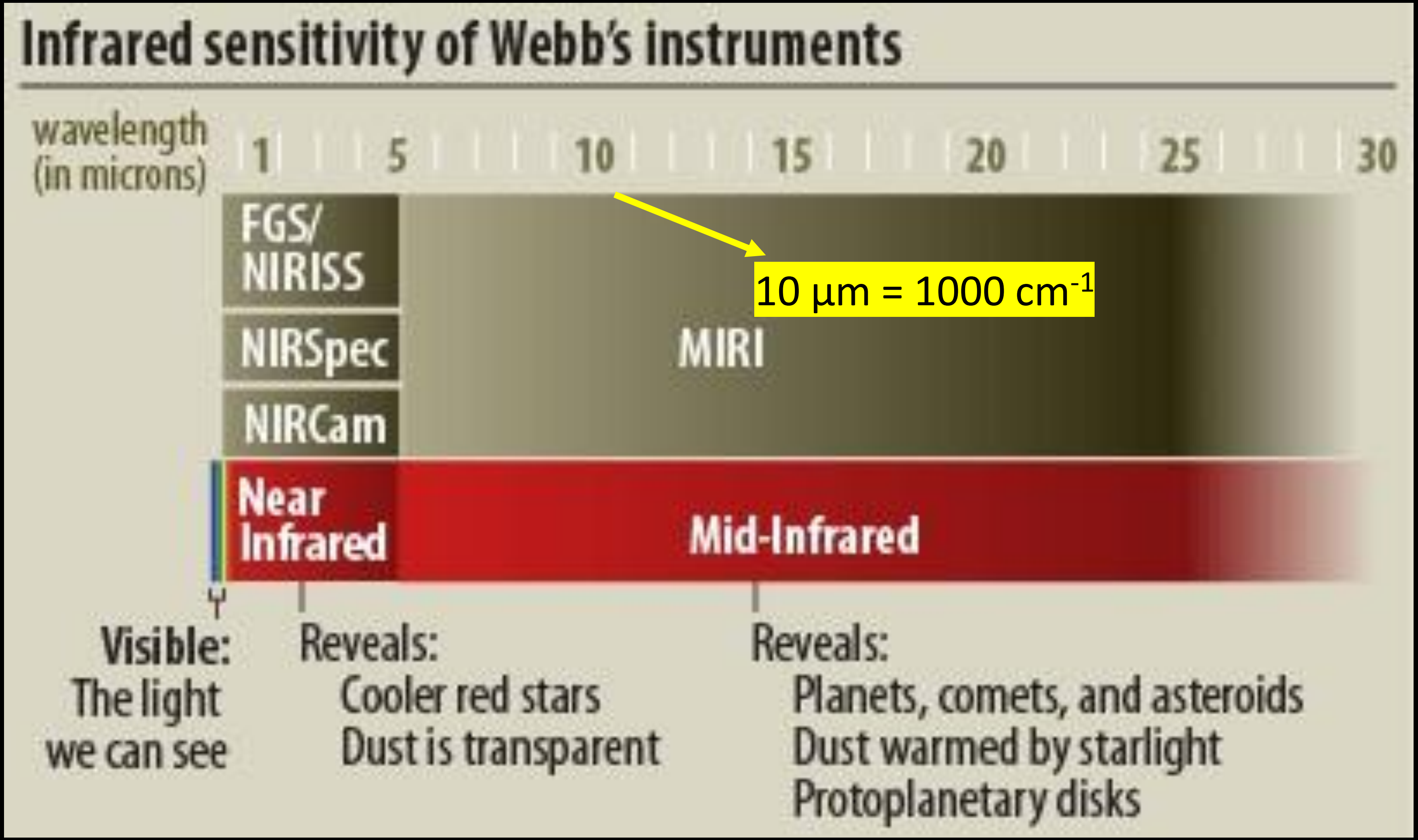
Connecting with observed IR spectra



NASA/Hubble NASA/Spitzer

Imaging cosmic dust with the James Webb Space Telescope (JWST)

Mid-Infrared observations with JWST

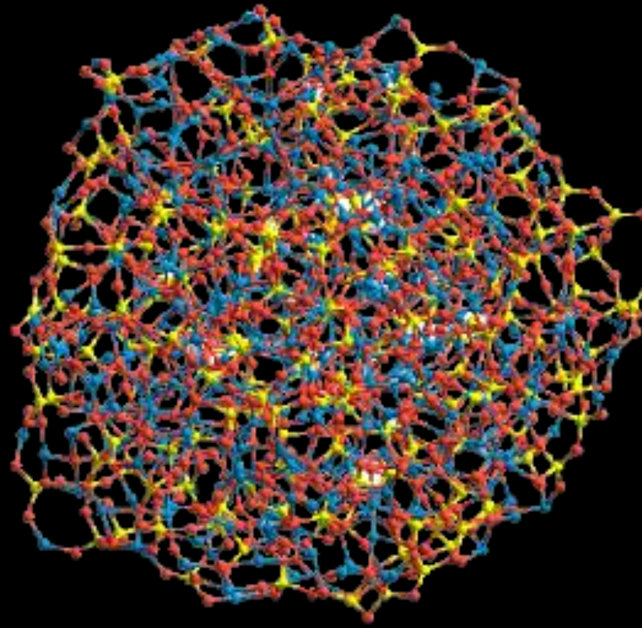
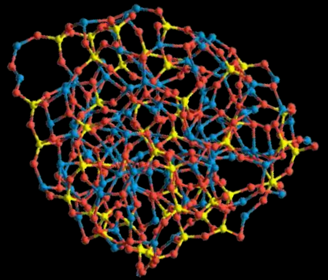
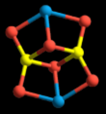
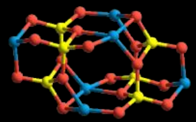
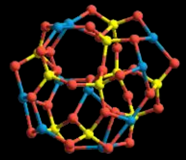
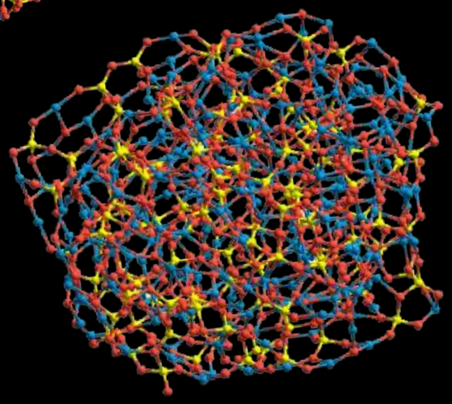


Computing average IR spectra of nanosilicate populations in the ISM

Variables to consider:

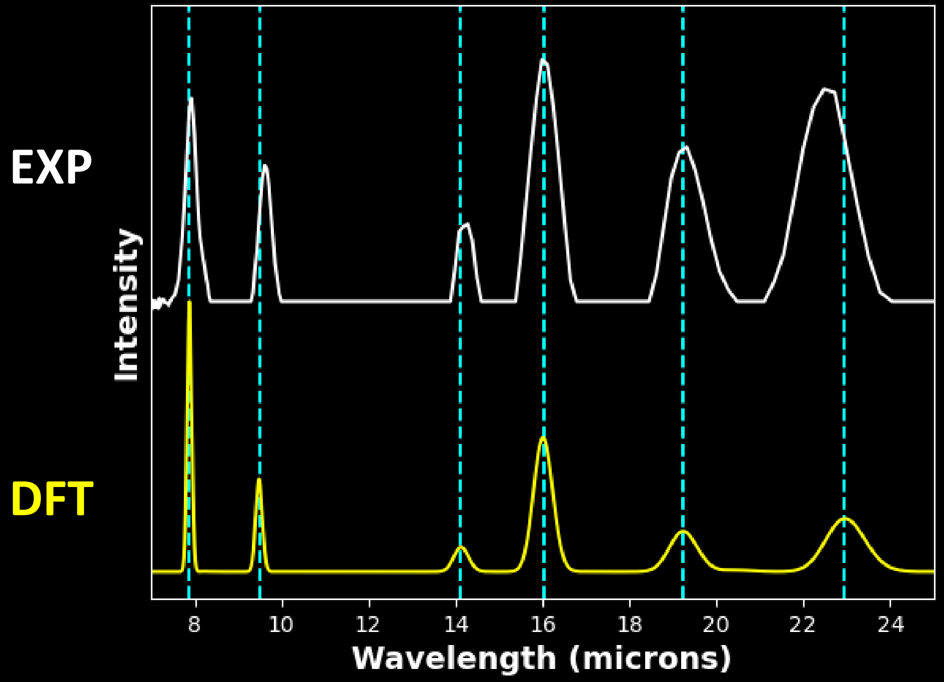
- Energetic stability (structure, morphology)
- Stoichiometry (e.g. pyroxenic, olivinic, Fe?)
- Size (sub-nm to nanometres)

