ASTROCHEMISTRY

FROM THE BIG BANG TO LIFE

Global Astrochemistry Lecture Series (GALS) 2024

LABORATORY ASTROCHEMISTRY. SOLID-STATE AND SURFACE PROCESSES

Martin McCoustra. *Heriot-Watt University, Scotland*

05.03.2024 | 15:00 - 17:00 CET

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Laboratory Astrophysics of Solids and Surfaces

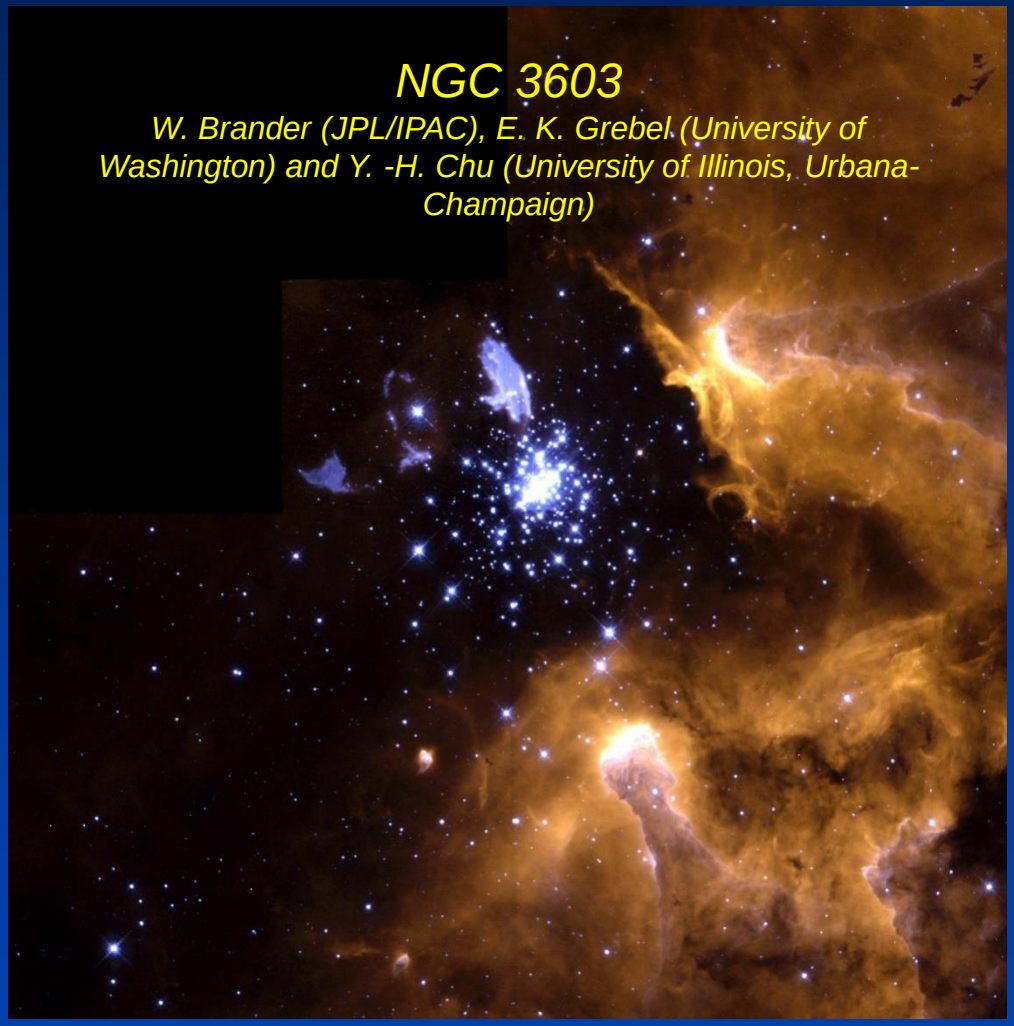
A Surface Science Perspective

Martin McCoustra

M.R.S.McCoustra@HW.AC.UK

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University

The Chemically-controlled Cosmos



Diffuse ISM

↓

Dense Clouds

↓

Star and Planet Formation (Conditions for Evolution of Life and Sustaining it)

↓

Stellar Evolution and Death

The Chemically-controlled Cosmos

- Astronomical spectroscopic observations stretching back over a century have reported different types of chemical species
- The first gas phase molecules were observed in the 1930s in comet tails
- The first reports of solid-state materials (H_2O, CO and CO_2) were in the early 1980s

The Chemically-controlled Cosmos

- Observations need experimental verification
- This is long-standing in the gas phase across the electromagnetic spectrum and is increasing supported by very high-quality computational chemistry
- More recently probed in the solid-state using matrix isolation methods as exemplified by the work of Allamandola, Greenberg etc. with laboratory work almost paralleling the observations

The Chemically-controlled Cosmos

- Today well over 200 species are known in the gas and solid phases
  - Atoms, Radicals and Ions, *e.g.,* H, N, O, …, OH, CH, CN, …, H_3^+, HCO^+, ...
  - Simple Molecules, *e.g.,* H_2, CO, H_2O, CH_4, NH_3, …
  - "Complex" Molecules, *e.g.,* HCN, CH_3CN, CH_3OH, C_2H_5OH, CH_3COOH, $(CH_3)_2CO$, glycine, other amino acids and prebiotic molecules(?)

https://cdms.astro.uni-koeln.de/classic/molecules

The Chemically-controlled Cosmos

- Molecules are found in many regions but the most complex are observed in the dense regions, which are themselves known to be sites of star and planet formation
- Molecules are crucial for
  - Maintaining the current rate of star formation
  - Ensuring the formation of small, long-lived stars such as our own Sun
  - Seeding the Universe with the chemical potential for life

The Chemically-controlled Cosmos

HERIOT WATT UNIVERSITY

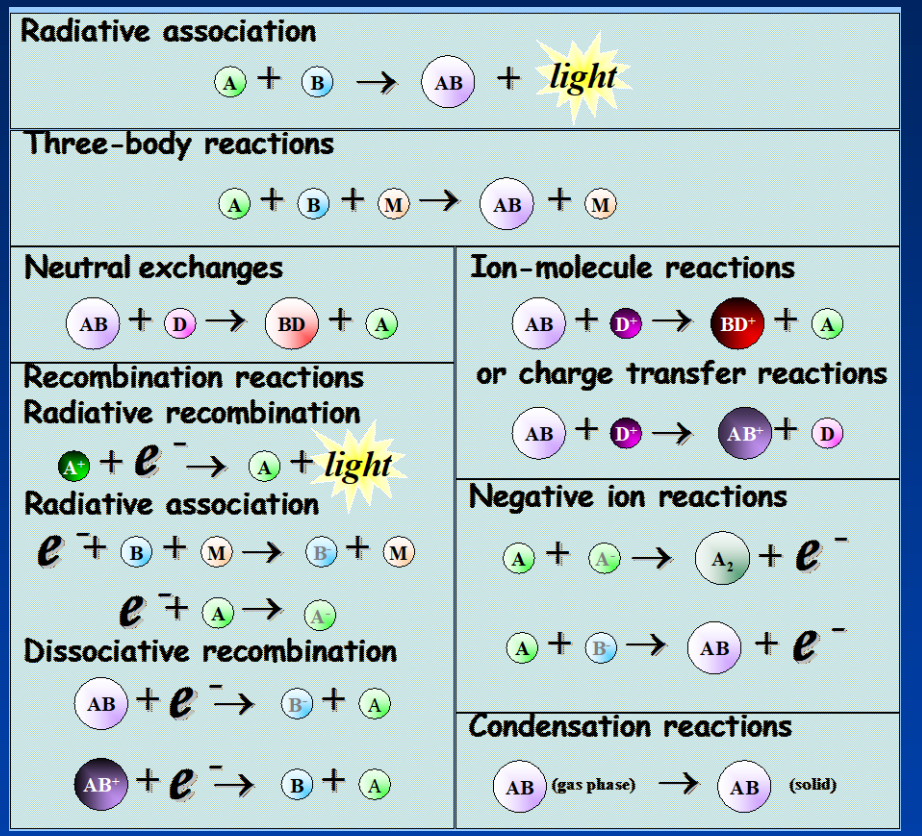
- Different environments support different conditions in which chemistry and physics occur

	Diffuse Medium	Dense Medium	Stellar Nebulae	Proto-planetary Disks	(Proto-) Planetary Atmospheres
Pressure / mbar	$< 10^{-14}$	$< 10^{-9}$	< 0.1	1 – 100	> 1000
Temperature / K	< 100	> 10	20 - 100	100 - 200	200 - 600
Radiation / nm	X-ray to Radio	IR to Radio with CR VUV	UV to Radio with CR VUV	UV to Radio with CR VUV	UV to Radio with CR VUV
H_2 : CO	H / H^+ Only	10^3 - 10^4	10^2 - 10^3	10 - 100	0.01 - 10

- Add in dust (silicaceous and carbonaceous) to this mix to provide surfaces for additional physics and chemistry to take place

The Chemically-controlled Cosmos

- Gas phase chemistry involving ion-molecule reactions and some types of reactions involving free radicals go a long way to explain what we see in all environments



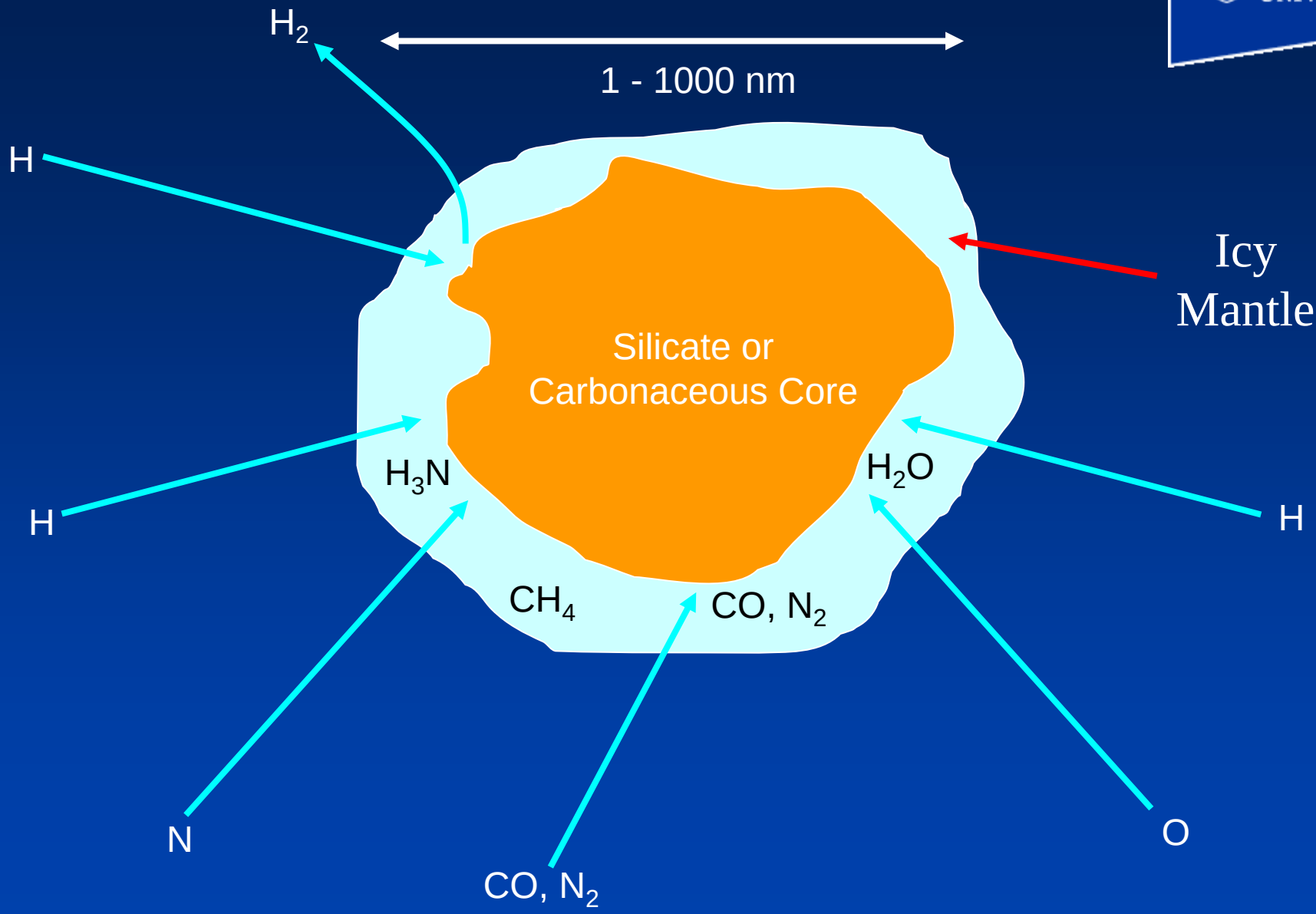
Adapted from Fraser, McCoustra & Williams, *Astronomy and Geophysics*, 2002, **43**(Issue 2), 210.

The Chemically-controlled Cosmos

- But ...
- Building chemical models of the evolution of space environments, such a dense gas clouds, involves networks of the 100s to 1000s of reactions and these often still fail to reproduce the observed concentrations of certain simple molecular species such as H_2 (the most abundant molecule in the Universe), H_2O, ...

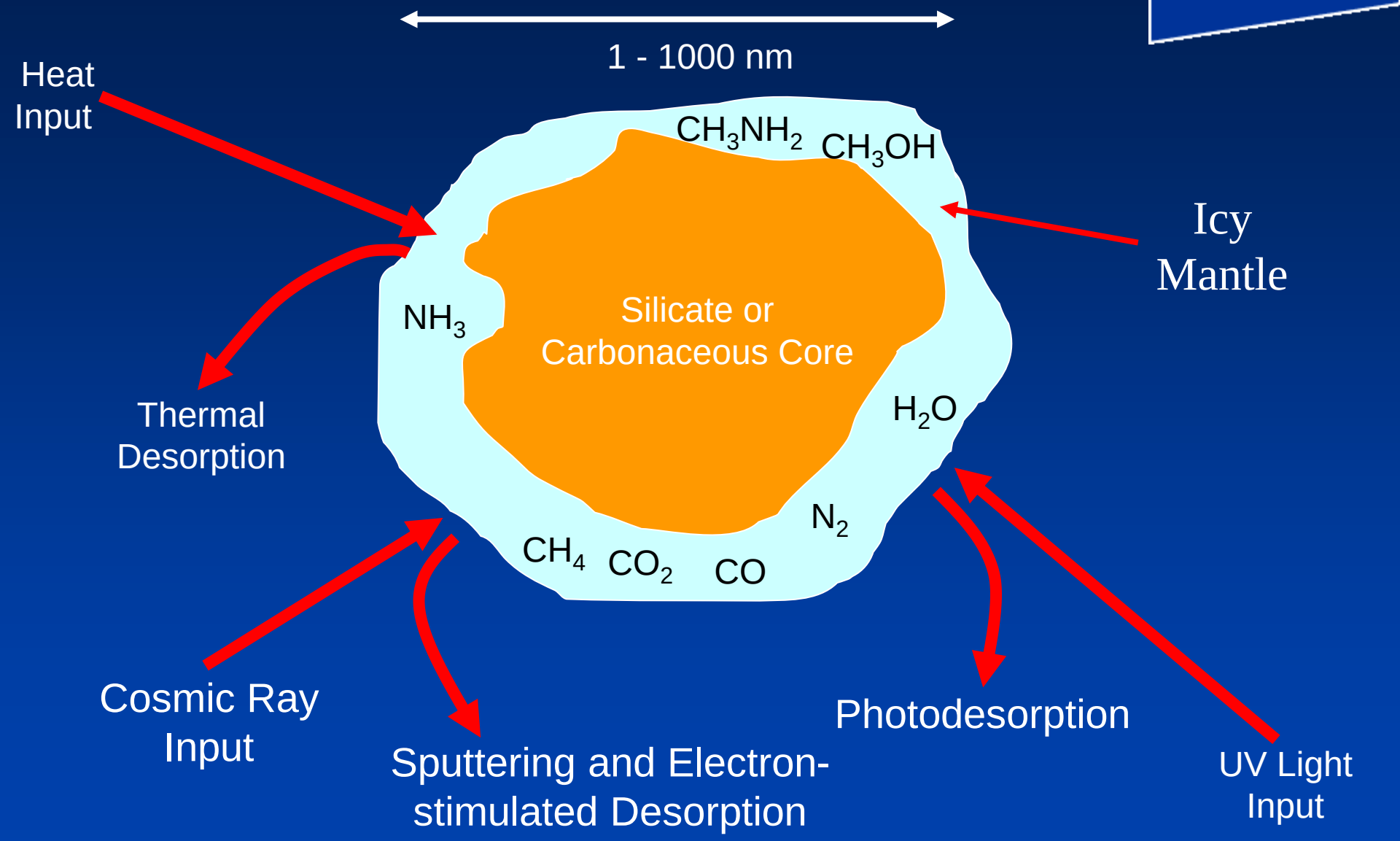
Dust is the Key Ingredient Necessary to Solve This Issue!

