Gas – Grain Interactions

A Surface Science Tutorial

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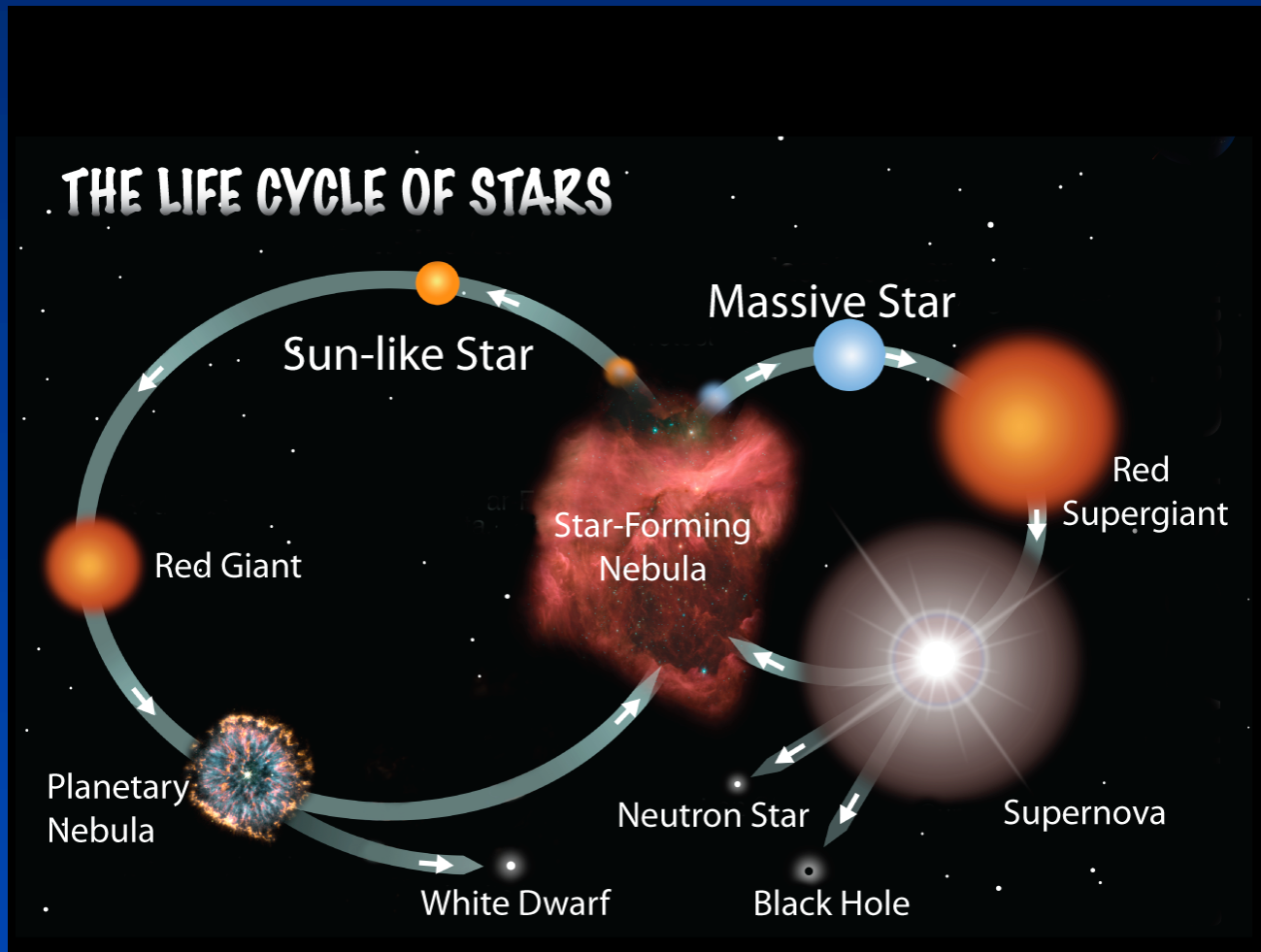
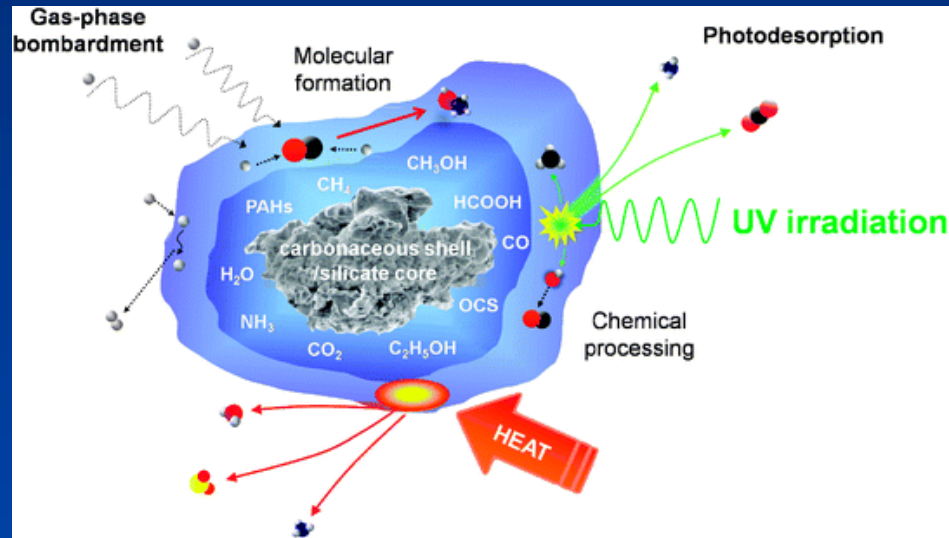# Astrochemistry…