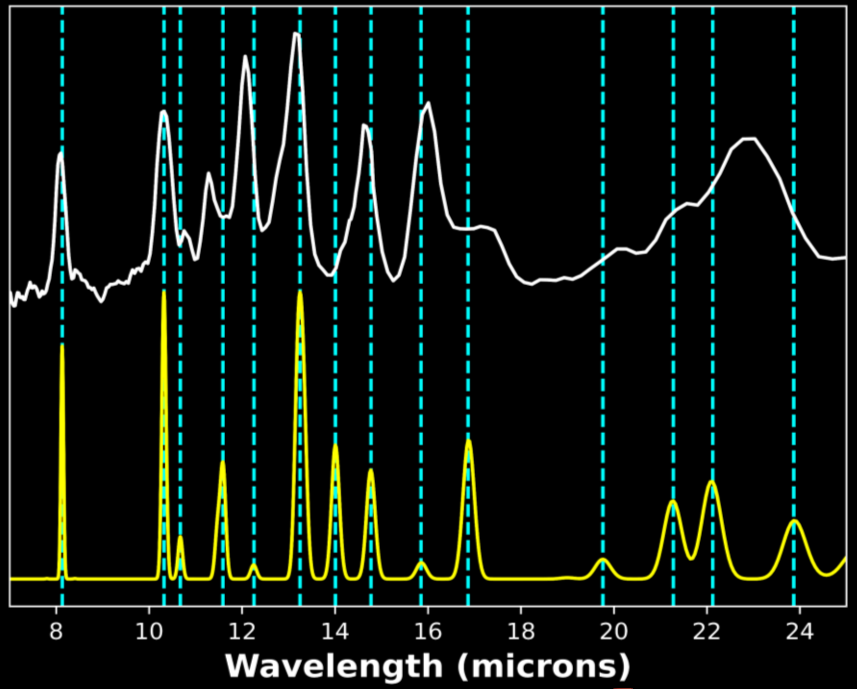
- Charge state (neutral, cationic, anionic)?
- Aggregated nanosilicates?

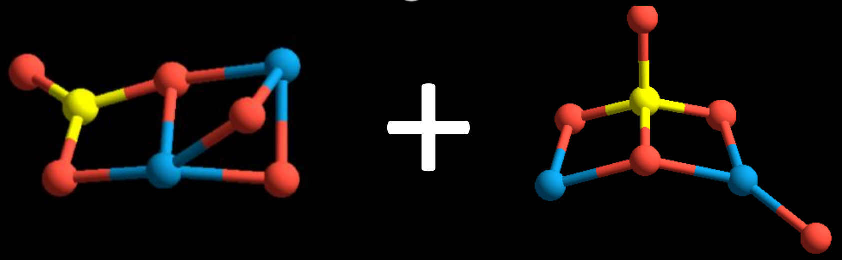







Reliability of DFT-computed IR spectra for populations

- Experimental IR spectra from cluster beam experiments on nanosilicates (FELIX)