The Chemically-controlled Cosmos



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The Chemically-controlled Cosmos



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The Chemically-controlled Cosmos

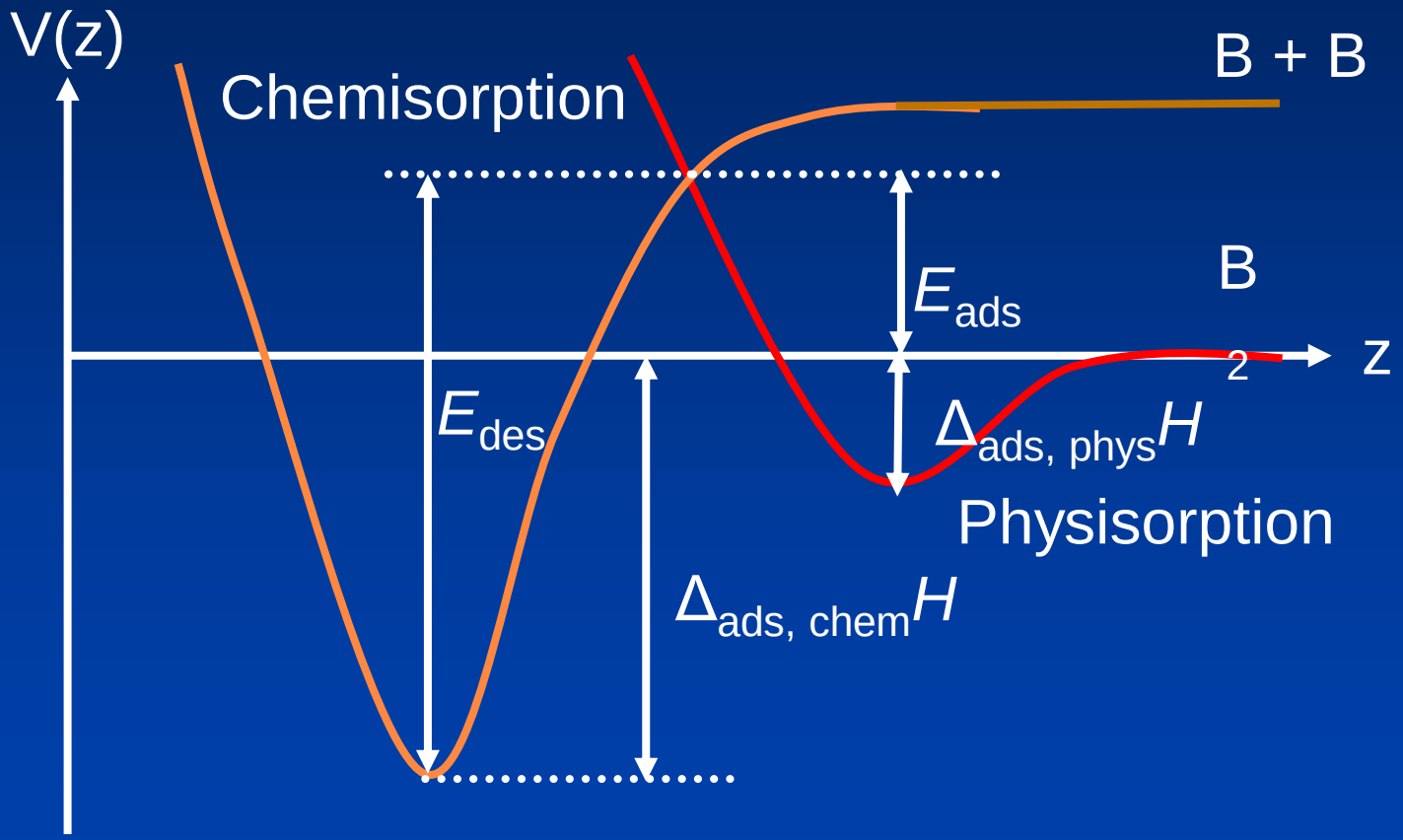
- Dust is crucial in many space environments; especially in cold dense environments
  - Assists in the formation of small hydrogen-rich molecules including H_2, H_2O, CH_4, NH_3, ... some of which will be trapped as icy mantles on the grains
  - Some molecules including CO, N_2, ... can condense on the grains from the gas phase
  - The icy grain mantle acts as a reservoir of molecules used to radiatively cool collapsing clouds as they warm
  - Reactions induced by VUV photons and cosmic rays in these icy mantles can create complex, even pre-biotic molecules

A Surface Science Perspective…

- A surface scientist will always ask several key questions…
  - What is the surface made of?
    - *Silicate Mineral, Graphite, Graphene, HAC, Metal atoms?*
    - *Use XPS, AES, IR*
  - What is the structure of the surface?
    - *Crystalline, Amorphous, Nano-structured?*
    - *Use S(T)EM, SPM, Computational methods*
  - What chemical species are interacting with the surface?
    - *Gas phase composition gives a guide to the dominant species*
    - *MS*
  - What physicochemical processes are occurring on the surface?
    - *Adsorption, Desorption, Diffusion, Reaction*

A Surface Science Perspective…

- Potential energy diagram for adsorbate-surface interactions due to Lennard-Jones



Processes of Adsorption and Diffusion on Solid Surfaces
J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1932, **28**, 333

Adsorption

- Classify the adsorption of atoms/molecules onto surfaces into two classes; *physical adsorption* (*physisorption*) and *chemical adsorption* (*chemisorption*)

PHYSISORPTION

- Long range
- Weak van der Waals interactions
- Binding energies < 50 kJ mol^{-1}
- Adsorbate largely unperturbed by interaction with the substrate

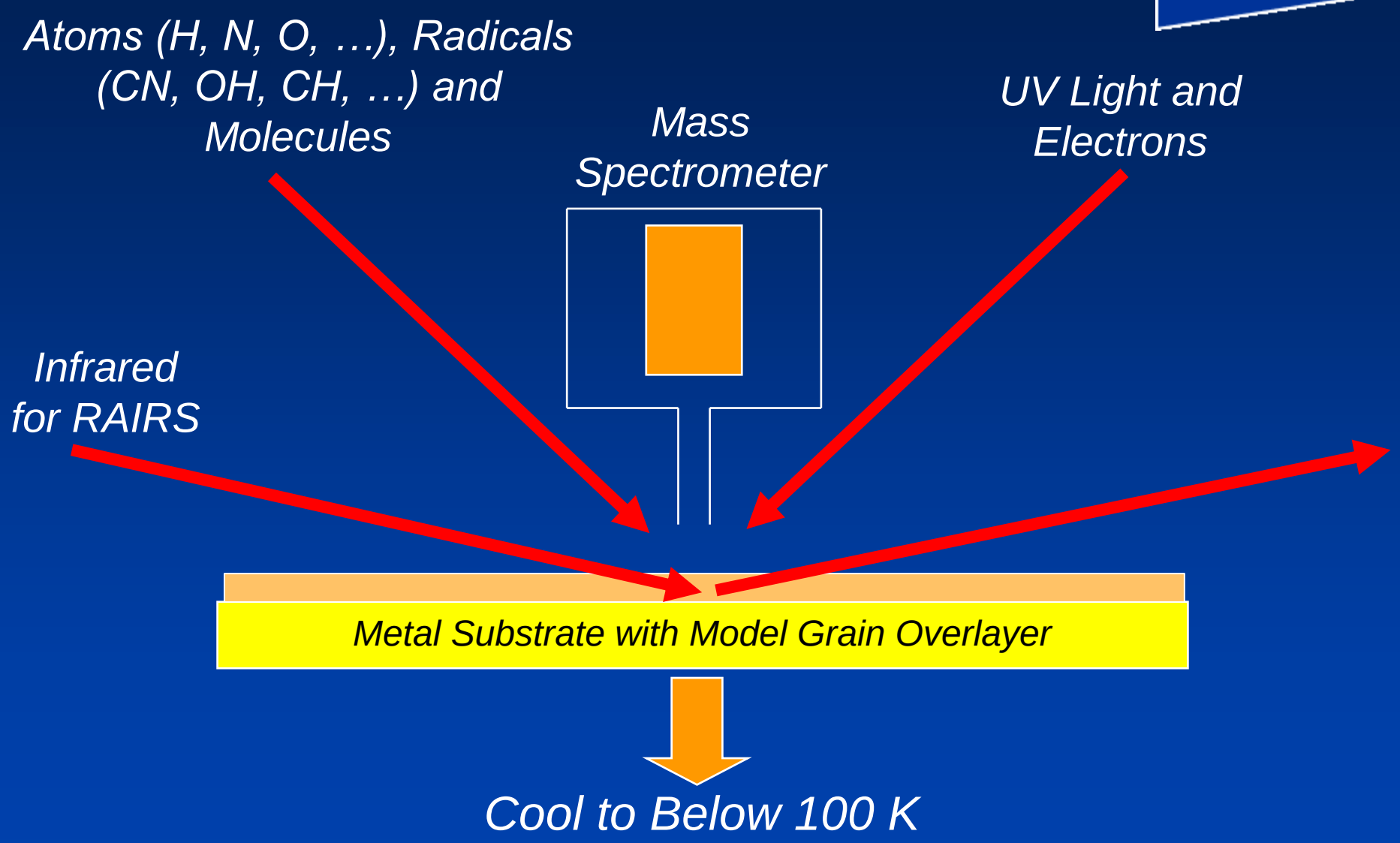
CHEMISORPTION

- Short range
- Exchange of electrons between adsorbate and substrate results in a covalent bonding interaction
- Binding energies > 100 kJ mol^{-1}
- Adsorbate largely, potentially, strongly perturbed by interaction with the substrate

A Surface Science Perspective…

Remember from the surface science perspective, what changes with the environment are the boundary conditions (temperature, composition, radiation field) NOT the basic physicochemical processes occurring at the surface?

Looking at Grain Surfaces



Looking at Grain Surfaces

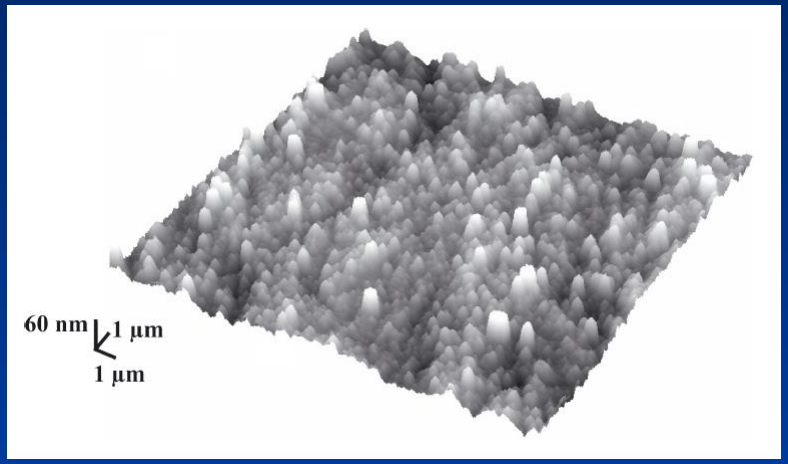


Laboratory Surface Astrophysics Experiment
H. J. Fraser, M. P. Collings and M. R. S. McCoustra, *Rev. Sci. Inst.*, 2002, **73**, 2161

Laboratory Surface Astrochemistry Experiments
V. L. Frankland, A. Rosu-Finsen, J. Lasne, M. P. Collings, and M. R. S. McCoustra, *Rev. Sci. Inst.*, 2015, **86**, 055103

Looking at Grain Surfaces

- Amorphous silica ($aSiO_2$)
- Produced by electron beam evaporation from solid silica on to a room temperature optically polished metal substrate
- Ideal for buried interface RAIRS
- Surface is polar!



Laboratory Investigations of the Interaction between Benzene and Bare Silicate Grain Surfaces
J. D. Thrower, M. P. Collings, F. J. M. Rutten and M. R. S. McCoustra, *Mon. Not. R. Astron. Soc*., 2009, **394**, 1510–1518

Adsorption on Grain Surfaces

- Adsorption is the first process, we need to consider and so let's have a look at the adsorption of a few simple molecules like CO, H_2O, or NH_3
- The key measurement in adsorption is the rate of adsorption

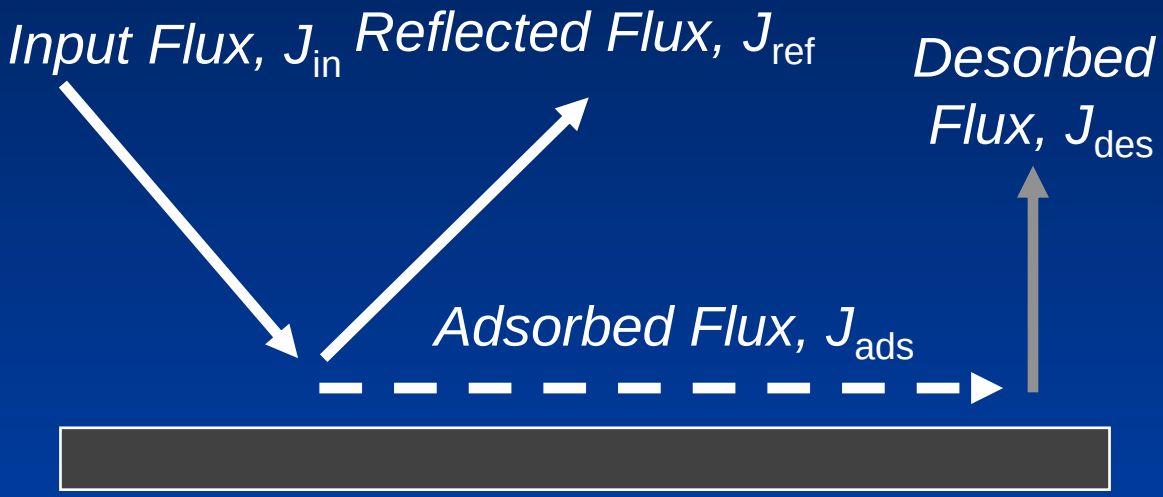
$$v_{ads} = S(\theta)\frac{P_i}{\sqrt{2\pi m_i k_B T_g}}$$

Adsorption on Grain Surfaces

- S, the sticking coefficient, varies from 0 to 1 and depends on θ, the coverage, and T_s, the surface temperature
  - Langmuir Adsorption (no interactions) => $S_0(1-\theta)$
  - Kisliuk Adsorption (interactions) => $S_0(1-\theta)/[1+\theta(K-1)]$

Adsorption on Grain Surfaces

- Most experiments designed to measure *S* do not do so; rather they measure the *uptake coefficient*, α