Astrochemistry…

☞ Icy grains grow by a combination of reactive accretion (*e.g.* H_2O, NH_3 etc.) and deposition (*e.g.* CO)

☞ Icy grains are cooked by a combination of optical radiation from the interstellar radiation field and charged particle radiation

☞ Thermal and non-thermal desorption returns material to the gas phase where it is readily observed

What is Surface Science?

At the crudest level, all of the physical and chemical changes that can occur at a surface can be summarized in three simple processes

Getting stuff on the surface

Getting stuff off the surface

Stuff happens on the surface

SURFACE

What is Surface Science?

☞ A way of thinking about surfaces and understanding them…

☞ Problem is one of both sensitivity and discrimination

☞ Commonly used tools in Laboratory Astrochemistry…

- Temperature programmed desorption
- Spectroscopy in both transmission and reflection-absorption
- Molecular beam methods for atom and radical dosing
- Laser spectroscopies for state-resolved methods with ToF or VMI

☞ Tools that new experiments might use…

- X-ray photoelectron spectroscopy
- Electron energy loss spectroscopy
- Kelvin Probe
- Surface kinetic tools such as LITD and MBMS

What is Surface Science?

☞ Many good text books cover the concepts and practice of surface science, most with a focus on single crystal surfaces but the ideas can be translated…

- Gasser, *An Introduction to Chemisorption and Catalysis by Metals* (Oxford University Press, 1985)
- Attard and Barnes, *Surfaces* (Oxford University Press, 1998)
- McCash, *Surface Chemistry* (Oxford University Press, 2001)
- Kolasinski, *Surface Science* (Wiley, 2002)

☞ A very useful book for the laboratory is

- Yates, *Experimental Innovations in Surface Science* (Springer, 2015)

Getting Stuff on the Surface…

☞ Adsorption…

☞ Rate of adsorption determined by

- Collision Frequency on the surface (Z_w)
- Sticking Coefficient (S) for adsorbate on surface
  - S = 1 for low temperature thin film deposition;
  - S = 0 for deposition above the desorption temperature and where no multilayer growth is permitted)
  - $S = S_0(1 - n_s/n_{s0})$ for Langmuir growth of a monolayer;

$$r_{ads} = SZ_w$$

$$Z_w = n_g \left(\frac{k_B T}{2\pi m} \right)^{1/2}$$

☞ Adsorption… is a dynamic process

☞ Dynamics are encompassed within S and how it depends on translational energy; and rotational, vibrational and electronic states

☞ Dynamics may be important where relative velocities of the gas and grains are high and collision energies may be substantial

☞ Subtle temperature effects in physisorption (where S is basically unity below the sublimation temperature) but often less so in chemisorption processes

☞ S will reflect nature of the adsorption process… physisorption or chemisorption… and it's balance with desorption (S or α)

Getting Stuff on the Surface…

☞ Unfortunately most experiments designed to measure S do not do so; rather they measure the *uptake coefficient*, α