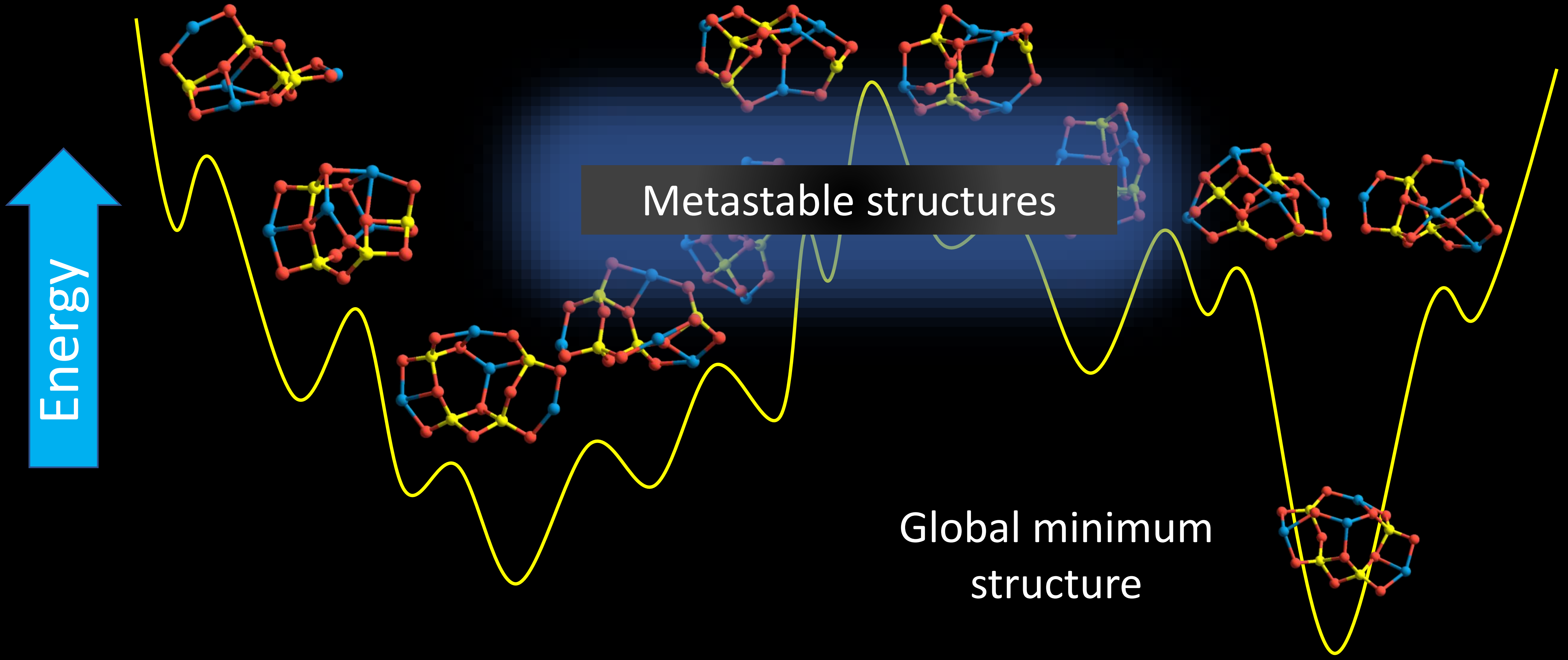




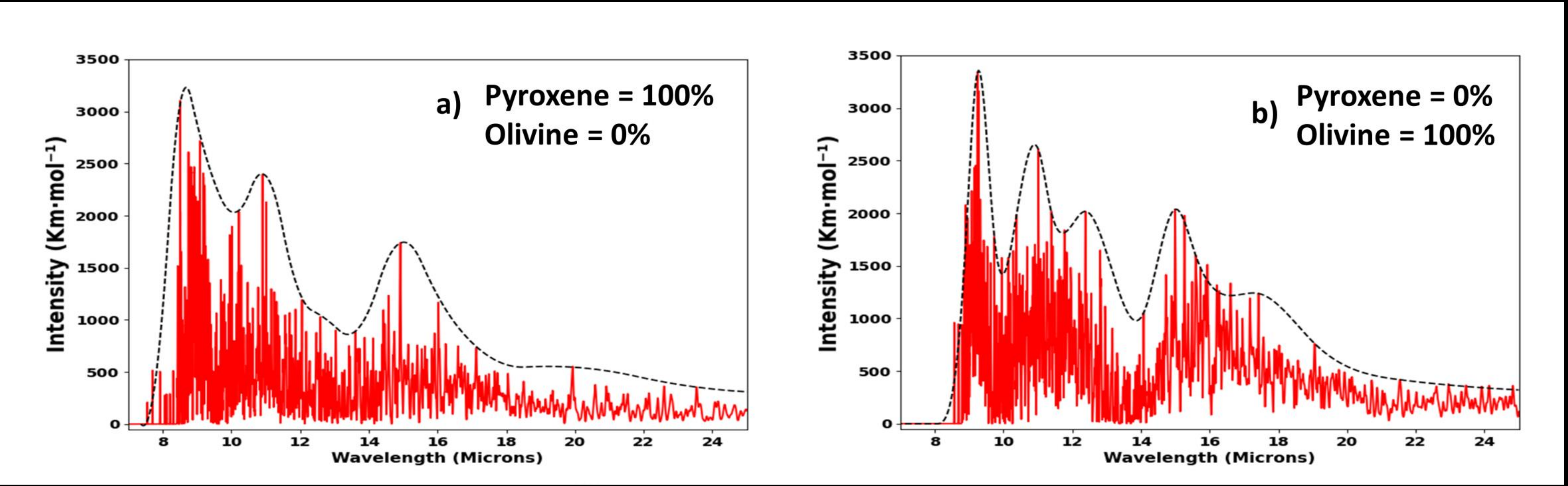


Average DFT error:
Δν ~0.1 microns

Energy landscapes of nanosilicates

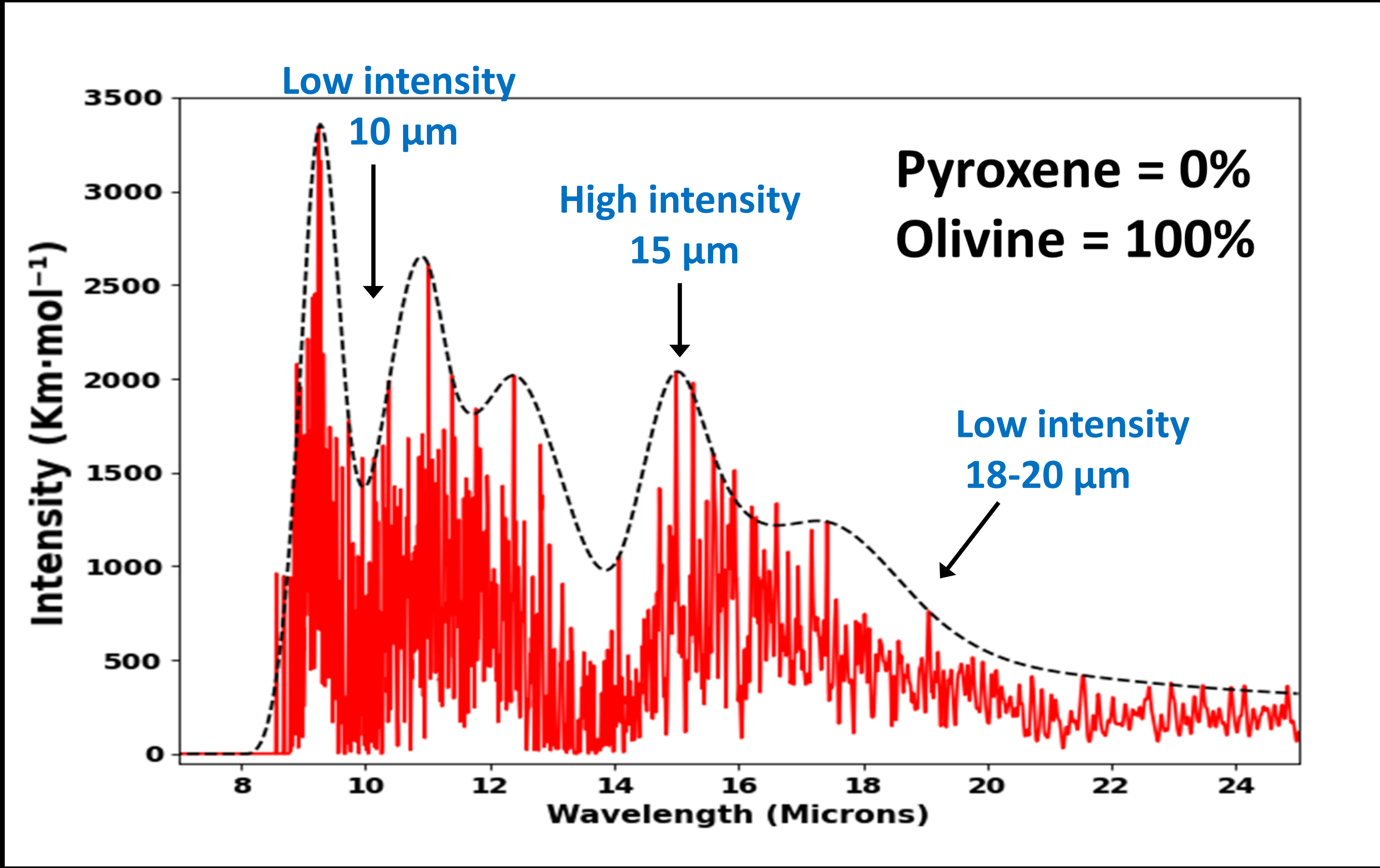


Average nanosilicate IR spectra



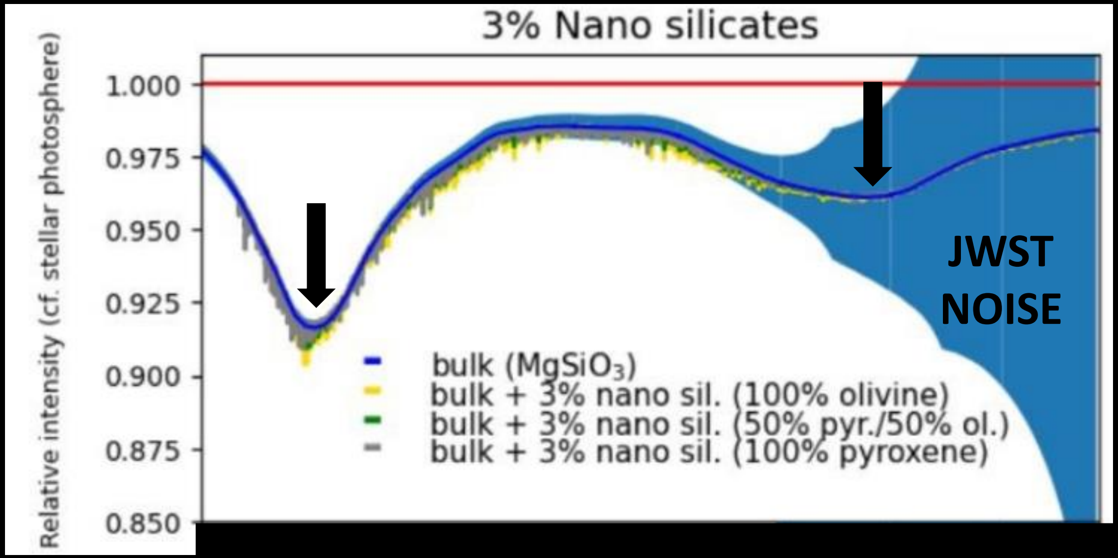
- 5 lowest energy nanosilicate from 10 sizes for pyroxenes and olivines
- Every nanosilicate produces 3*n*-6 vibrational lines (where *n* = number of atoms)
- ~100 nanosilicates leads to ~1800 lines

Are Nanosilicates Observable With JWST?



S. T. Zeegers, J. Mariñoso Guiu, F. Kemper, J. P. Marshall, S. T. Bromley, *Faraday Discuss.* (2023)

Are Nanosilicates Observable With JWST?



DIFFUSE ISM

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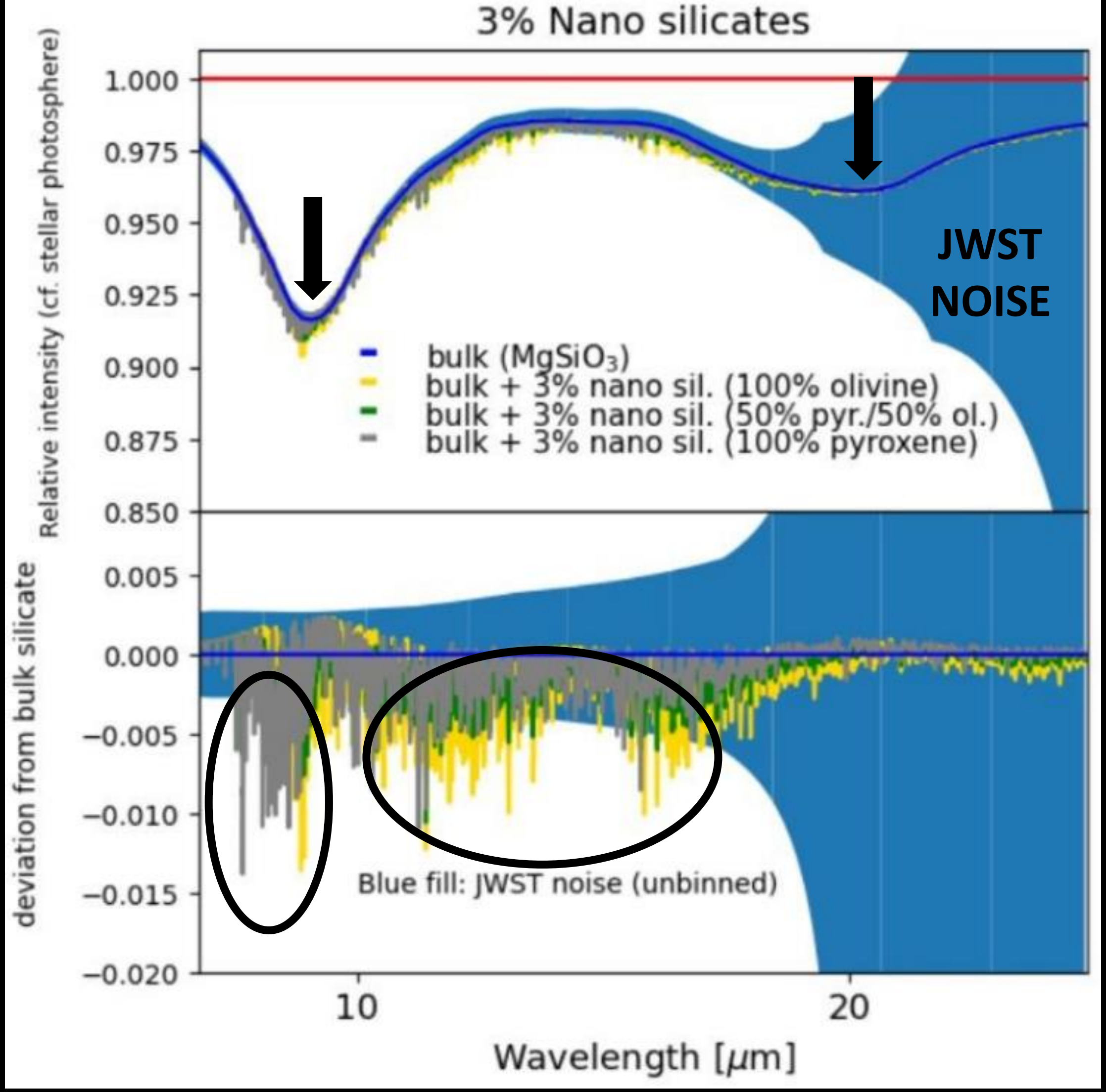