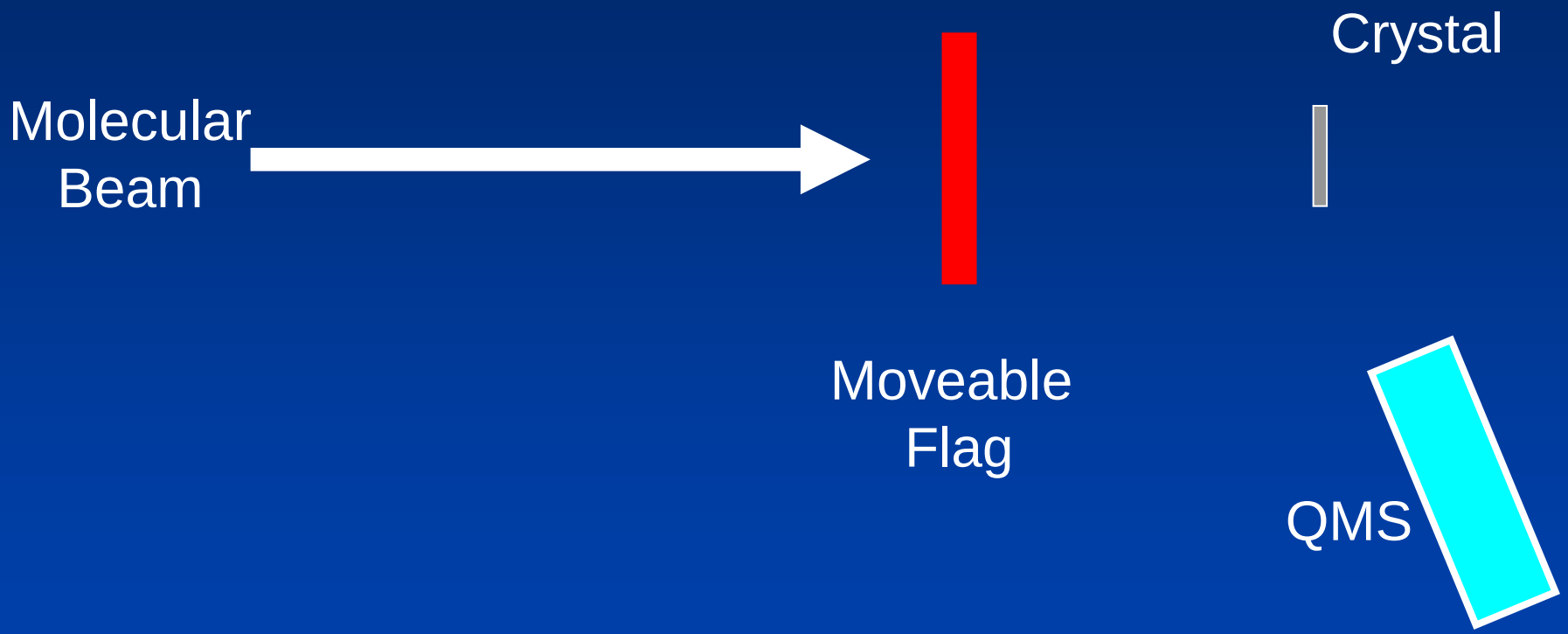


$$\alpha(T) = S(T) - \frac{k_{des}(T)}{AJ_{in}}$$

Only measurements of α under conditions where desorption is negligible give *S*!

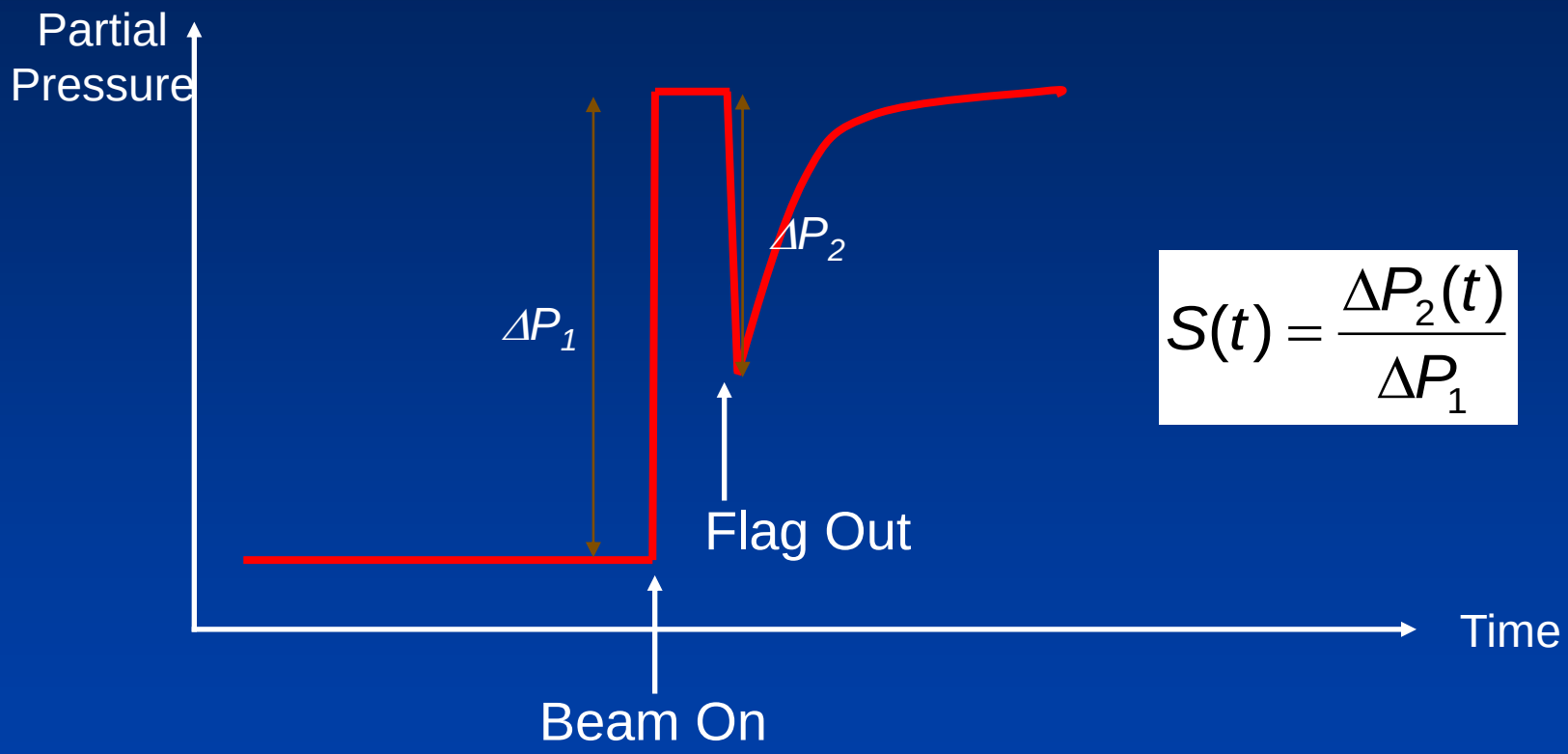
Adsorption on Grain Surfaces

- The King & Wells method is probably most common method for determining $S(\theta)$ for $S > 0.05$



Molecular Beam Investigation of Adsorption Kinetics on Bulk Metal Targets: Nitrogen on Tungsten
D. A. King and M. G. Wells, *Surf. Sci.*, 1972, **29**, 454

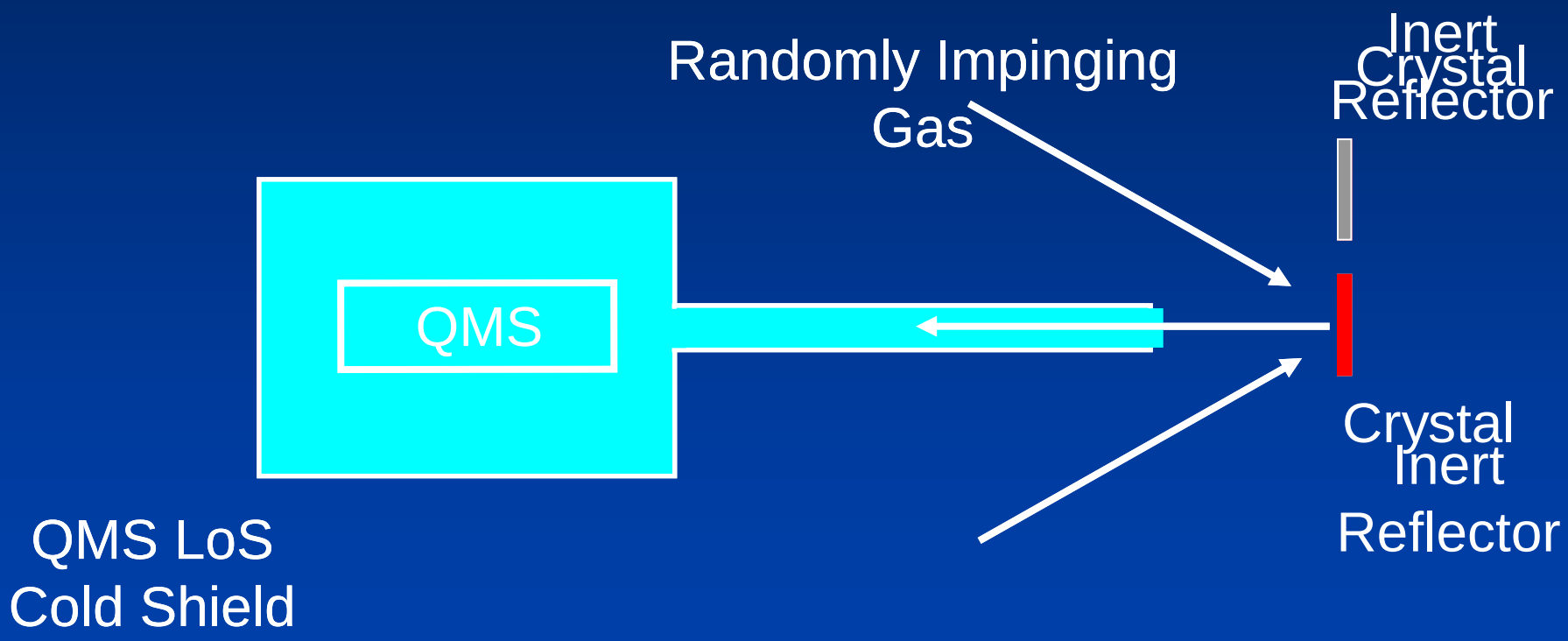
Adsorption on Grain Surfaces



$$S(t) = \frac{\Delta P_2(t)}{\Delta P_1}$$

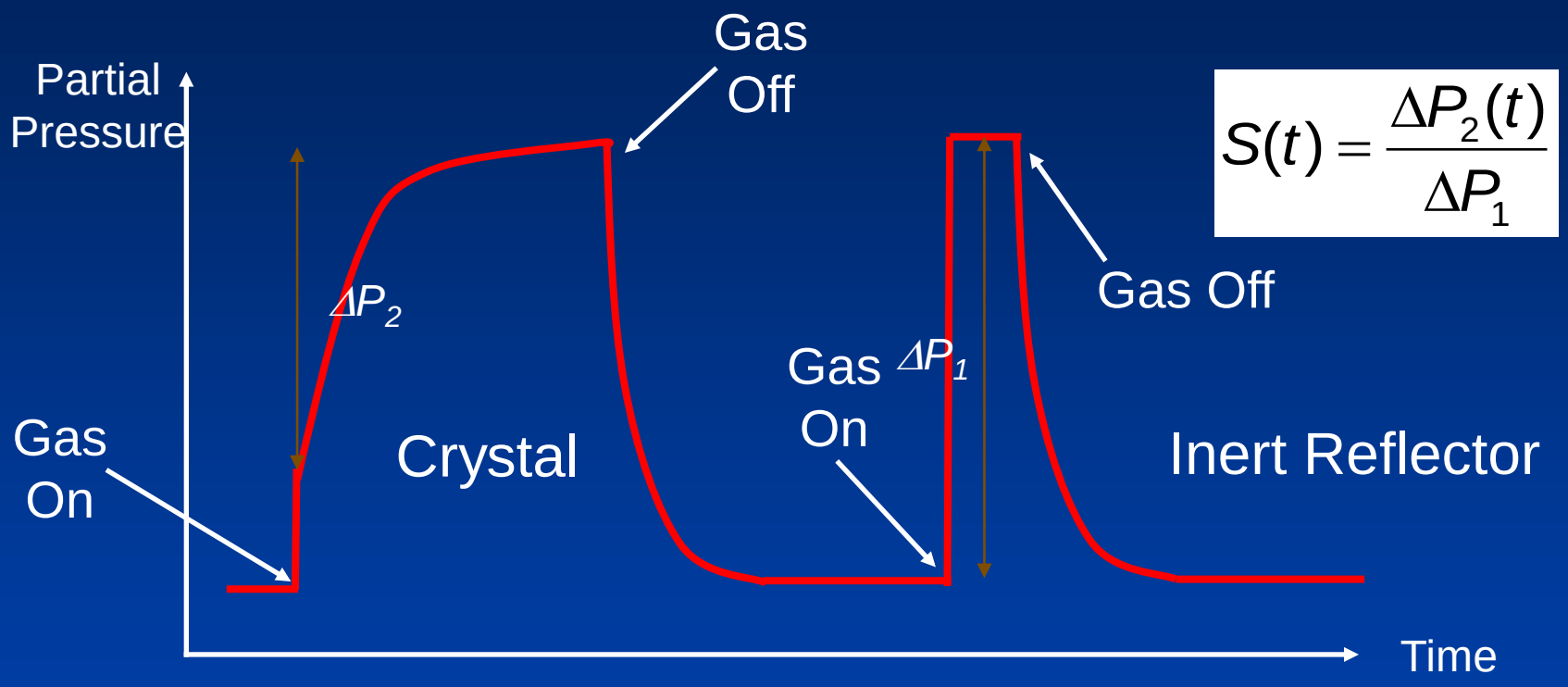
Adsorption on Grain Surfaces

- The LoS-SP Method turns the King & Wells method on its head and offers an alternative tool for measuring $S(\theta)$ for $S > 0.05$



Reaction and Sticking Probabilities using Line of Sight Techniques: Iodine on Al (111)
Jones and Fisher, *Surf. Sci.*, 1999, **424**, 127

Adsorption on Grain Surfaces



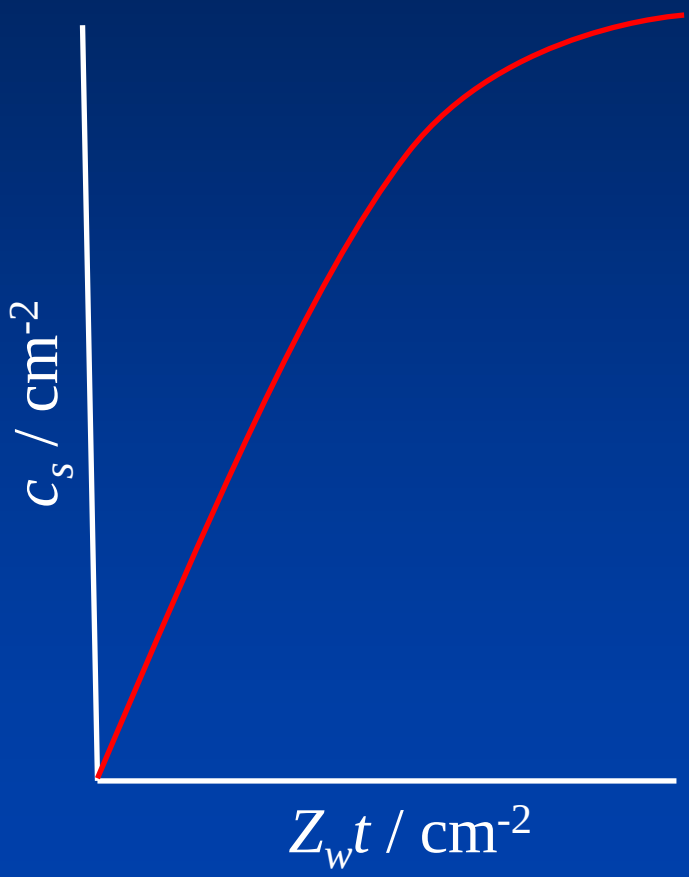
$$S(t) = \frac{\Delta P_2(t)}{\Delta P_1}$$