Input Flux, J_{in} Reflected Flux, J_{ref} Desorbed Flux, J_{des}

Adsorbed Flux, J_{ads}
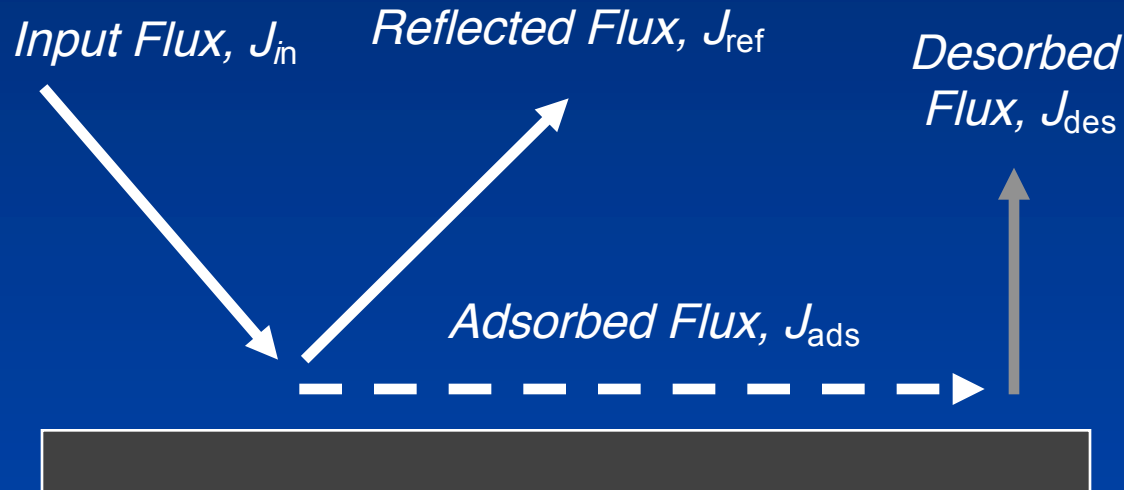
$$\alpha(T, J_{in}) = S(T) - \frac{k_{des}(T)}{J_{in}}$$

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

Stuff Happens on the Surface…

☞ Diffusion…

☞ Difficult to measure but potentially crucial in determining the chemistry

☞ How can we study diffusion?

- Direct observation by Scanning Probe Microscopy
- Indirect measurements using change in spectroscopic signal with time after an initial event (a temperature jump or regional cleaning)
  - Isothermal time-resolved FTIR
  - Isothermal time-resolved LITD

Stuff Happens on the Surface…

☞ Time-resolved RAIRS of O-H stretch of H_2O on silica

☞ Arrhenius analysis suggests…

- Barrier to H_2O diffusion on amorphous silica is around 2 kJ mol⁻¹

- De-wetting of H_2O from silica even at the lowest of temperatures on relatively short timescales (a few 100s of years)

- Activation barrier drops to zero above 25 K coincident with the start of the pore-collapse process in ballistically deposited porous amorphous solid water (p-ASW)

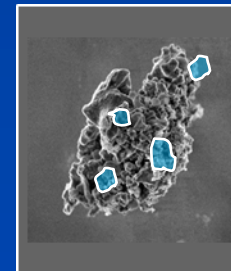- Above 100 K, line profile changes due to phase change
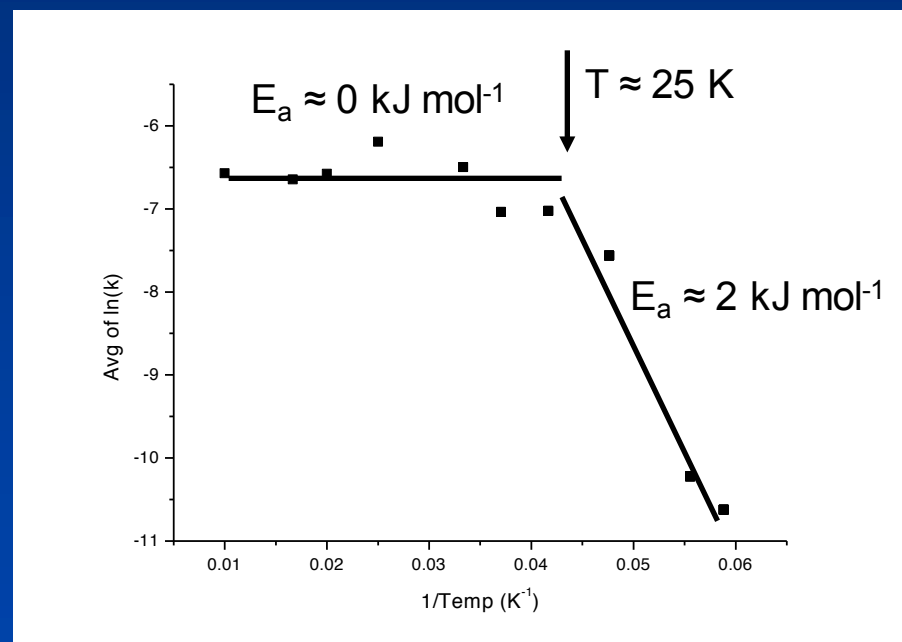
A. Rosu-Finsen, D. Marchione, T. L. Salter, J. W. Stubbing, W. A. Brown and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31930-31935