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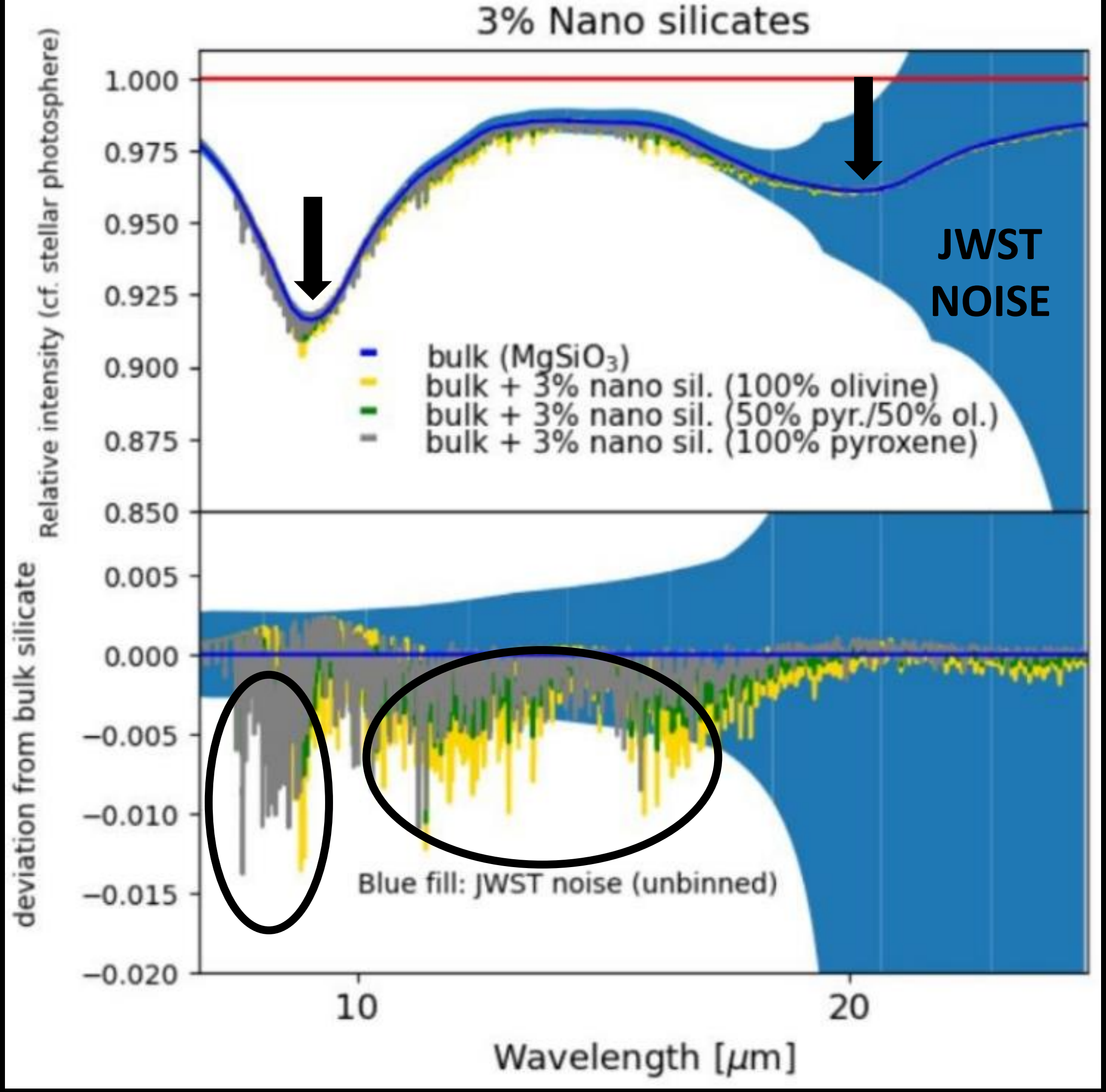

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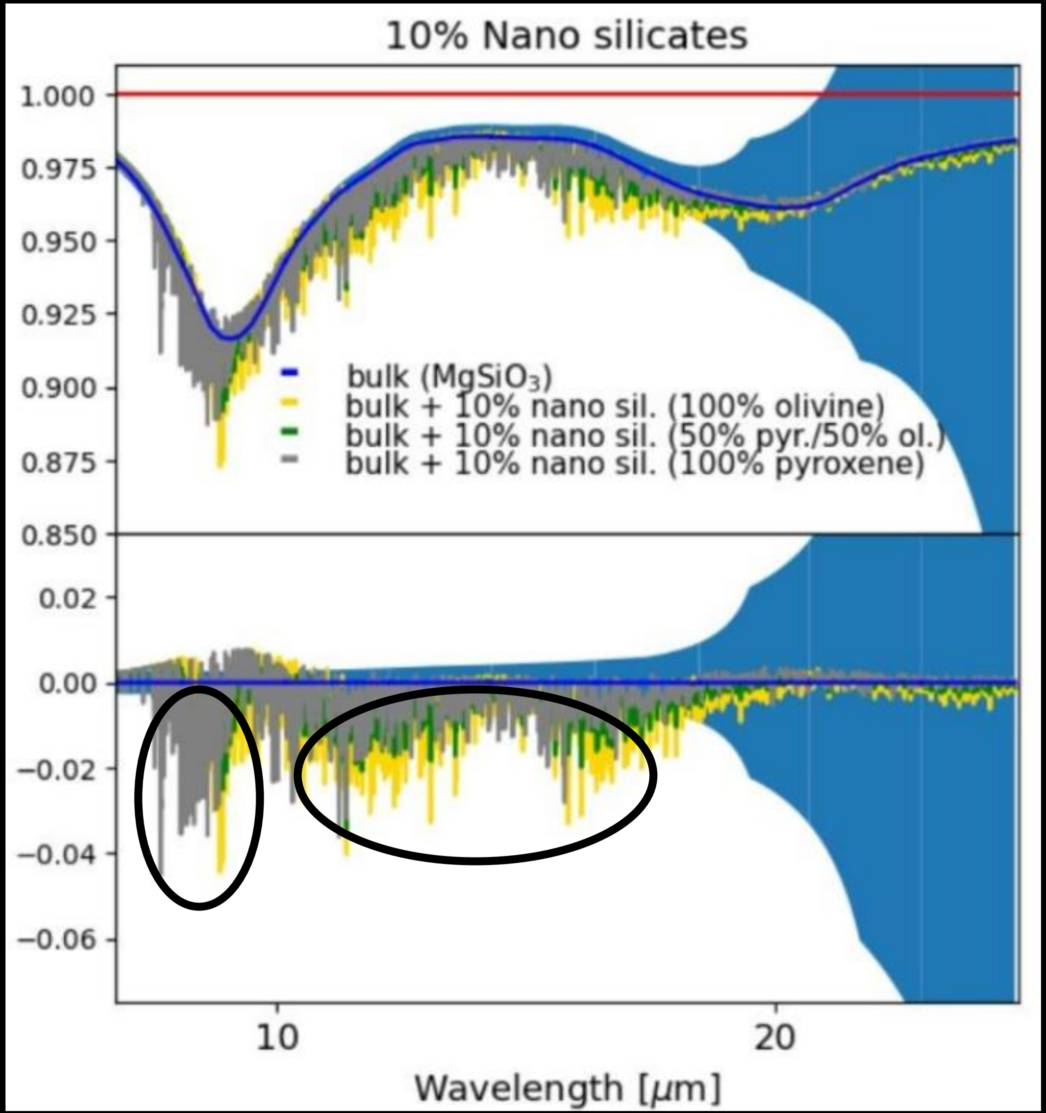