Adsorption on Grain Surfaces

- To measure S < 0.05, we use calibrated uptake measurements
  - Measure surface concentration (c_s) using a calibrated surface sensitive spectroscopy
  - Plot *versus* exposure, *i.e.* the total number of incident molecules incident in time t (= $Z_w t$) as in the figure on the right
- S is then defined in terms of

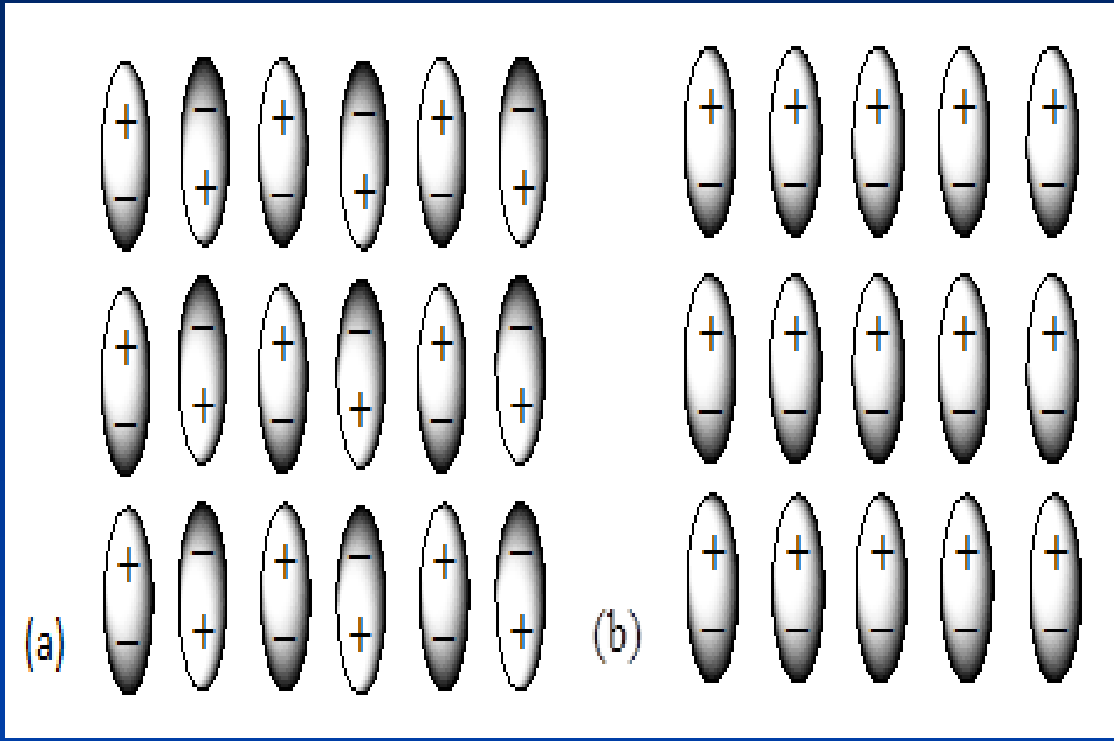
$$S = \frac{dc_s}{d(Z_w t)}$$

i.e. the slope of the curve at any value of $Z_w t$



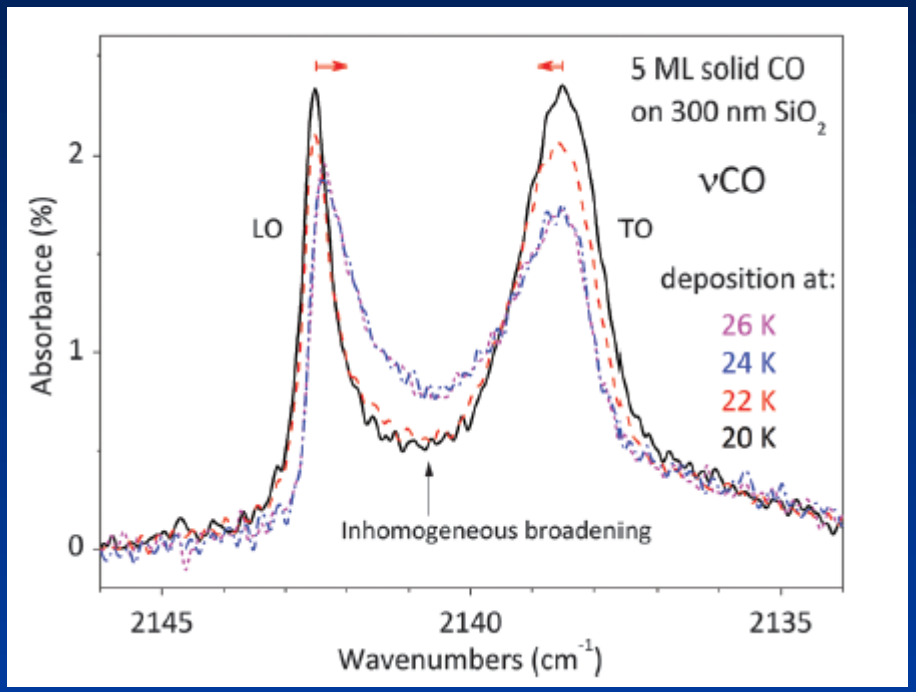
Depositing Dipolar Molecular Thin Films…

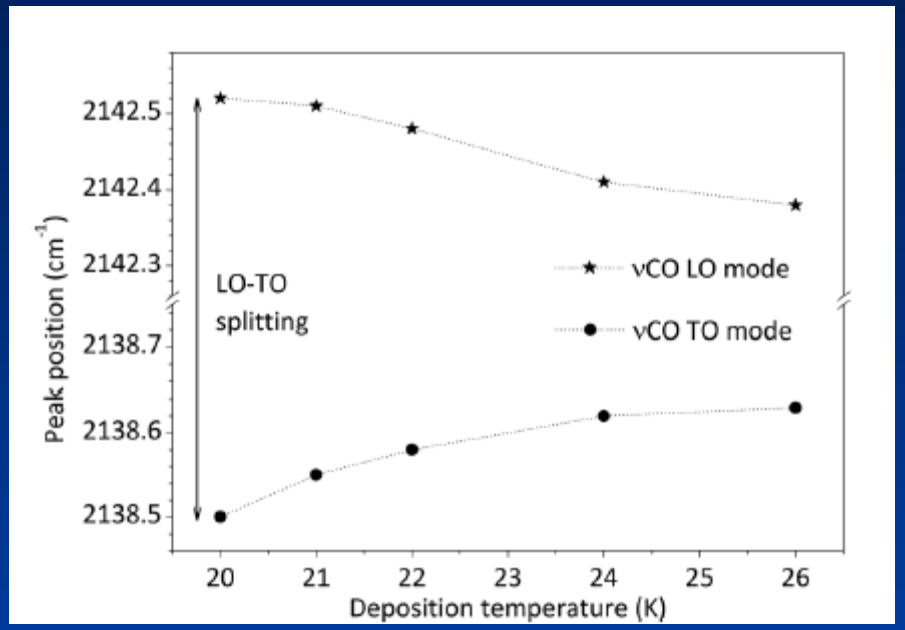
- Chemical intuition would tell us dipolar molecules would absorb as in (a)



- Experimental measurement shows us… (b)

Depositing Dipolar Molecular Thin Films…





Still Don't Understand Why This Happens?

Spontaneous Electric Fields in Solid Carbon Monoxide

J. Lasne, A. Rosu-Finsen, A. Cassidy, M. R. S. McCoustra, and D. Field, *Phys. Chem. Chem. Phys.*, 2015, **17**, 30177-30187

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University

Adsorption on Grain Surfaces

- Carbon monoxide, amorphous solid water, ammonia, methanol all show this behaviour at cryogenic temperatures and express a bulk electric fields up to 10^8 V/m
  - Vibrational Stark Effect
  - Surface Potentials
- We can express this in terms of $<\mu_z/\mu>$, the average dipole orientation perpendicular to the thin solid film
  - Potentials increase with increasing film thickness
  - Decrease with increasing deposition temperature

Spontaneous Electric Fields in Solid Films: Spontelectrics
D. Field, O. Plekan, A. Cassidy, R. Balog, N.C. Jones and J. Dunger, *Int. Rev. Phys. Chem.*, 2013, **32**, 345-392

A Review of Recent Progress in Understanding the Spontelectric State of Matter
O. Plekan, A. Rosu-Finsen, A. M. Cassidy, J. Lasne, M. R. S. McCoustra and D. Field, *Eur. Phys. J. D*, 2017, **71**, 162

So What with Spontelectric Ices?

- We have demonstrated that spontelectric behaviour in solid CO can be used to fill important gaps in our understanding of the evolution of pre-stellar cores
- Dust grains with a CO ice mantle reduce the degree of ionization of pre-stellar cores by a factor of between 5 and 6
- This reduces the timescale for expulsion of magnetic fields from cores, a key step in promoting gravitational collapse, by a similar factor suggesting an explanation for the discrepancy between observed and calculated timescales for star formation

Enabling Star Formation Via Spontaneous Molecular Dipole Orientation In Icy Solids
A. Rosu-Finsen, J. Lasne, A. Cassidy, M. McCoustra and D. Field, *Astrophys. J.*, 2016, **832**, 1

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Molecule Formation on Grain Surfaces

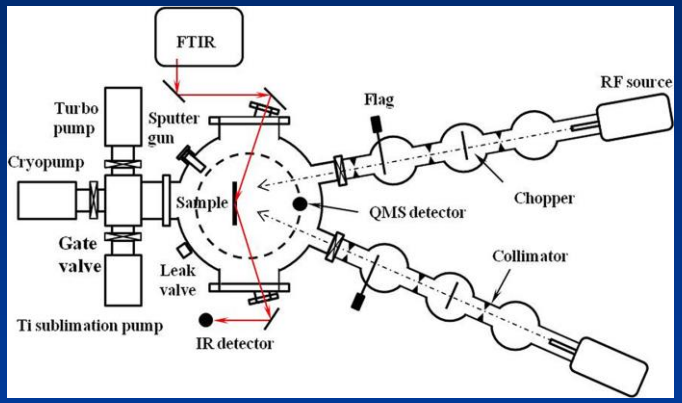
- Let now briefly consider how to make molecules on surfaces… and to transform simple molecules into more complex species by reactions started by light or cosmic rays in icy solids

Molecule Formation on Grain Surfaces

- Key aspects to consider
  - Environment… Cold and Dense *versus* Warm and Diffuse
  - Substrates… Silicaceous *versus* Carbonaceous *versus* Ices
- What do we need to measure?
  - Reaction efficiencies and their temperature dependence
  - Reaction mechanisms and dynamics including energy disposal

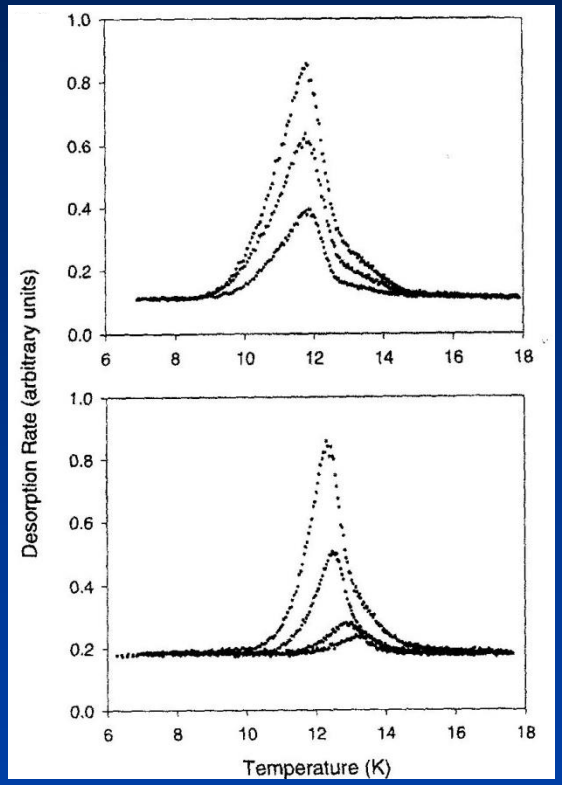
Molecule Formation on Grain Surfaces

- H_2 formation is a nice example
  - Physisorption dominates H/D atom adsorption at low (< 20 K) temperatures
  - Rates established using a combination of beam dosing of H/D atoms and TPD to follow Langmuir-Hinshelwood Mechanism on all surfaces
  - Reaction is efficient enough to account for most of the H_2 formation in cold, dense environments

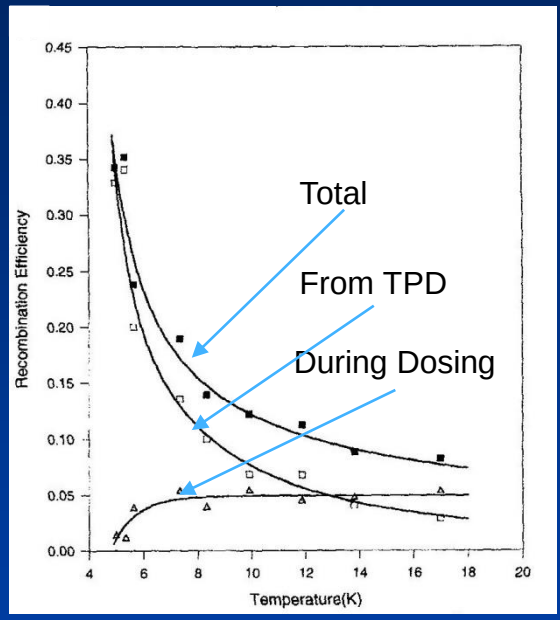


H_2 Formation on Interstellar Grains
G. Vidali, *Chem. Rev.*, 2013, **113**, 8762

Molecule Formation on Grain Surfaces



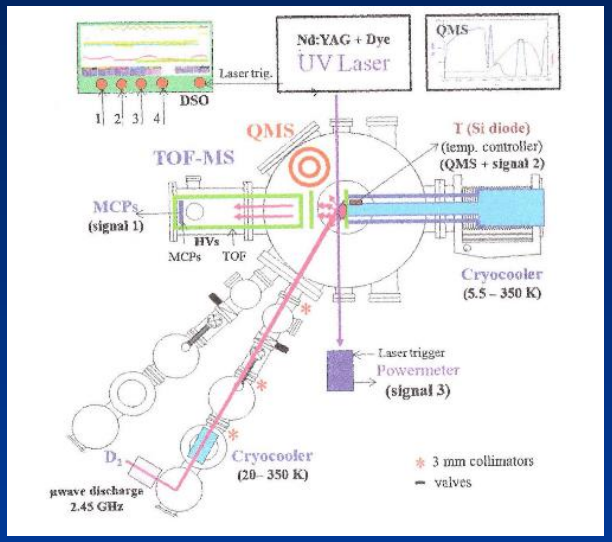
HD TPD data as a function of H/D dosing time from 0.07 to 8 minutes



HD recombination efficiency as a function of surface temperature

Molecule Formation on Grain Surfaces

- H_2 formation is a nice example
  - Formation of the H-H bond releases something like 4.2 eV
  - Dynamical studies reveal substantial vibrational and rotational excitation in the H_2 product consistent with dynamical simulations
  - Key input to energy balance of the cold, dense regions and has prompted observational work looking for hot H_2