Stuff Happens on the Surface…

☞ Simple kinetic model based on these observations assuming a cooling environment…
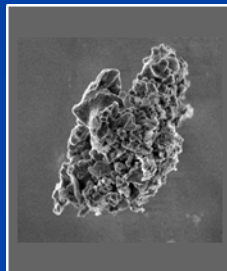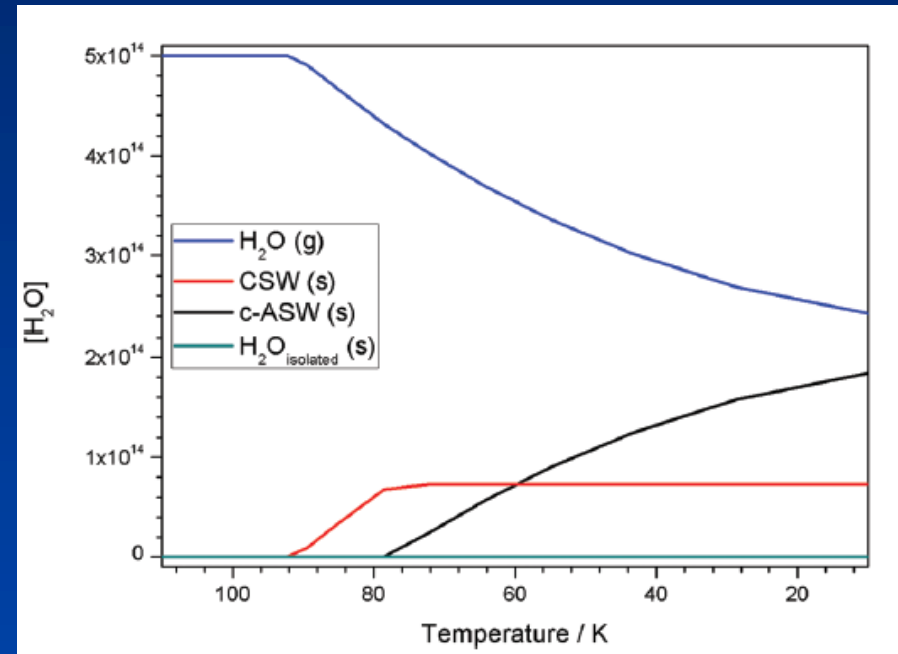
Time ↑

Temperature ↓

Stuff Happens on the Surface…

☞ Chemical reactions…

☞ Careful study has established three reaction mechanisms for reaction processes occurring on solid surfaces

Eley-Rideal Reactions

*Langmuir-Hinshelwood Reactions*

Kasemo-Harris Reactions

Stuff Happens on the Surface…

☞ Developed in the 1940s by Eley and Rideal (see *Nature*, 1946, **146**, 401) from measurements of *ortho-para* exchange in H_2 and isotope exchange between H_2 and D_2 over tungsten surfaces (*e.g. Proc. Roy. Soc. (London)*, 1941, **178A**, 429)