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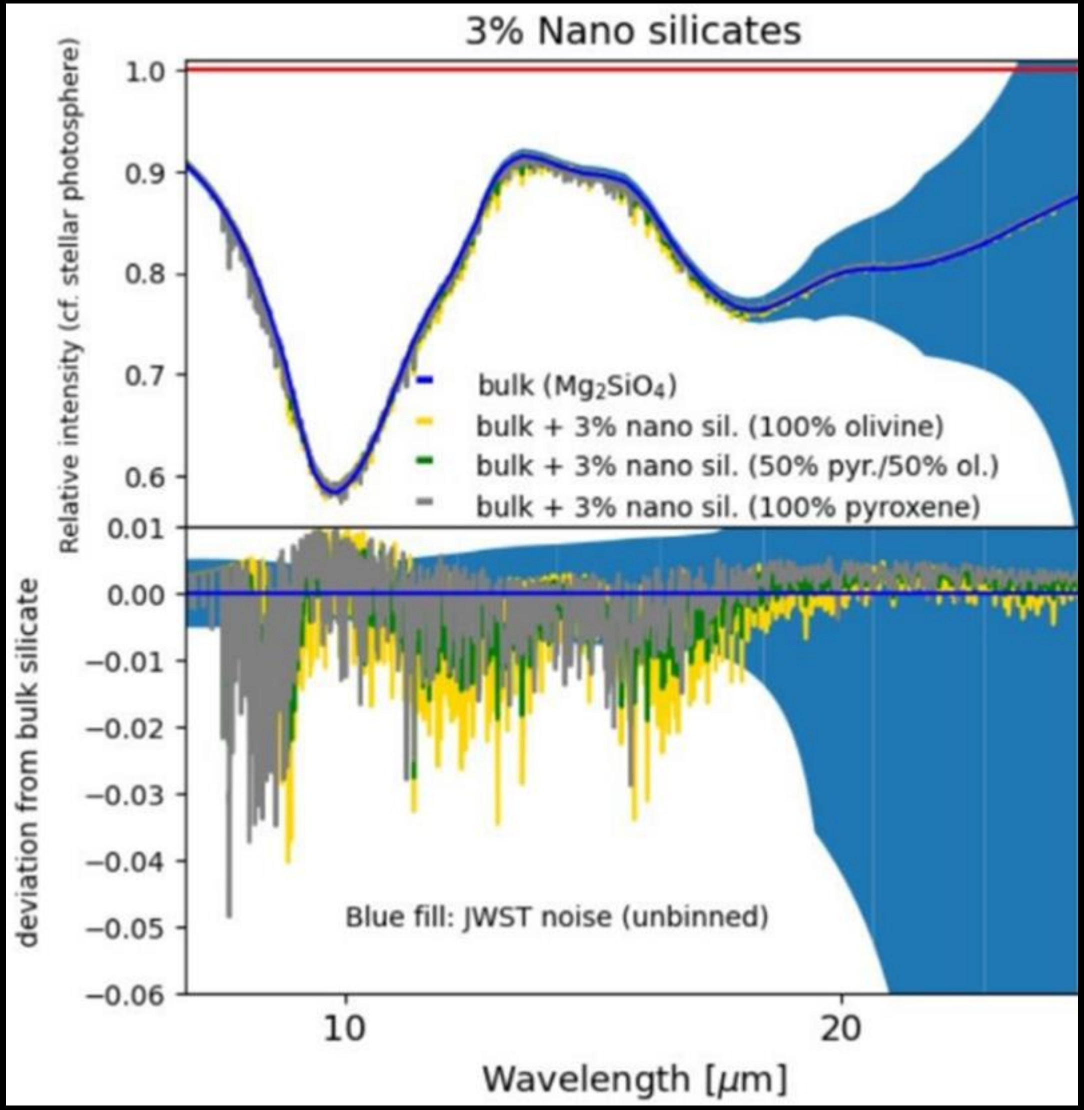
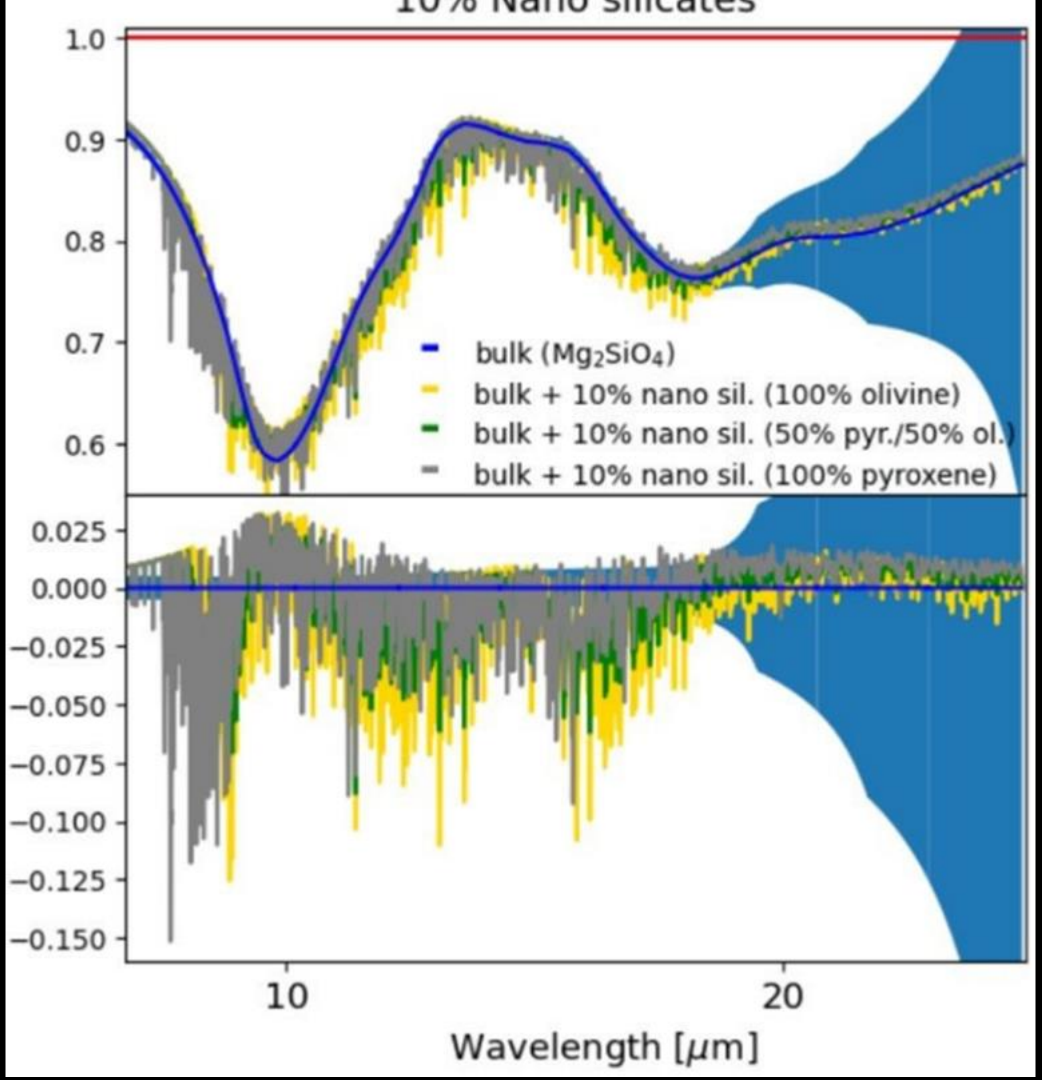
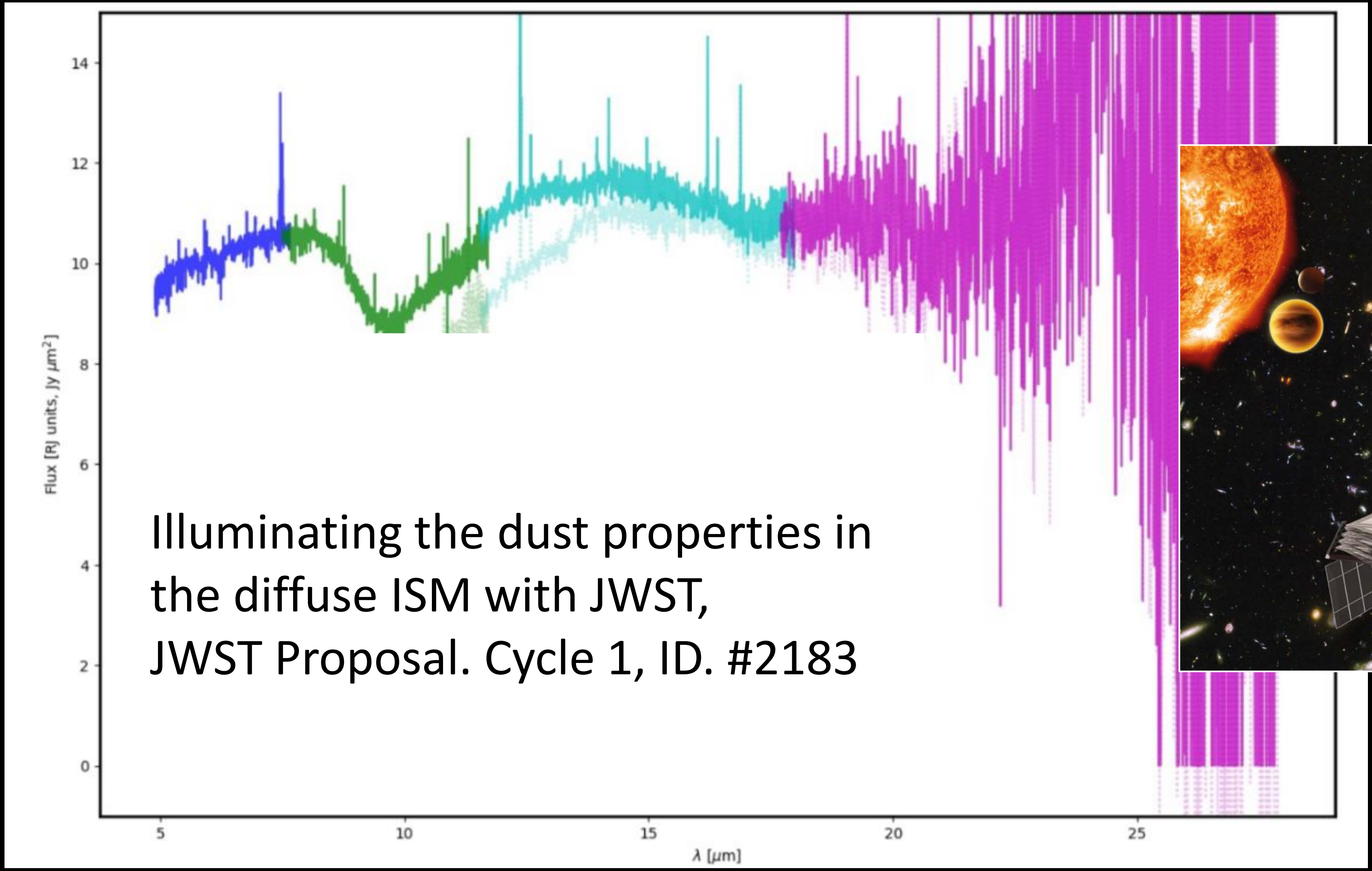