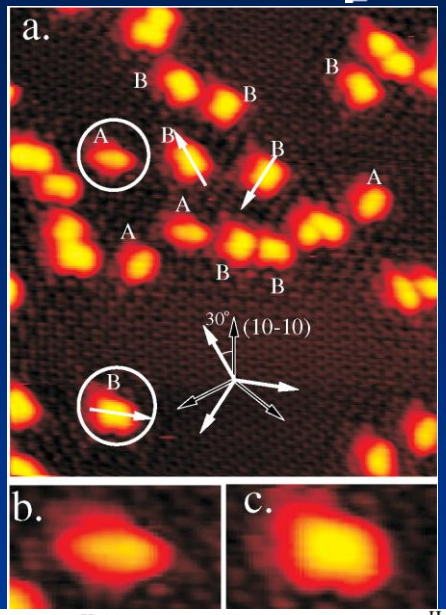


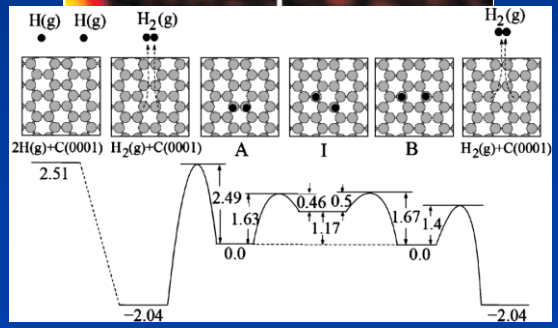
Competing Mechanisms of Molecular Hydrogen Formation in Conditions Relevant to the Interstellar Medium

F. Islam, E. R. Latimer and S. D. Price, *J. Chem. Phys.*, 2007, **127**, 064701; J. –L Lemaire, G. Vidali, S. Baouche, M. Chehrouri, H. Chaabouni and H. Mokrane, *Astrophys. J.*, 2010, **725**, L156

Molecule Formation on Grain Surfaces

- H_2 formation is a nice example
  - H_2 formation also observed in warm, diffuse environments
  - Formation likely involves chemisorbed H/D on graphitic/graphenic/PAH surfaces
  - STM studies have established role of H_2 dimers on the hexagonal carbon surface and agree with high quality DFT studies of these systems

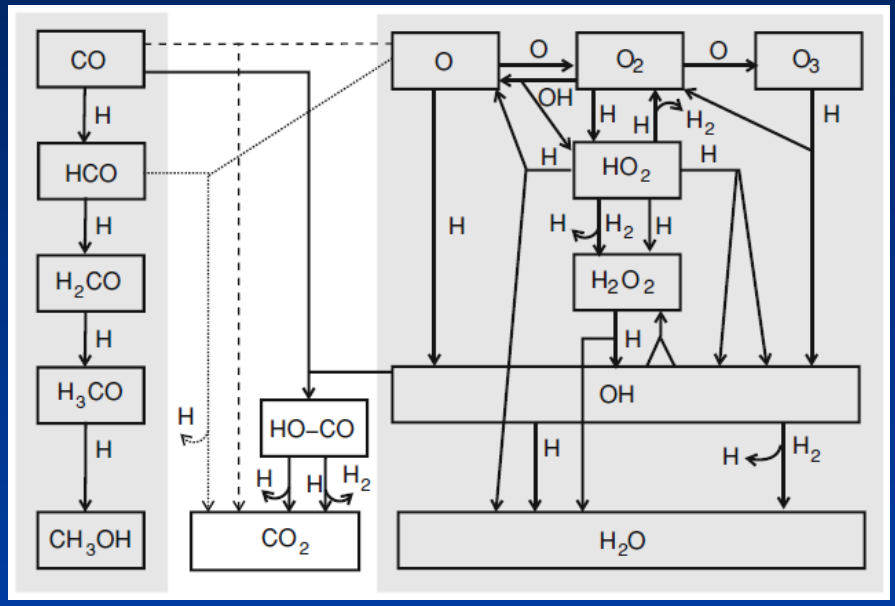




Metastable Structures and Recombination Pathways for Atomic Hydrogen on the Graphite (0001) Surface
L. Hornekær, Z . Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Lægsgaard, B. Hammer and F. Besenbacher, *Phys. Rev. Lett.*, 2006, **96**, 156104

Molecule Formation on Grain Surfaces

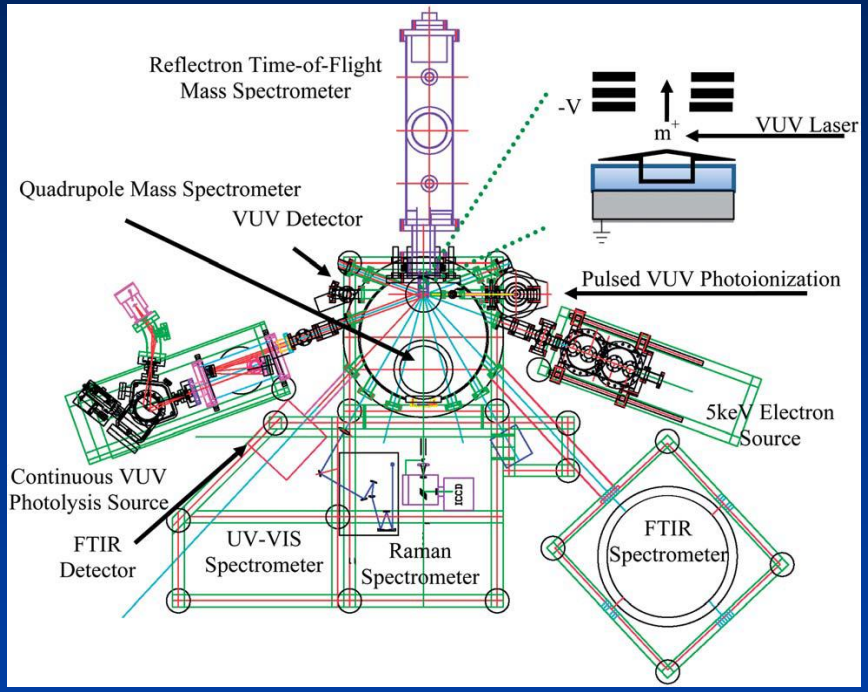
- The chemistry of cold, dense environments changes with time
  - H atoms dominate the gas phase but H_2 formation efficient
  - Early chemistry is dominated by hydride (H_2O, NH_3,…) formation and H atom addition reactions
  - Observe products of that chemistry directly from IR spectra of solids



Surface Formation of HCOOH at Low Temperature
S. Ioppolo, H. M. Cuppen, E. F. van Dishoeck and H. Linnartz, *Mon. Not. Roy. Astron. Soc.*, 2011, **410**, 1089

Molecule Formation on Grain Surfaces

- The chemistry of cold, dense environments changes with time
  - H_2 dominates the gas phase
  - Late chemistry associated with formation of complex organic molecules by radiation induced chemistry
  - Observe products of that chemistry in the gas phase

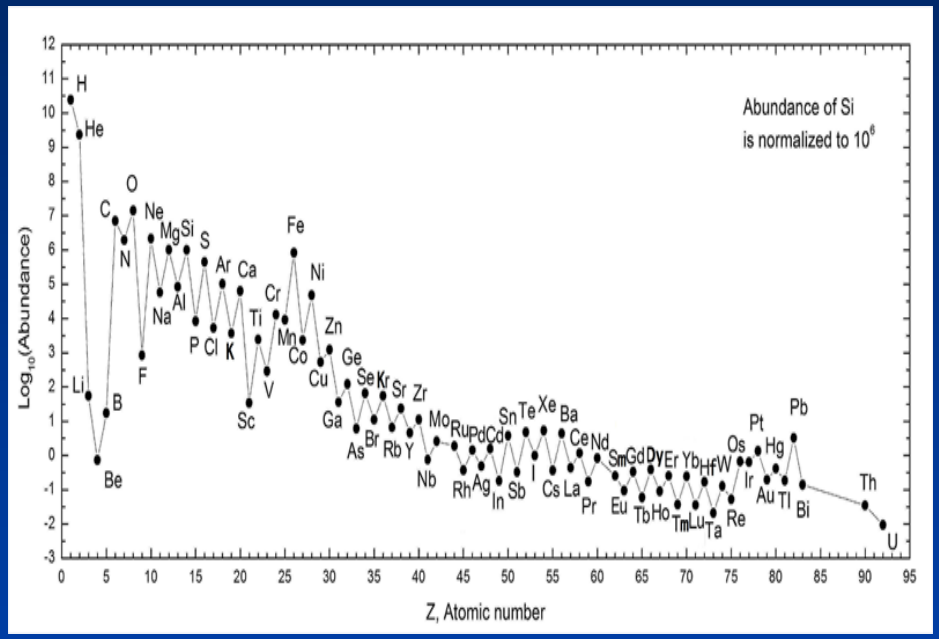


Infrared and Reflectron Time-of-flight Mass Spectroscopic Study on the Synthesis of Glycoaldehyde in Methanol (CH_3OH) and Methanol-Carbon Monoxide (CH_3OH-CO) Ices Exposed to Ionising Radiation

S. Maity, R. I. Kaiser and B. M. Jones, *Faraday Discuss.*, 2014, 168, 485

Molecule Formation on Grain Surfaces

- Catalytic elements are abundant in space and on grains (as single atoms and nanoclusters)
- Astrocatalysis involving Fischer-Tropsch and Haber-Bosch chemistries may be an important contributor to chemical evolution in some denser and higher temperature environments



Diffusion on and Desorption from Grains

- Then we need to understand how they are returned to the gas phase where they are most readily detected… especially with the molecule hunting telescope ALMA
  - Collisions
  - Thermal Processes
  - Non-Thermal (Light and Radiation Induced) Processes

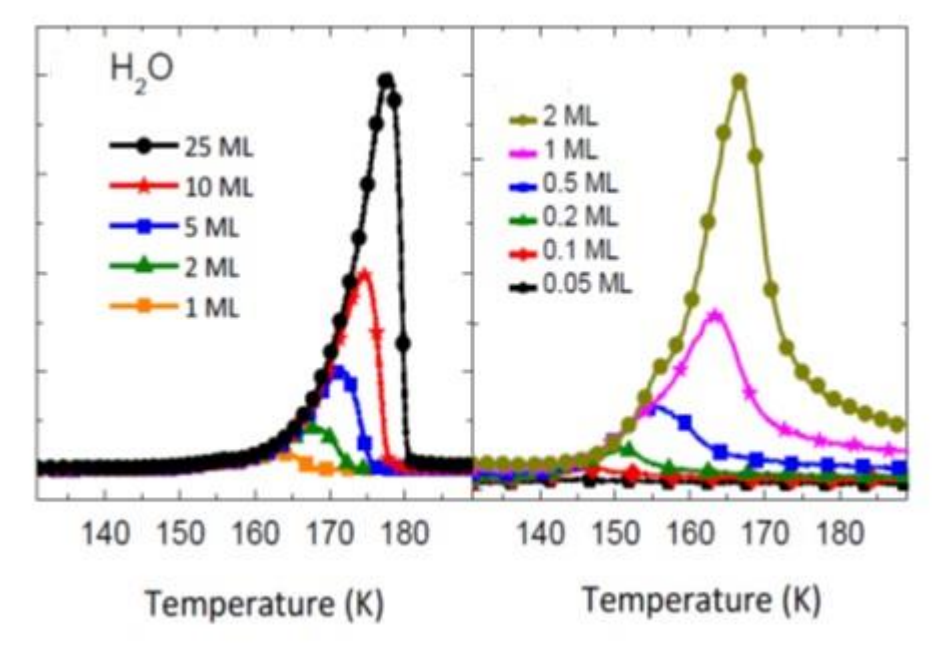
Collision-induced Diffusion and Desorption

- Collisions can promote diffusion
  - Thermal energies (meV) at relevant temperatures are too small to induce desorption but may induce diffusion
  - But it hasn't been studied!
- Collisions can promote desorption
  - Super-thermal energies (meV – few eV) can induce desorption and may be relevant in shocked regions
  - Cosmic Ray energies from a few eV to TeV can induce chemical changes while above a few 100s of eV sputtering is common
  - Grain-grain collisions? (single particle surface science?)

Thermal Diffusion and Desorption

- Heating…
  - Activates diffusion…
  - … and we need to understand diffusion as it is at the centre of the issue of whether adsorbates wet or de-wet from substrates

Water Diffusion on Silica



- Water is a polar molecule … it should wet the silica surface!
- But TPD shows zero order behaviour at all exposures consistent with de-wetting!

Water does not wet the Silica Surface!

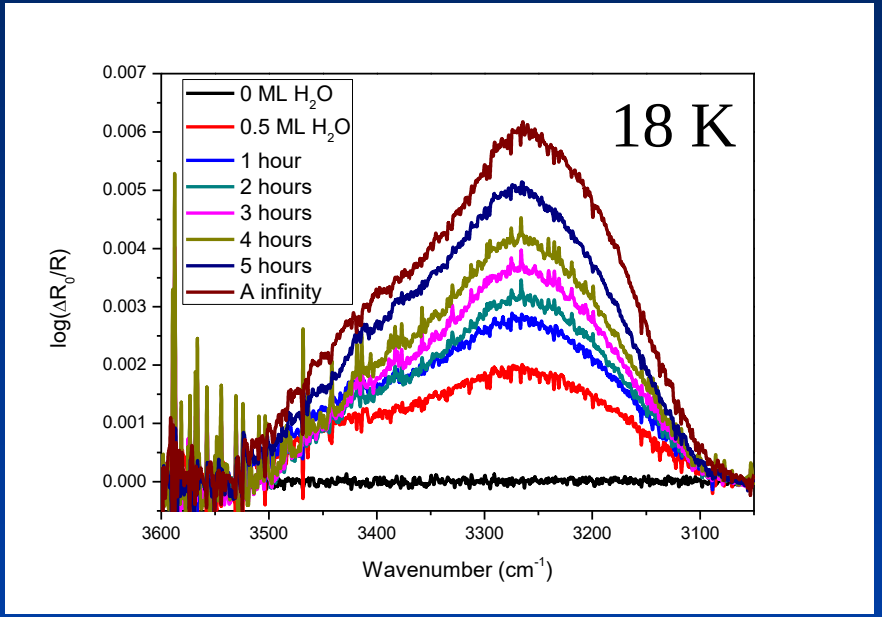
Peeling the Astronomical Onion

A. Rosu-Finsen, D. Marchione, T. L. Salter, J. W. Stubbing, W. A. Brown, and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.,* 2016, **18**, 31930-31935

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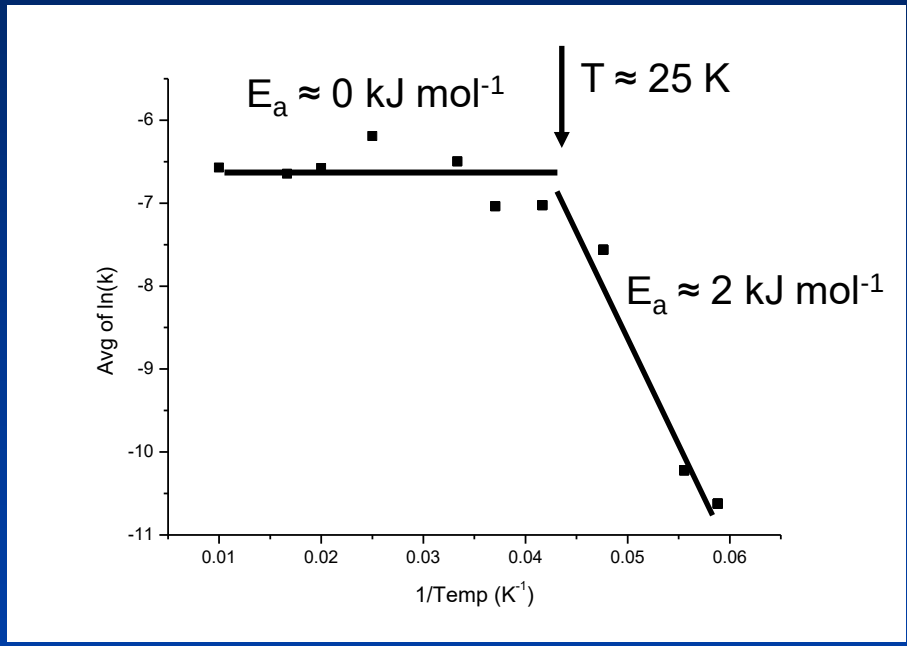
Water Diffusion on Silica

- A simple RAIRS experiment
  - Fix temperature at 15 K
  - Deposit sub-monolayer quantity of H_2O
  - Anneal to 18 K and wait for an hour and cool to 15 K, record spectrum and repeat…
  - Intensity of O-H stretching band increases with time in a regime where there is no increase in the number of H_2O on the surface!
- Agglomeration of isolated H_2O and small clusters of H_2O into bulk islands on the silica!