Adsorption

Gaseous Diffusion and Reaction

Desorption
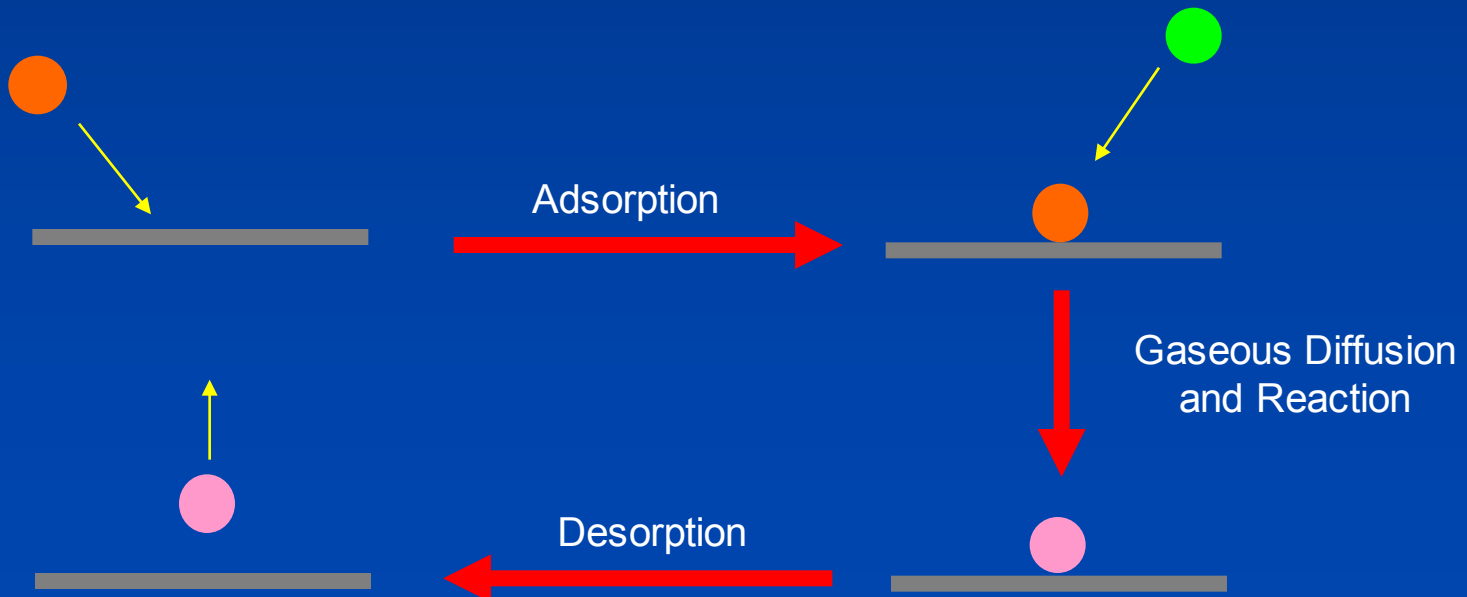
Stuff Happens on the Surface…

☞ The second mechanism we will consider bears the names of Langmuir (http://en.wikipedia.org/wiki/Irving_Langmuir) and Hinshelwood (http://en.wikipedia.org/wiki/Cyril_Norman_Hinshelwood) and involves the reaction of one or two adsorbed species

Adsorption

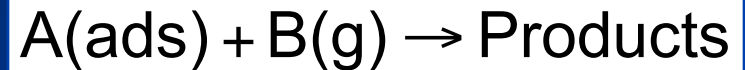Surface Diffusion and Reaction

Desorption
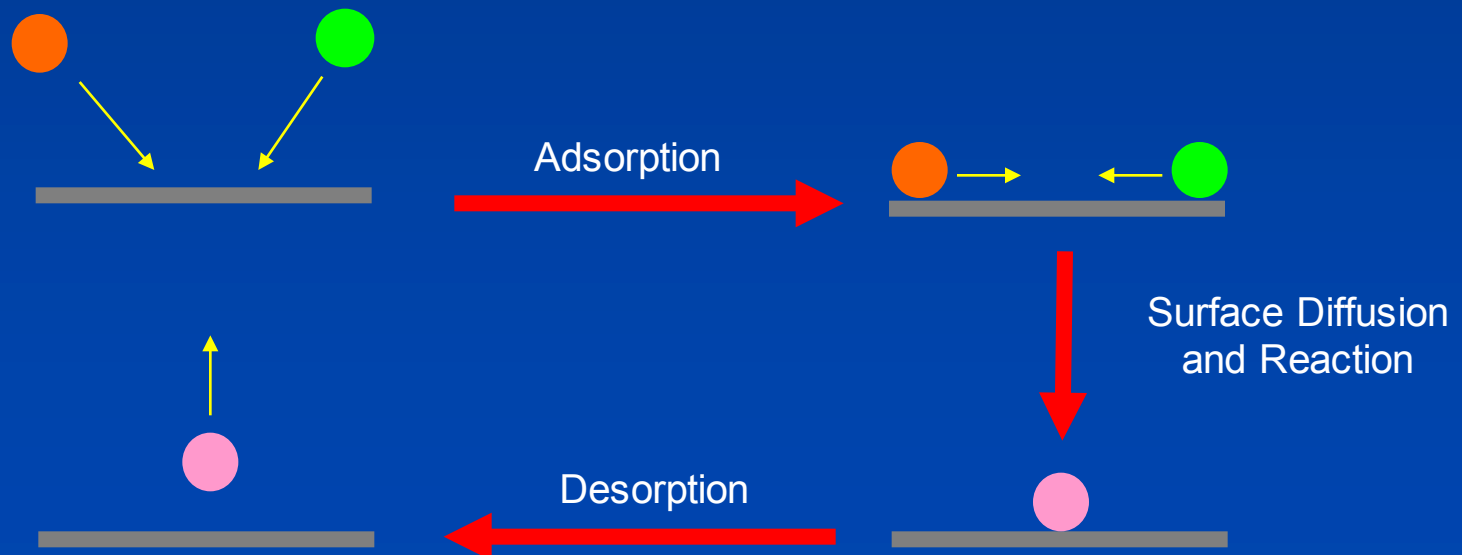
Stuff Happens on the Surface…