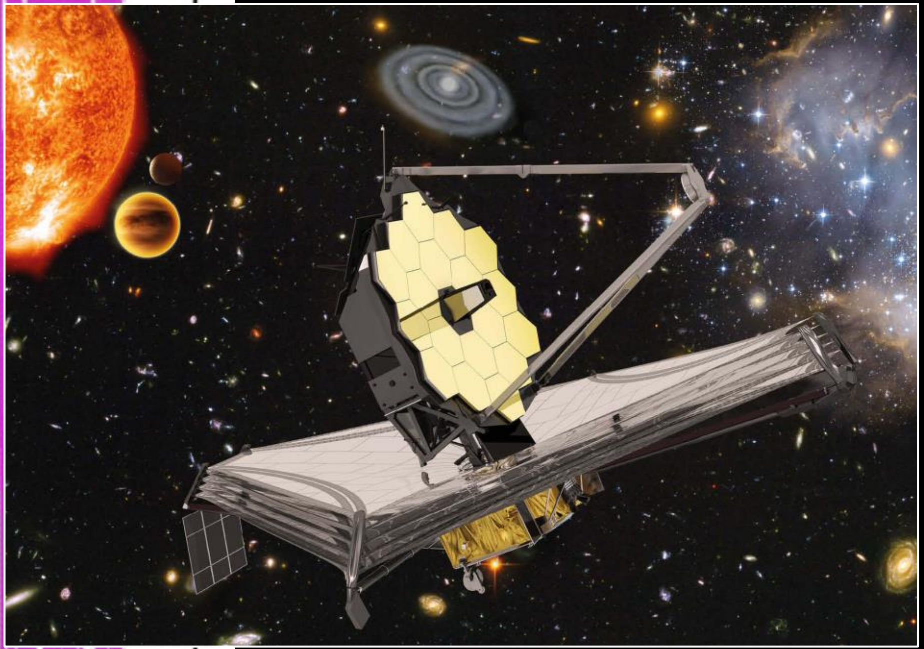
DENSE ISM



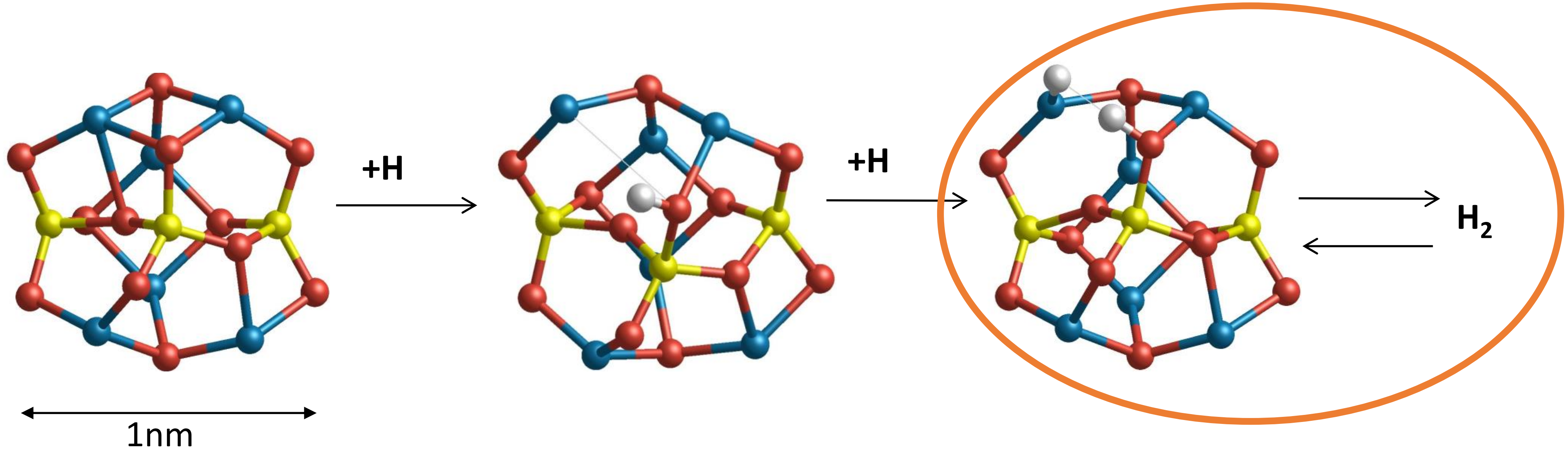
Preliminary MIRI data – being processed…



Illuminating the dust properties in the diffuse ISM with JWST,
JWST Proposal. Cycle 1, ID. #2183



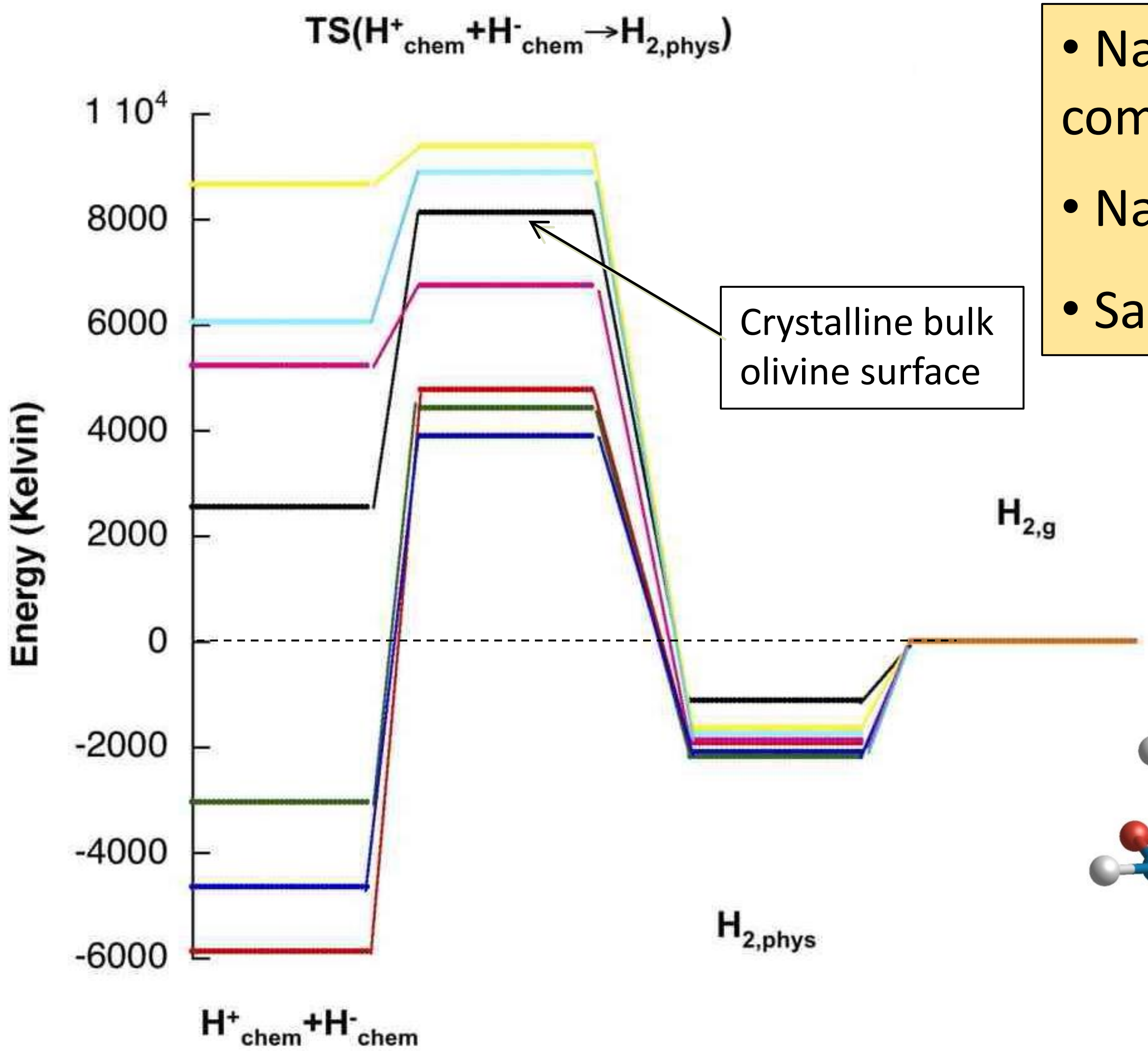
Nanosilicates as promoters of H_2 formation?