Water Diffusion on Silica

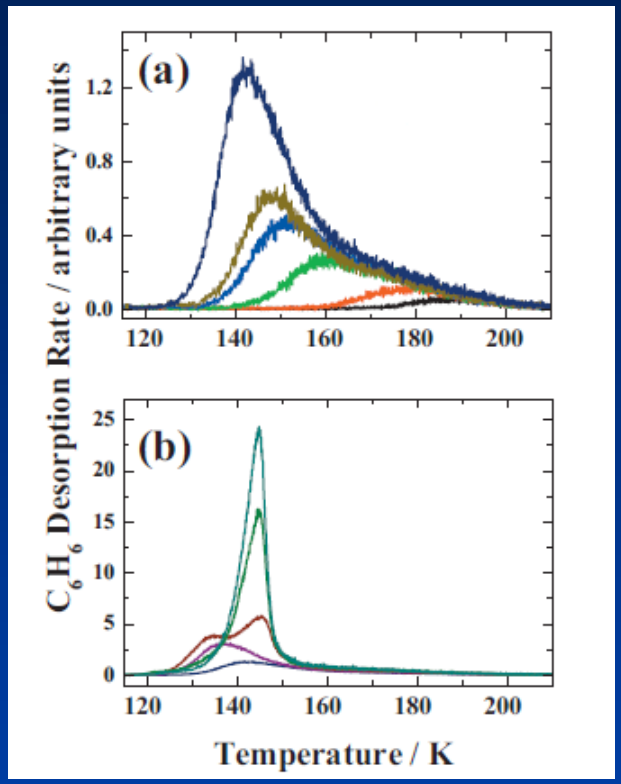
- First order kinetics analysis straight from the undergraduate laboratory
- Repeat at new temperature!
- Arrhenius analysis as a function of annealing temperature



Barrier to Agglomeration of 2 kJ/mol Below 25 K

Benzene Diffusion on Silica

- Benzene is a non-polar molecule … it should not wet the silica surface!
- But TPD shows a clear monolayer growing before the multilayer.



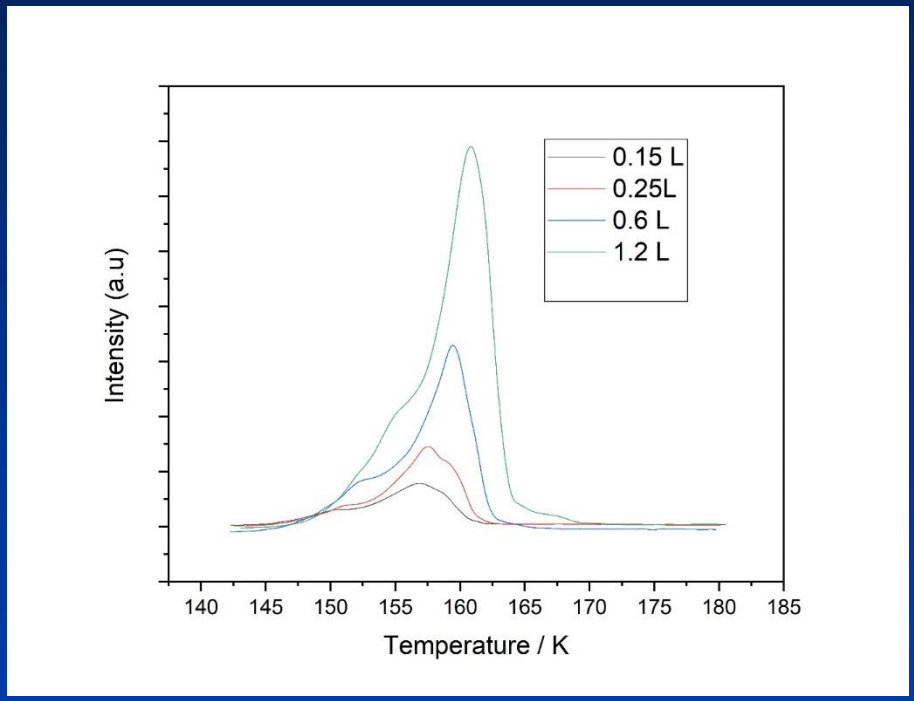
Chemical Intuition Doesn't Work as Benzene Wets Silica Surface!

Laboratory Investigations of the Interaction between Benzene and Bare Silicate Grain Surfaces
J. D. Thrower, M. P. Collings, F. J. M. Rutten and M. R. S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2009, **394**, 1510–1518

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Cyclohexane Diffusion on Silica

- Cyclohexane is a non-polar molecule … it should not wet the silica surface!
- TPD is consistent with de-wetting in showing zero order kinetics at all exposures.

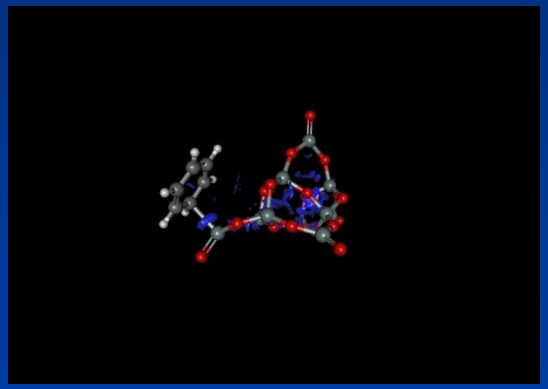


Chemical Intuition Works!

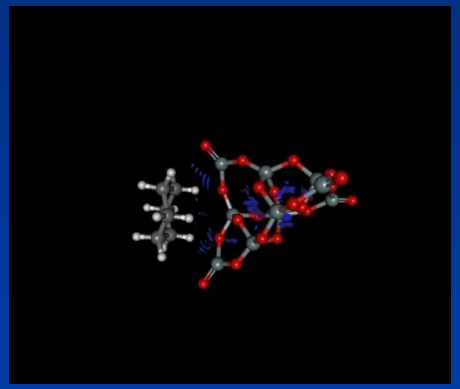
R. Senevirathne, *MPhil* ***Thesis*** (Heriot-Watt University, Edinburgh, Scotland, 2024)

Adsorption and Diffusion

- A deeper perspective comes from modest *ab initio* calculations…
  - Silica clusters from work of Bromley and co-workers (*Comp. Theo. Chem.*, 2017, **1102**, 38-43)
  - Simple HF calculations with 6.311G** basis using GAMESS-US



ΔE_{BSSE} = -75.77 kJ/mol



ΔE_{BSSE} = -11.31 kJ/mol

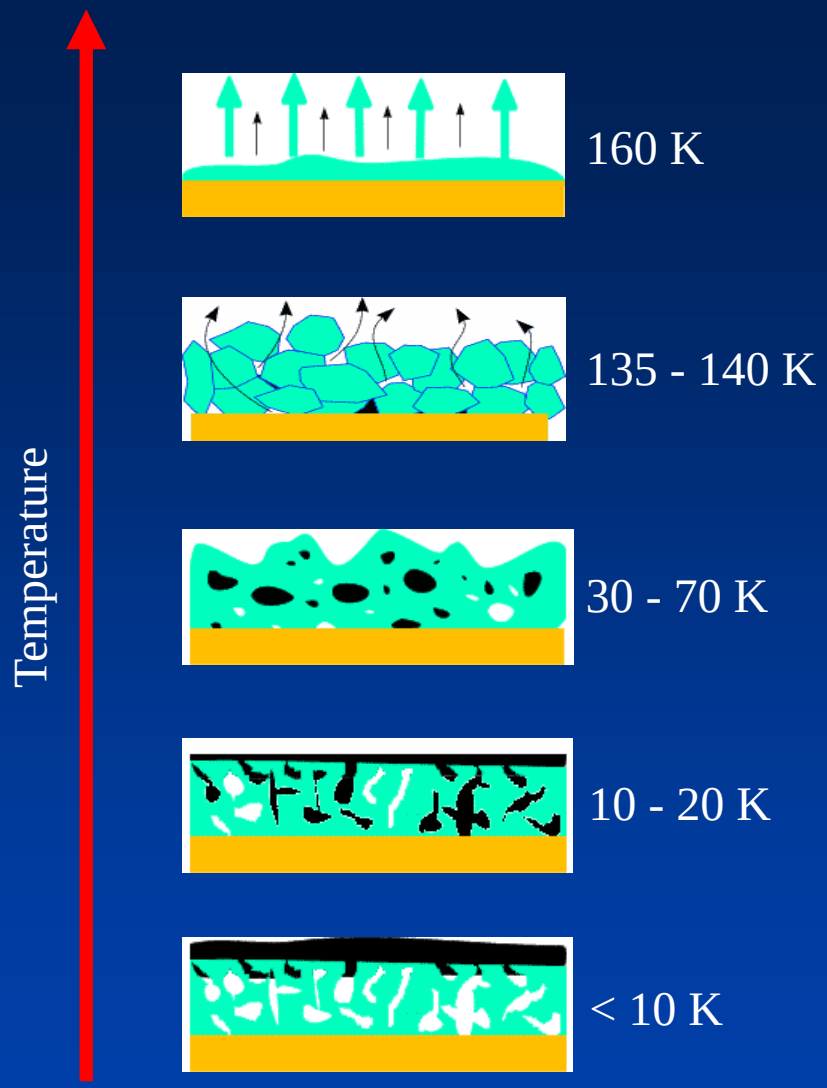
Balance of Binding Energy to Surface and to Molecular Solid

R. Senevirathne, *MPhil* ***Thesis*** (Heriot-Watt University, Edinburgh, Scotland, 2024)

Thermal Diffusion and Desorption

- Heating…
  - Activates diffusion…
  - Promotes thermal desorption…

An Example…

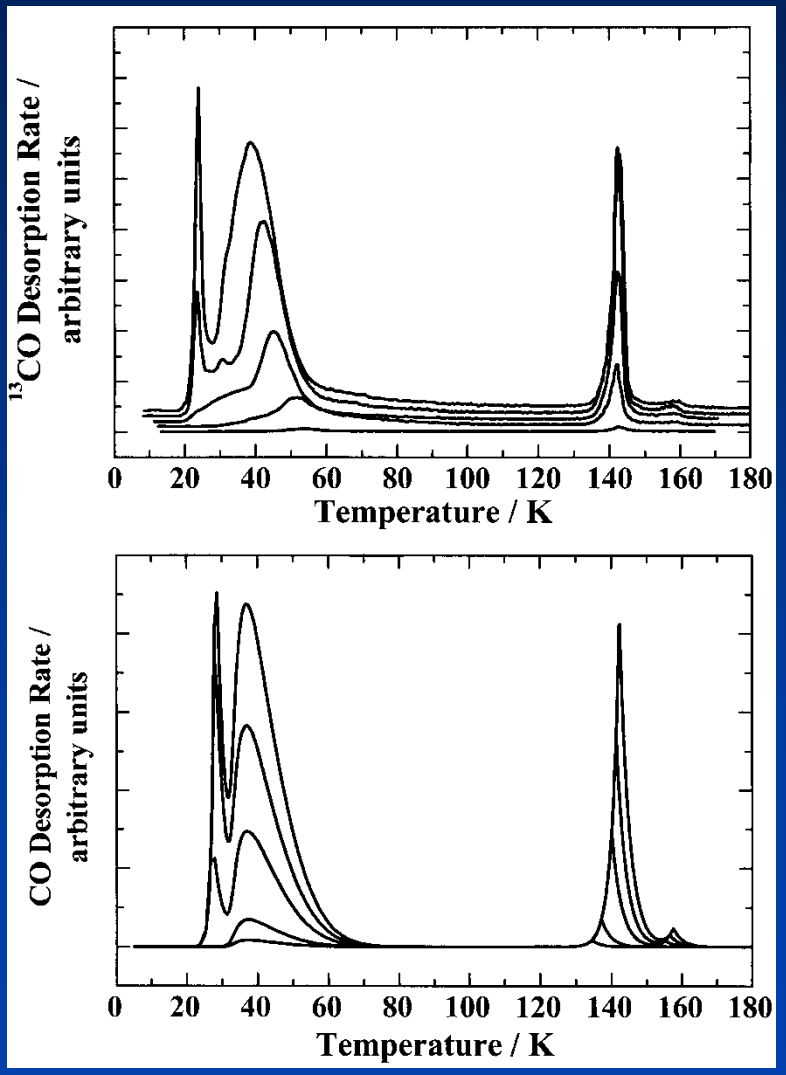


Carbon Monoxide Entrapment in Interstellar Ice Analogs
M. P. Collings, H. J. Fraser, J. W. Dever, M. R. S. McCoustra and D. A. Williams
Astrophys. J., 2003, **583**, 1058-1062

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University

An Example…

- Constructed a kinetic model to describe this process which reproduces well our experimental observations.
- We are now using it in a predictive manner to determine what happens at astronomically relevant heating rates, *i.e.* A few 10s of pK s^{-1} *cf.* 80 mK s^{-1} in our TPD studies

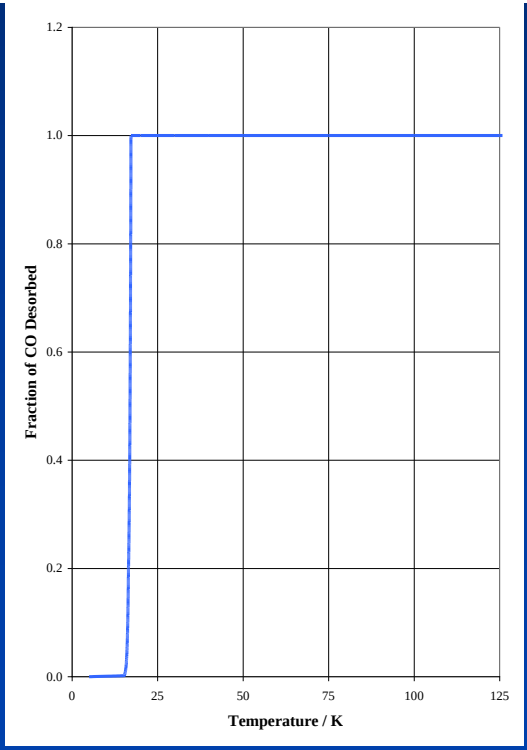


An Example…

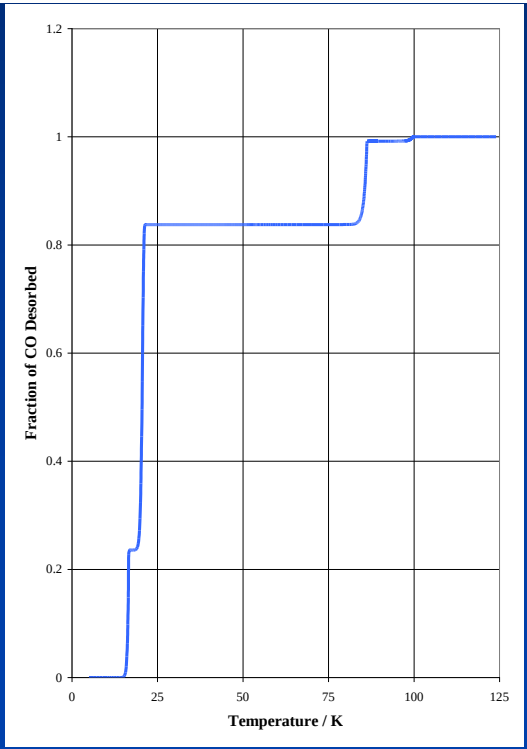
- What do these observations mean to those modelling the chemistry of the interstellar medium?