☞ Our final example of a surface reaction mechanism is the relatively recently identified Hot Atom or Harris-Kasemo Reaction on surfaces
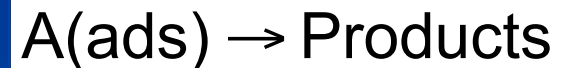

Adsorption

Hot Atom Formation

Hot Atom Reaction

Desorption
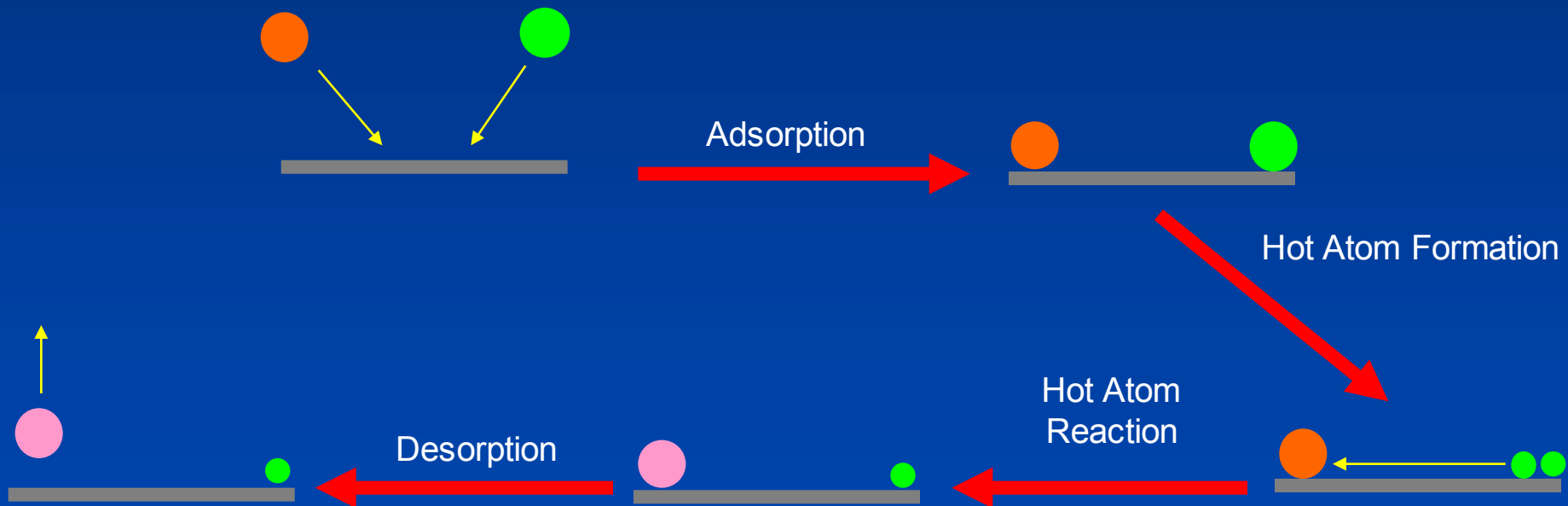
Stuff Happens on the Surface…

☞ Rates of these processes can be defined in terms of relevant gas phase (n_g) and surface (n_{ads}) concentrations

☞ These elementary reactions are always coupled with either gaseous transport (Eley-Rideal) or surface transport (Langmuir-Hinshelwood) processes