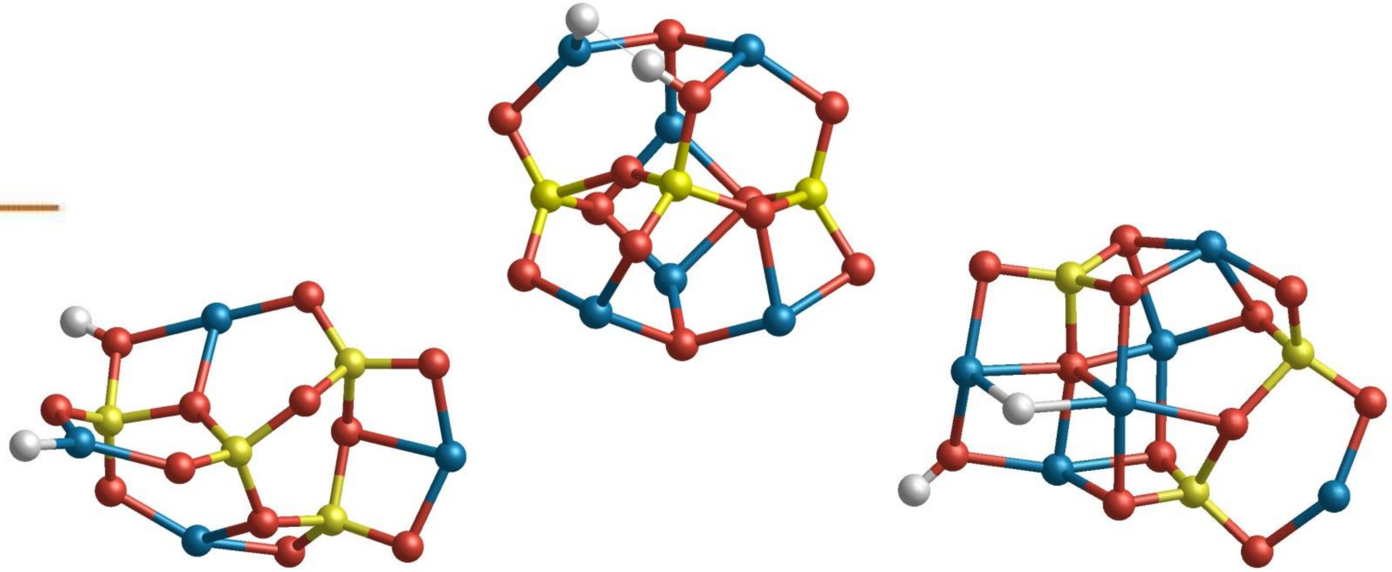
- Silicate grains assumed to be essential third body for enabling H + H → H_2 reaction
- H_2 formation from free H atoms entails a step-wise energy release of ~4.5 eV
- For rapid H_2 formation and a 50:50 H_2/grain division of energy, a nanosilicate will be heated by ~700K

B. Kerkeni and S. T. Bromley, MNRAS, 435, 1486 (2013).

Nanosilicates as promoters of H_2 formation?

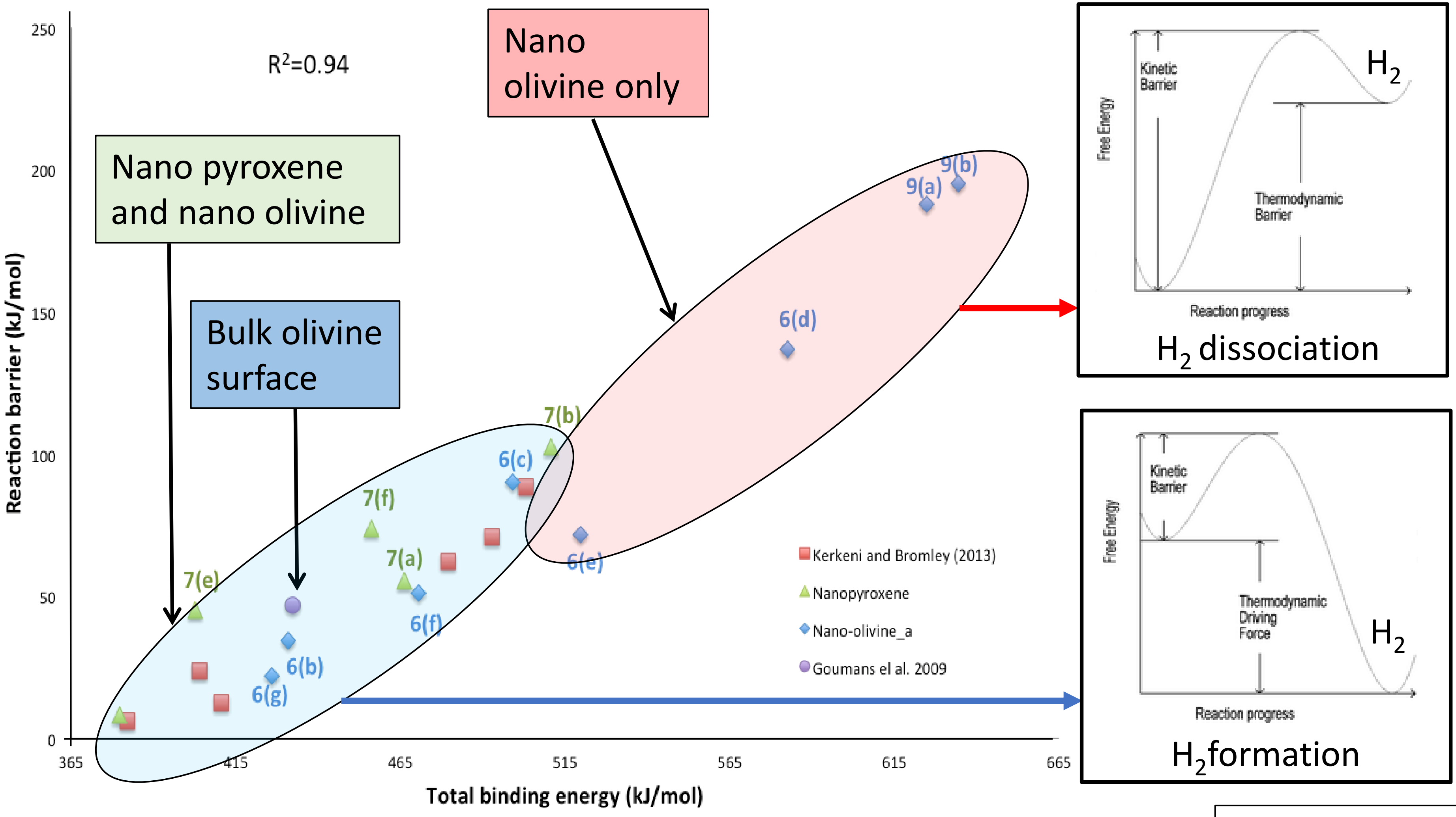


- Nanosilicates have a richer range of adsorption sites compared to bulk crystalline surfaces
- Nanosilicates mimic chemistry of large amorphous grains
- Same generic reaction as on crystalline silicate surfaces



B. Kerkeni and S. T. Bromley, MNRAS, 435, 1486 (2013).

H_2 formation and dissociation on nanosilicates



I.Oueslati, B. Kerkeni, S. T. Bromley, PCCP 2015

Summary

Nanosilicate dust grains are likely to be found in many astronomical environments

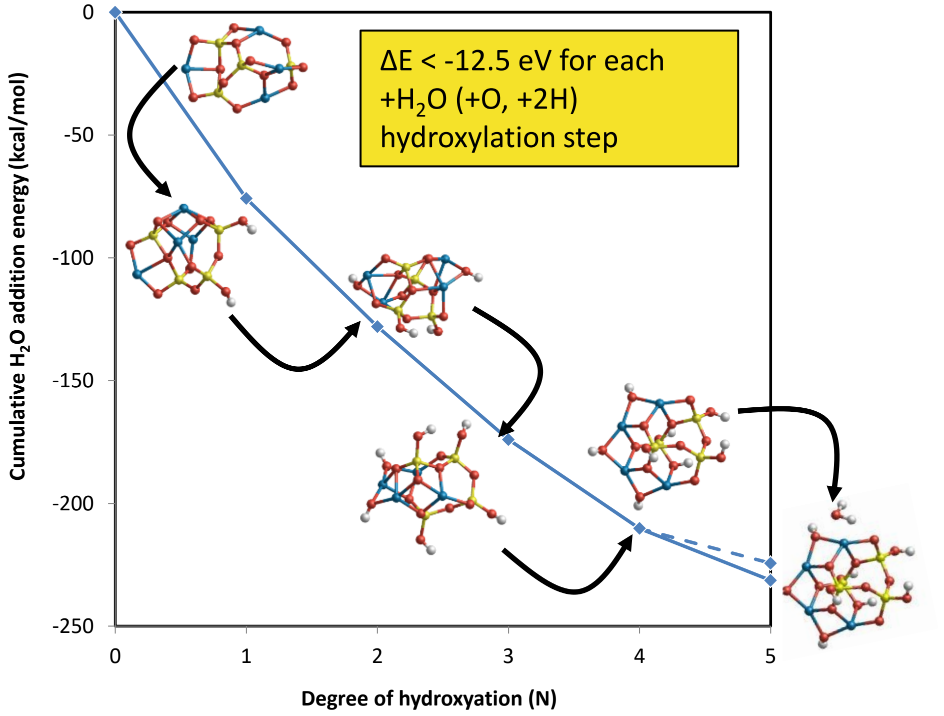
Good nanodust models are required due to assist laboratory characteristion and observations – getting ready for JWST!