Assume Heating Rate of 1 K millennium^{-1}

Old Picture of CO Evaporation

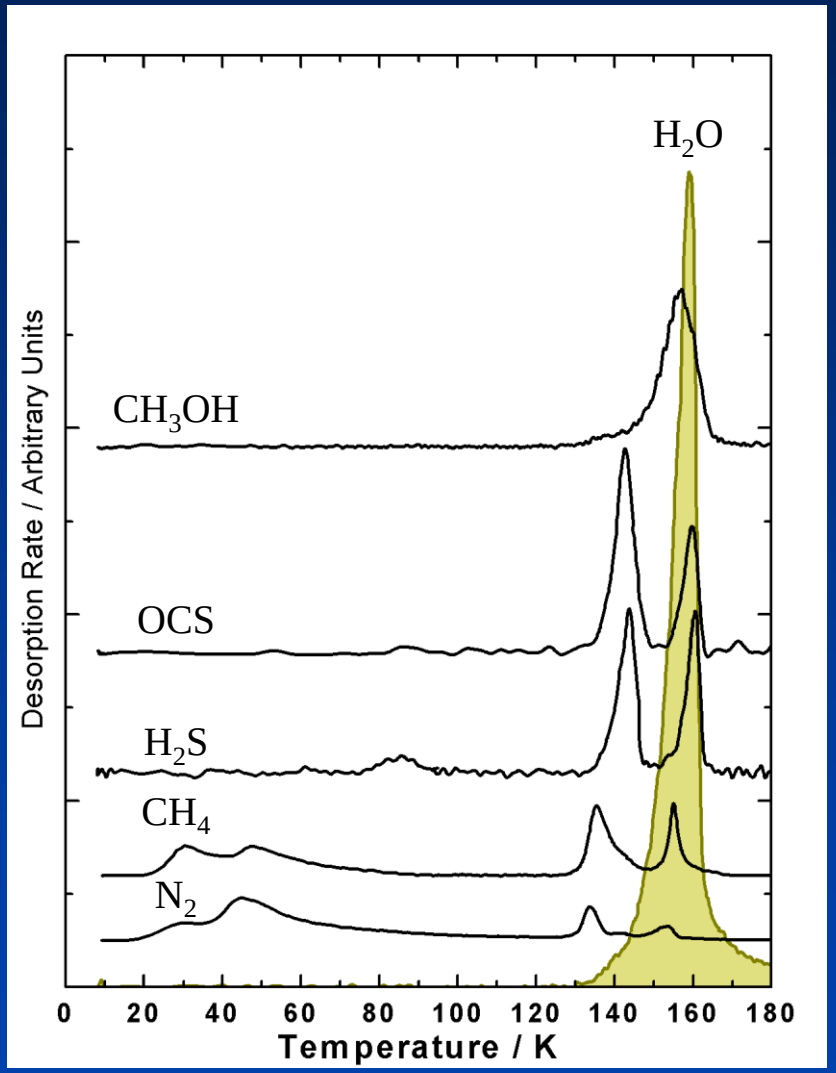


New Picture of CO Evaporation



Extending the Example…

- Qualitative survey of TPD of grain mantle constituents
  - **Type 1**
    - Hydrogen bonding materials, *e.g.* NH_3, CH_3OH, …, which desorb only when the water ice substrate desorbs
  - **Type 2**
    - Species where $T_{sub} > T_{pore\ collapse}$, *e.g.* H_2S, CH_3CN, …, have a limited ability to diffuse and hence show only molecular desorption and do not trap when overlayered on water ice but exhibit largely trapping behaviour in mixtures
  - **Type 3**
    - Species where $T_{sub} < T_{pore\ collapse}$, *e.g.* N_2, O_2, …, readily diffuse and so behave like CO and exhibit four TPD features whether in overlayers or mixtures
  - **Type 4**
    - Refractory materials, *e.g.* metals, sulfur, *etc.* desorb only at high temperatures (100s of °C)



Non-Thermal Diffusion and Desorption

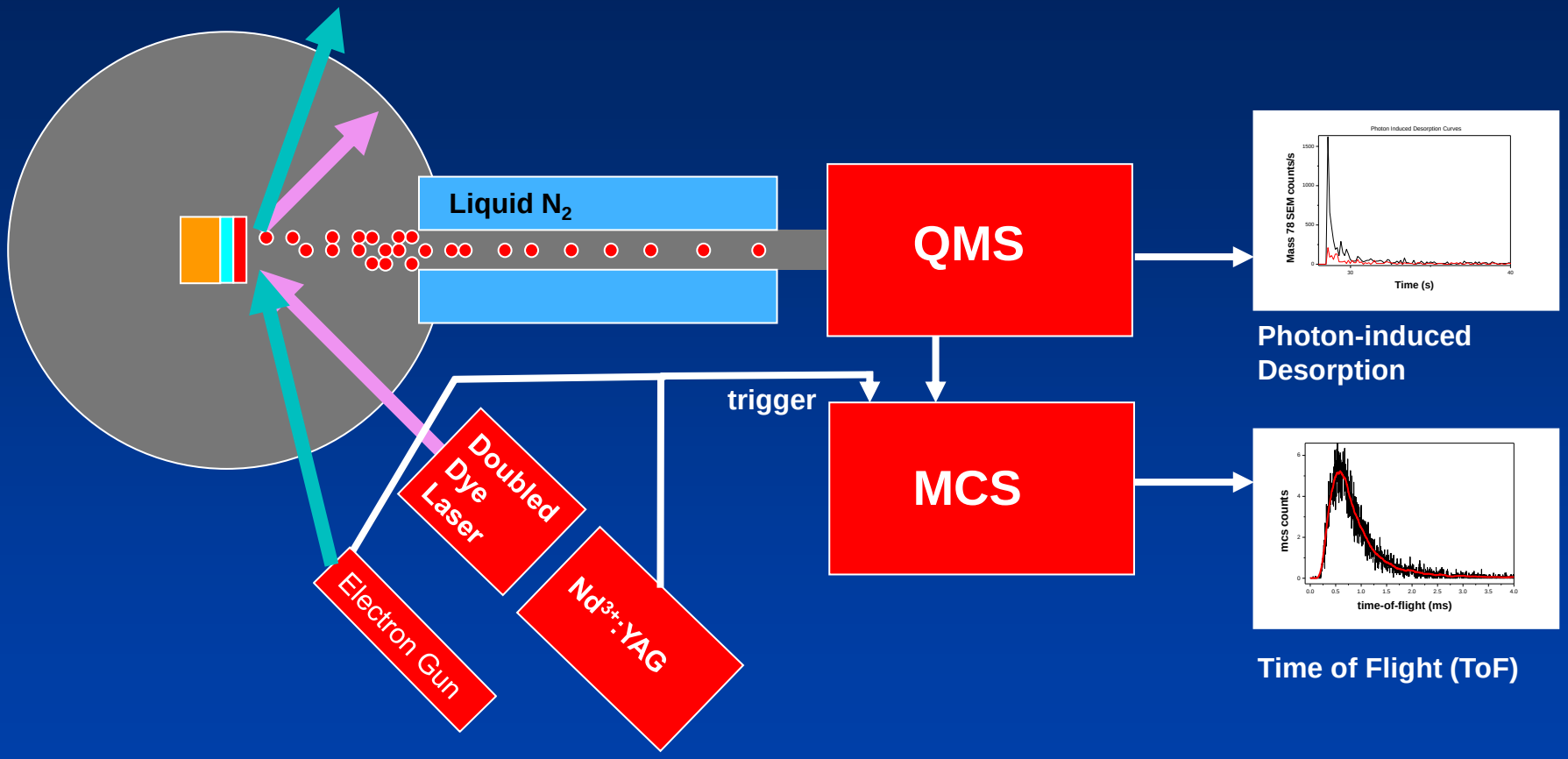
- What about Vibrational Excitation?
  - Abundance of IR wavelengths in the interstellar radiation field
  - Also more readily penetrates dense environments than shorter wavelengths
  - Mid-IR photons have energies in excess of typical weak physisorption interaction and so should be able to promote diffusion and desorption

Watch this Space!

Non-Thermal Diffusion and Desorption

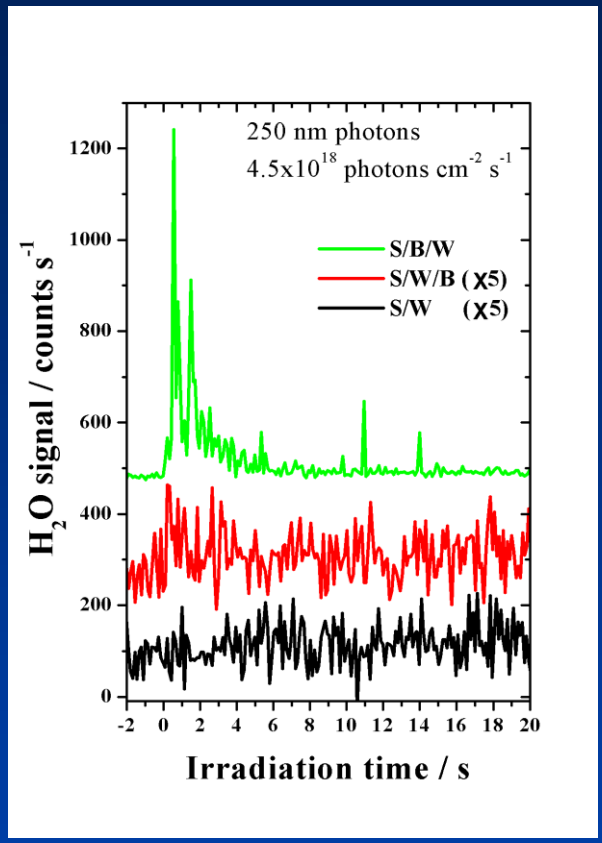
- What about Electronic Excitation?
  - Photons… Typically VUV (around 10 eV) but also visible as the maximum flux in the interstellar radiation field is in the visible
  - Cosmic Rays and their secondary electrons… Secondary electrons are the key to understanding Cosmic Ray effects on icy solids… Of course each Cosmic Ray can produce many secondary electrons
  - Need to measure both reaction efficiencies and their temperature dependence and reaction mechanisms and dynamics including energy disposal as the later is important in the environmental energy balance

Shining a Little Light or Electrons…



UV Photons… Desorption Kinetics

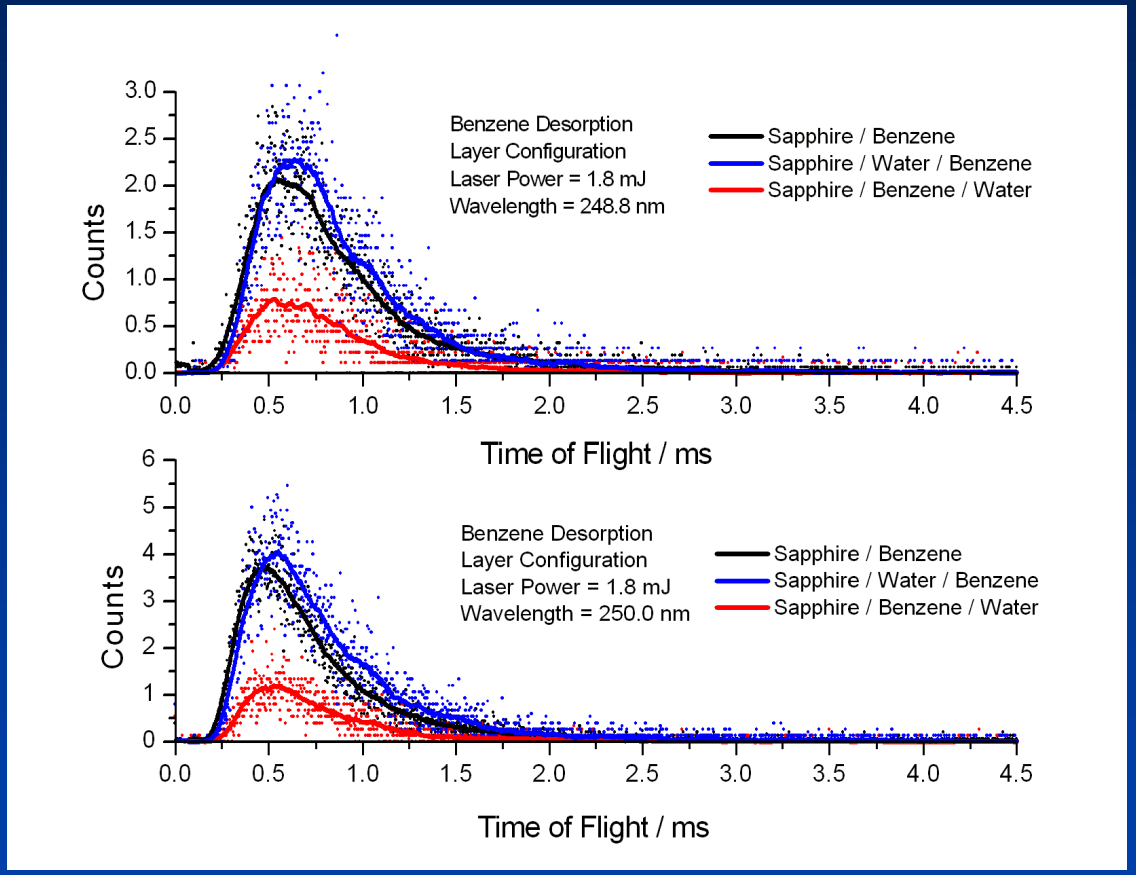
- System studied, C_6H_6 on amorphous solid H_2O
- Presence of C_6H_6 promotes H_2O desorption
- Cross-section for the process can be estimated from PSD curves 1×10^{-19} cm^2 at 250 nm *cf.* 4×10^{-19} cm^2 for C_6H_6 itself
- Suggests an efficiency approaching 0.25!



Photon-and Electron-stimulated Desorption from Laboratory Models of Interstellar Ice Grains
J. D. Thrower, A. G. M. Abdulgalil, M. P. Collings, M. R. S. McCoustra, D. J. Burke, W. A. Brown, A. Dawes, P. J. Holtom, P. Kendall, N. J. Mason, F. Jamme, H. J. Fraser, and F. J. M. Rutten, *J. Vac. Sci. Technol. A*., 2010, **28**, 799.