☞ Elementary rate law for Kasemo-Harris is essentially the same as Langmuir-Hinshelwood only difference in the hot fragment transport

$$A(ads) + B(g) \rightarrow Products$$

$$v_r = k_{ER} n_{ads,A} n_{g,B}$$

$$A(ads) \rightarrow Products$$

$$v_r = k_{ULH} n_{ads,A}$$

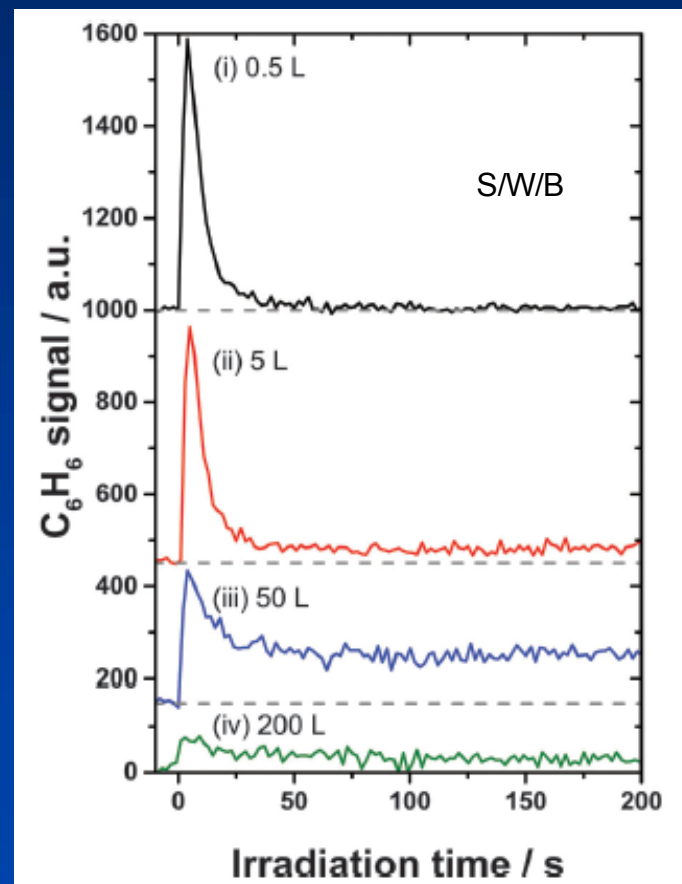$$A(ads) + B(ads) \rightarrow Products$$

$$v_r = k_{BLH} n_{ads,A} n_{ads,B}$$

Stuff Happens on the Surface…

☞ Photochemistry and radiochemistry are the key processes that govern the chemical evolution of ices

☞ Three key points to remember

- Have a common underpinning – electronic excited states (excitons) drive these processes

J. D. Thrower and M. R. S. McCoustra, *Exciton-promoted Desorption from Solid Water Surfaces* in *Encyclopaedia of Interfacial Science* (Elsevier, New York, 2017), in print
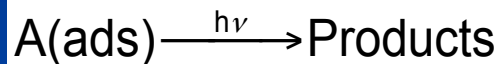
Stuff Happens on the Surface…

☞ H$_2$O ice is a unique substrate when it comes to non-thermal interactions involving high-energy photons and charged particles

☞ Long-lived excitons generated by these radiations can promote efficient desorption of species weakly hydrogen bound to the ice surface (*e.g.* C$_6$H$_6$)

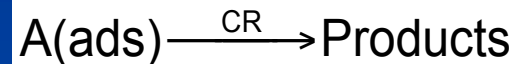☞ Cross-section *ca.* 10^{-16} cm^2

D. Marchione, J. Thrower and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 4026-4034

Stuff Happens on the Surface…

☞ Photochemistry and radiochemistry are the key processes that govern the chemical evolution of ices

☞ Three key points to remember

- Have a common underpinning – electronic excited states (excitons) drive these processes
- These processes have cross sections (σ) which are strongly dependant on the energy of the photons or charged particles

$$A(ads) \xrightarrow{h\nu} Products$$

$$-\frac{dn_{A(ads)}}{dt} = \left[\sum_{\lambda} f(\lambda)\sigma(\lambda) \right] n_{A(ads)}$$

$$A(ads) \xrightarrow{CR} Products$$

$$-\frac{dn_{A(ads)}}{dt} = \left[\sum_{E_{CR}} f(E_{CR})\sigma(E_{CR}) \right] n_{A(ads)}$$

$$= \left[\sum_{E_{CR}} f(E_{CR}) \left(\sigma(E_{CRn}) + \sum_{E_{CRe}} f(E_{CRe})\sigma(E_{CRe}) \right) \right] n_{A(ads)}$$

C. Shingledecker and E. Herbst, *Phys. Chem. Chem. Phys.*, in print

☞ Branching ratios in such energetically-driven processes are crucial

☞ Nicely illustrated with a comparison of electron-promoted desorption *versus* electron-induced chemistry in H_2O ice