Accurate quantum chemical and classical modelling can give important and unrivalled insights into…

…chemical structure and grain morphology, dust nucleation processes, IR/microwave spectra, astrochemistry and much more…

Between bare silicates and ice-covered grains?

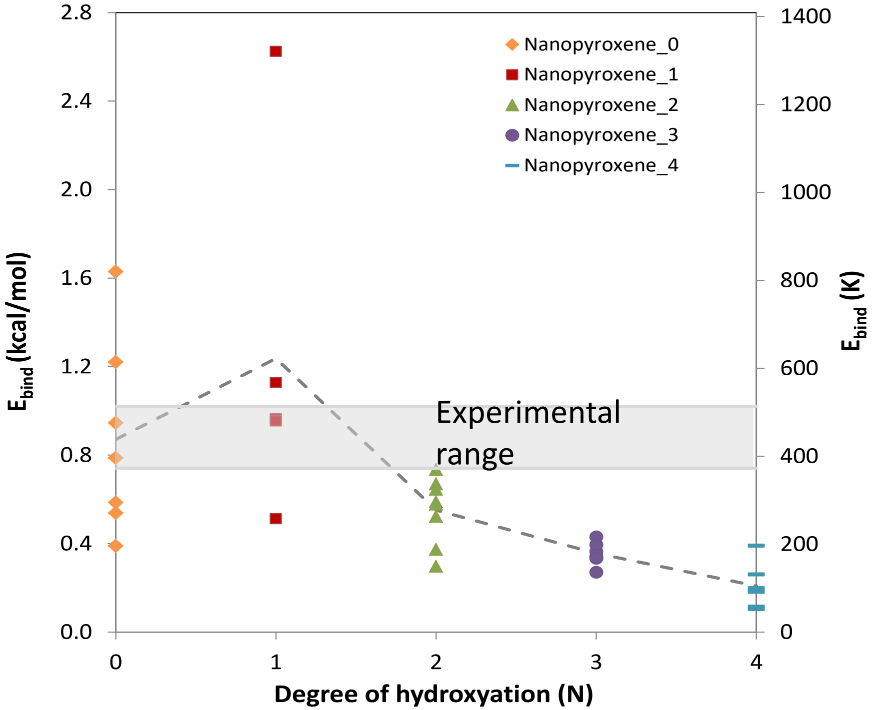
Hydroxylation of silicates



- Addition of O and H produces hydroxylated grains
- More favourable than production of H_2 or H_2O
- -OH (E_{ads}~2.8 eV) resists photodisorption?

F. Goumans and S. T. Bromley, MNRAS 2011

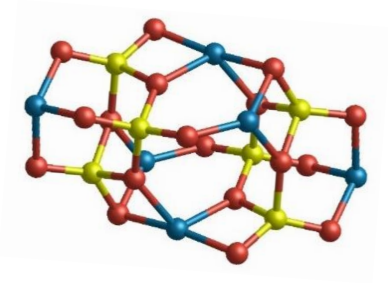
H physisorption on hydroxylated silicates



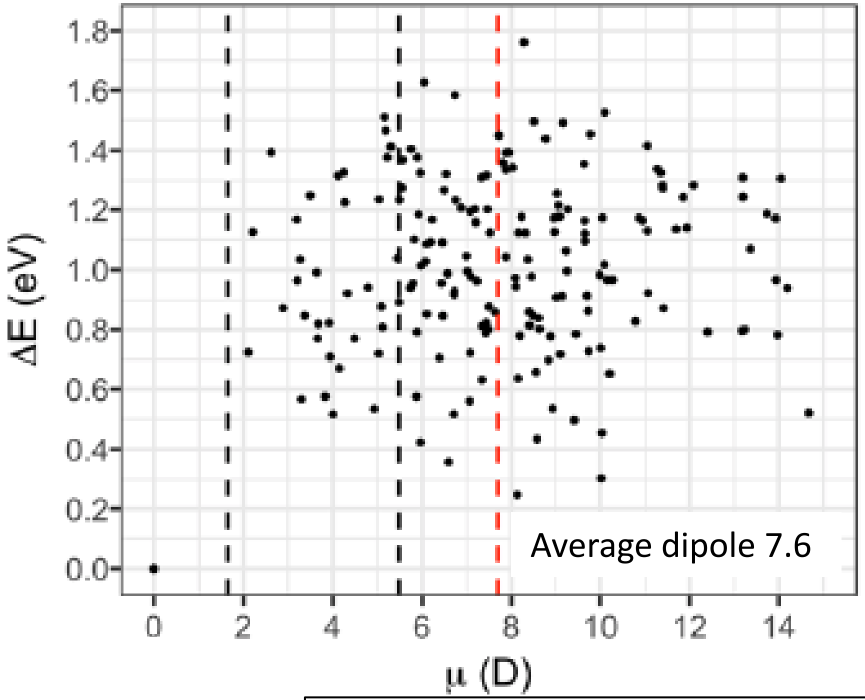
- Physisorption becomes closer to exp. data
- Hydroxylated grains also produce H_2
- Tendency for smaller barriers

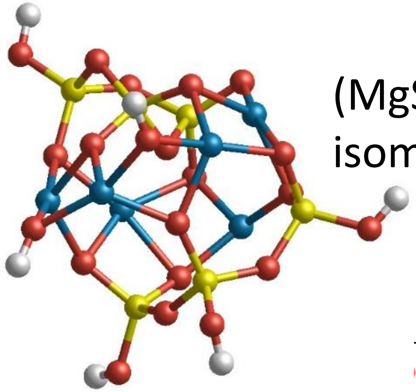
B. Kerkeni, M-C. Bacchus-Montabonel, S. T. Bromley Molecular Astrophys. submitted

Role of water adsorption on average dipoles?

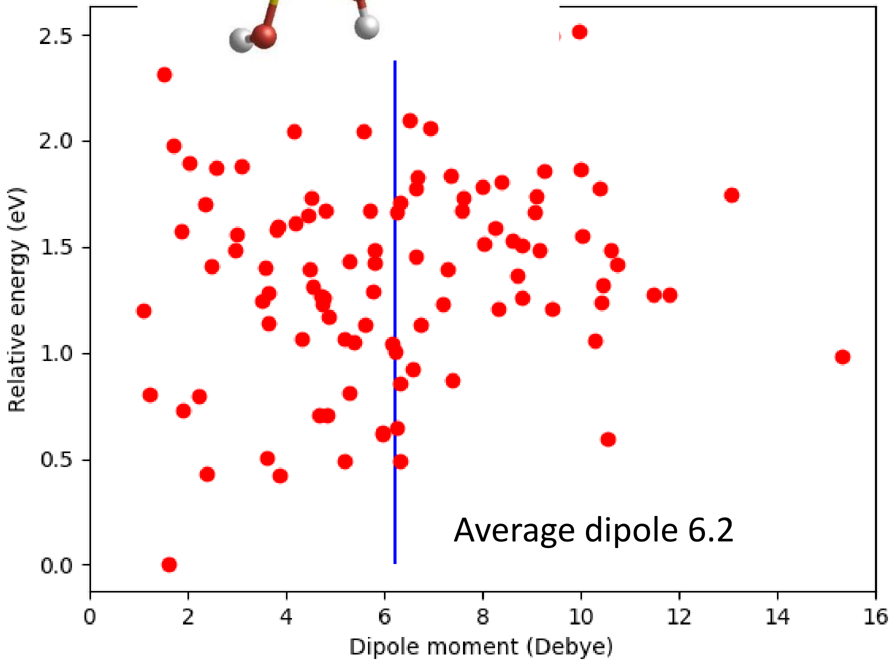


$(MgSiO_3)_6$ isomers





$(MgSiO_3)_6(H_2O)_3$ isomers



Mariñoso, Ferrero, Rimola, Bromley, Frontiers in Astronomy and Space Sciences (2021)