UV Photons… Mechanism and Dynamics

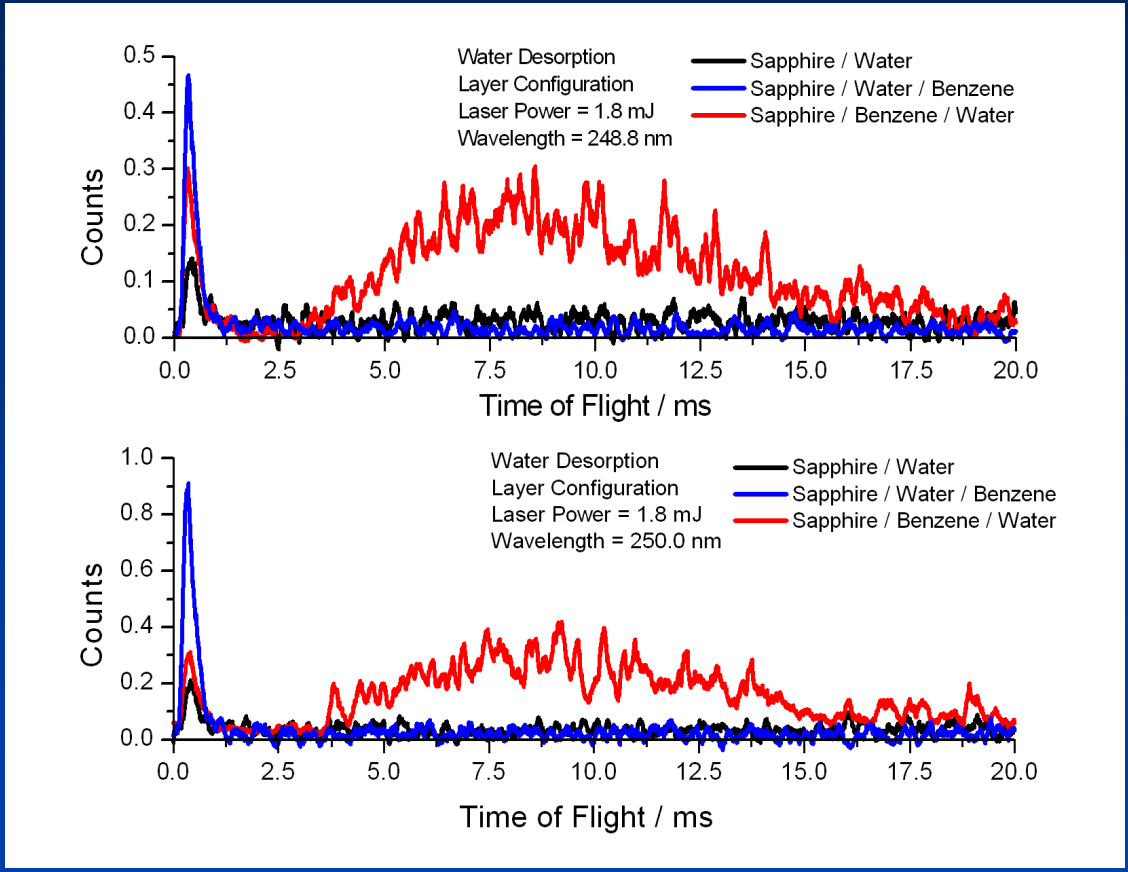
- C_6H_6 desorption observed at all wavelengths
  - Substrate-mediated desorption weakly dependent on wavelength
  - Adsorbate-mediated desorption reflects absorption strength of C_6H_6
- Yield of C_6H_6 is reduced by the presence of a H_2O capping layer12



Surface Science Investigations of Photoprocesses in Model Interstellar Ices
J. D. Thrower, M. P. Collings, M. R. S. McCoustra, D. J. Burke, W. A. Brown, A. Dawes, P. D. Holtom, P. Kendall, N. J. Mason, F. Jamme, H. J. Fraser, I. P. Clark and A. W. Parker, *J. Vac. Sci. Technol. A*, 2008, **26**, 919.

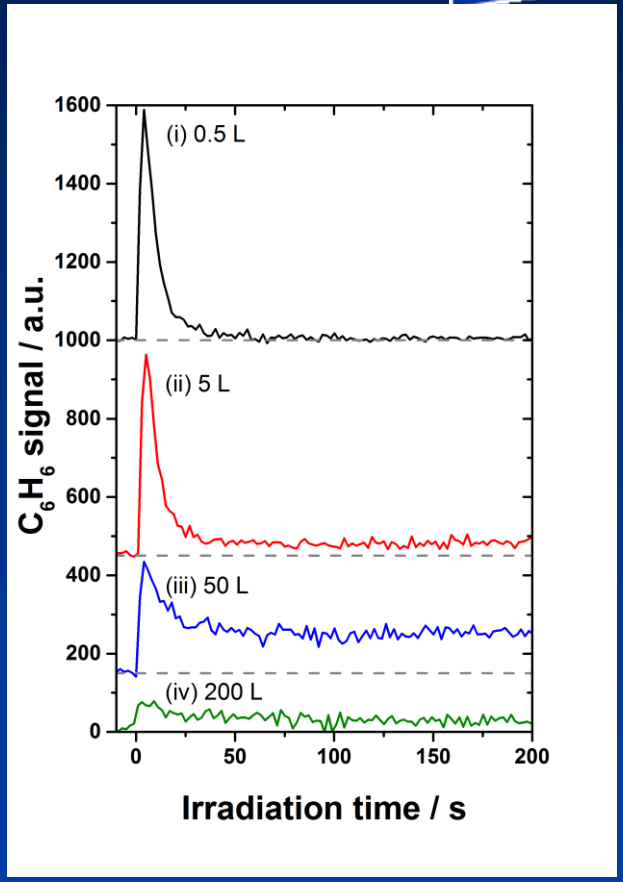
UV Photons… Mechanism and Dynamics

- H_2O desorption echoes that of C_6H_6
- But H_2O does not absorb at any of these wavelengths and so desorption is mediated *via* the substrate and the C_6H_6
- Yield of H_2O is increased by the presence of a C_6H_6 layer



Secondary Electrons… Desorption Kinetics

- C_6H_6 on amorphous solid H_2O were irradiated with electrons of energies of between 100 and 400 eV
- Desorption of C_6H_6 mediated by the H_2O ice and the formation of excitons
- Desorption of C_6H_6 diffusing between islands has a massive cross-section of around 2×10^{-15} cm^2 in this range *cf.* 5×10^{-18} cm^2 for H_2O
- We see no evidence for any chemical transformations only desorption

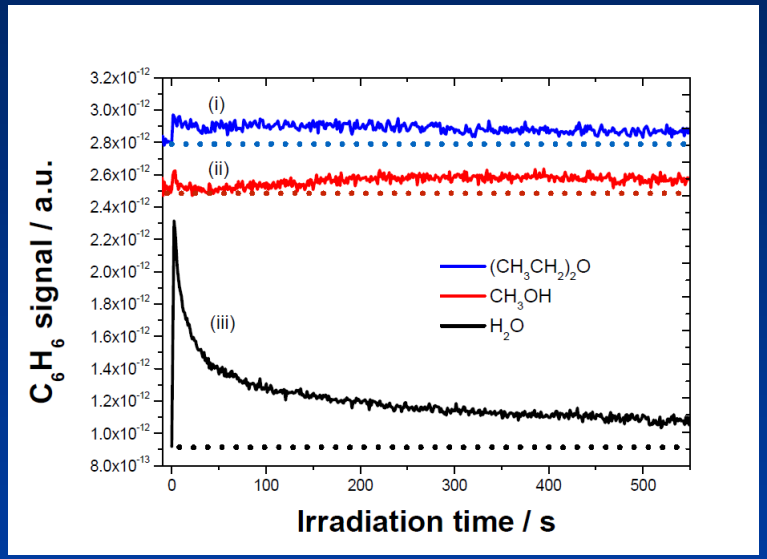


Highly Efficient Electron-stimulated Desorption of Benzene from Amorphous Solid Water Ice

J. D. Thrower, M. P. Collings, F. J. M. Rutten, and M. R. S. McCoustra, *Chem. Phys. Lett.*, 2011, **505**, 106-111

Secondary Electrons… Mechanism

- Hint of a fast desorption from CH_3OH (red)
  - Linear hydrogen bonded chains
  - CH_3OH has no dangling OH groups at the surface so CH_3OH must re-orientate on surface if C_6H_6 is to π hydrogen bond to the surface and the long-time rise in signal is probably due to that!
- No evidence for fast process on $(CH_3CH_2)_2O$ (blue)
  - No intermolecular hydrogen bonding
  - C_6H_6 interacts with the $(CH_3CH_2)_2O$ *via* van der Waals forces
- Hydrogen bonding is crucial!



A Toy Astrophysical Model

- Context is important in this work as we must convince astronomers and astrophysicists of the value of the work
- Kinetic simulations based on the realistic assumptions of photon and electron fluxes

$$H_2O(s) \xrightarrow{\Delta T} H_2O(g)$$

$$-\frac{dn_{H_2O(s)}}{dt} = \nu_{des} e^{-E_{des}/RT}$$

$$H_2O(s) \xrightarrow{h\nu_{ISRF}} H_2O(g)$$

$$-\frac{dn_{H_2O(s)}}{dt} = \left[\sum_{\lambda} f_{ISRF}(\lambda)\sigma_{ISRF}(\lambda)\right] n_{H_2O(s)}$$

$$H_2O(s) \xrightarrow{h\nu_{CRI}} H_2O(g)$$

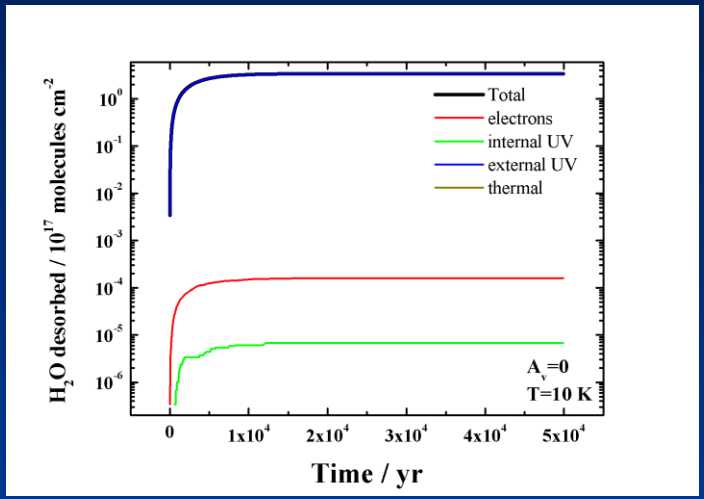
$$-\frac{dn_{H_2O(s)}}{dt} = \left[\sum_{\lambda} f_{CRRF}(\lambda)\sigma_{CRRF}(\lambda)\right] n_{H_2O(s)}$$

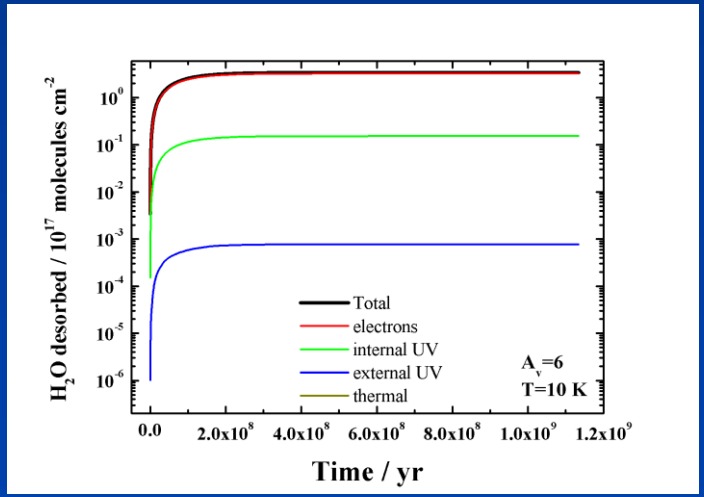
$$H_2O(s) \xrightarrow{e^-_{CRI}} H_2O(g)$$

$$-\frac{dn_{H_2O(s)}}{dt} = \left[\sum_{E} f_{CRIE}(E)\sigma_{des,CRIE}(E)\right] n_{H_2O(s)}$$

A Toy Astrophysical Model

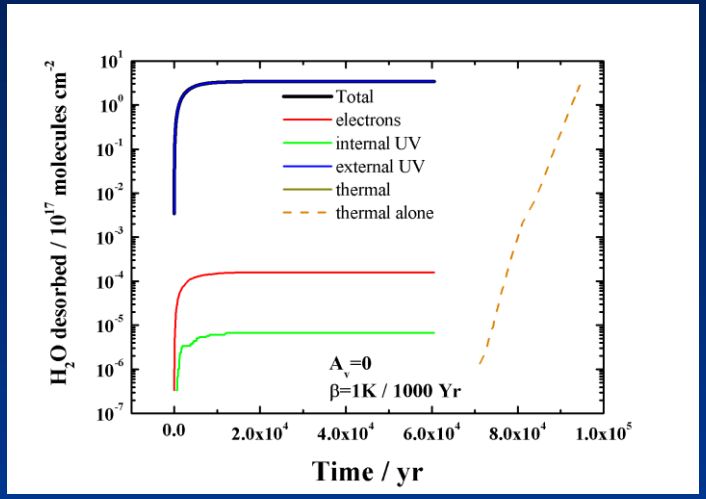
- Kinetic simulations based on the assumptions of photon and electron fluxes on the previous slides
  - Steady-state

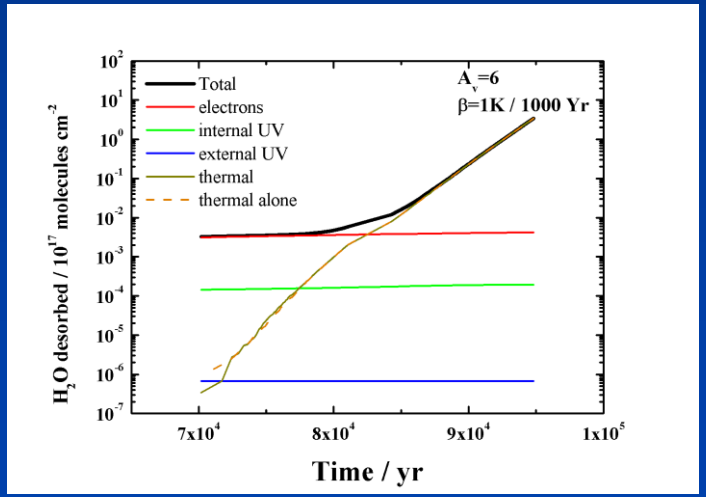




A Toy Astrophysical Model

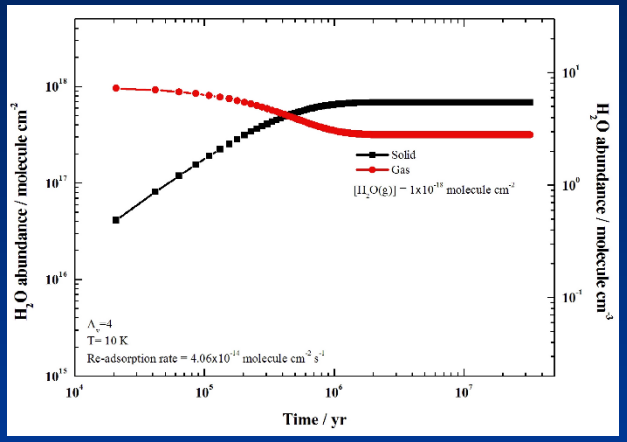
- Kinetic simulations based on the assumptions of photon and electron fluxes on the previous slides
  - Steady-state
  - Thermal desorption

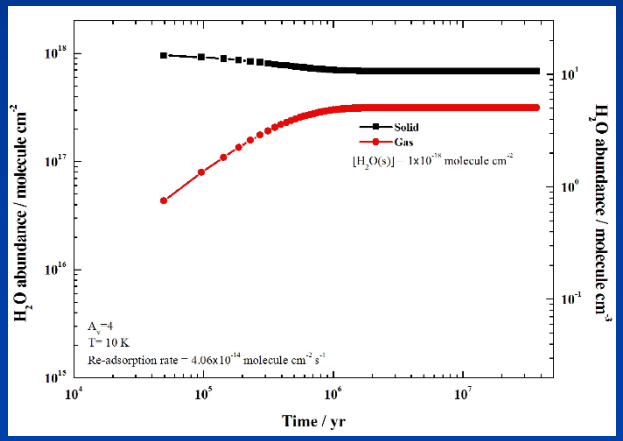




A Toy Astrophysical Model

- We can add re-adsorption to this simulation and use our model to look at simple systems approaching equilibrium if we ignore thermal desorption
  - From the gas phase
  - From the solid state





Conclusions…

- Surface Science has a key role to play in understanding the physics and chemistry of astrophysical environments
- The physics and chemistry that we model in our laboratories and in our computers is universal and that includes the process of taking chemical complexity to the edge of life
- Astronomers have now found in excess of 3400 planets orbiting distant stars in the Milky Way… Some are massive Jupiter-like planets, perhaps with strange orbits about their star, but others are small and Earth-like
- New telescopes and space missions are planned to seek out smaller Earth-like planets in the Goldilocks' Zone around remote stars
- Surface Science can help us address the origins of life!

Conclusions… And An Advert!

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