- H_2O is not observed rather we see H_2, O_2 and other species from dissociation in the exciton state at or near the surface
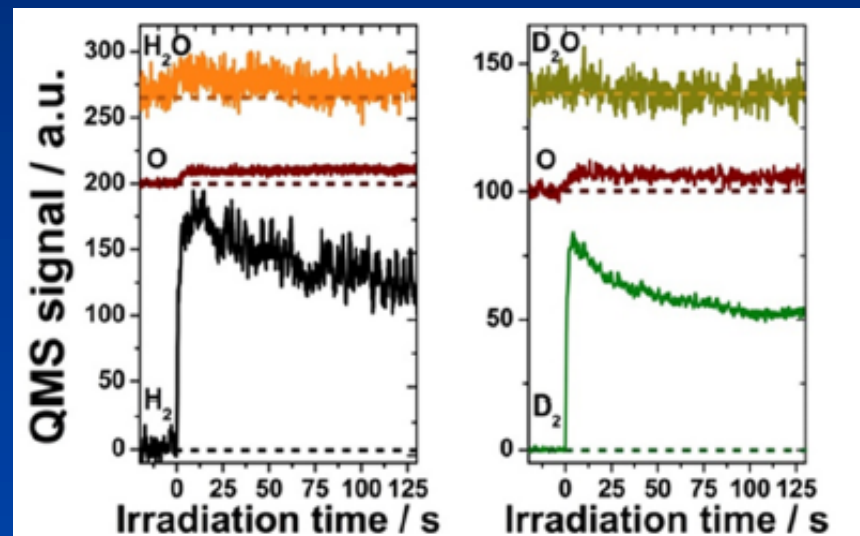
A. G. G. M. Abdulgalil, A. Rosu-Finsen, D. Marchione, J. D. Thrower, M. P. Collings and M. R. S. McCoustra, *ACS Earth Space Chem.,* 2017, **1**, 209-215

K. A. K. Gadallah, D. Marchione, S. P. K. Koehler and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.*, 2017, **19**, 3349-3357

Stuff Happens on the Surface…

☞ Photochemistry and radiochemistry are the key processes that govern the chemical evolution of ices

☞ Three key points to remember

- Have a common underpinning – electronic excited states (excitons) drive these processes
- These processes have cross sections (σ) which are often strongly dependant on the energy of the photons or charged particles
- Limited penetration depth of certain radiations and limited escape depth of volatile reaction products points us in the direction of a selvedge (a near surface region which is strongly coupled to the gas phase)

Stuff Happens on the Surface…

☞ Illustrative example of a comparison of MeV H+ and 250 eV e- irradiation of CH_3CN

- Proton irradiation leads to no measurable loss of CH_3CN but extensive chemical conversion with a measured cross-section of 4.0×10^{-18} cm^2

- Electron irradiation leads to desorption of CH_3CN (as what is unknown but likely H_2 loss) with a cross-section of 0.8 to 3.2×10^{-15} cm^2

☞ Only reconciled if we assume that desorption occurs only from a selvedge a few molecules thick
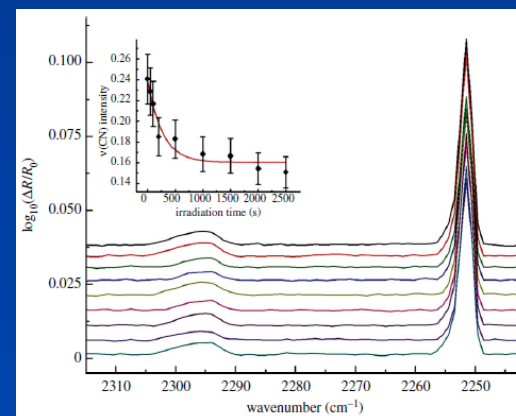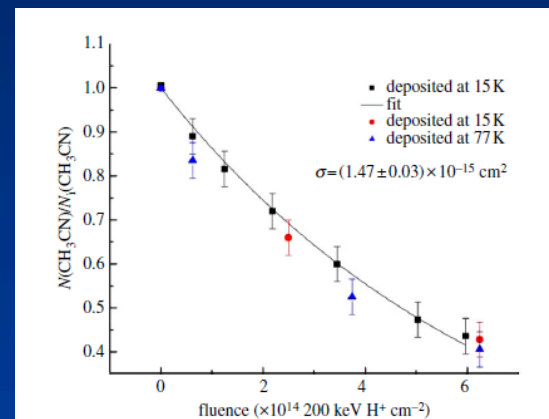
A. G. M. Abdulgalil, D. Marchione, J. D. Thrower, M. P. Collings, M. R. S. McCoustra, F. Islam, M .E. Palumbo, E. Congiu and F. Dulieu, *Phil. Trans. Roy. Soc. A*, 2013, **371**, 20110586
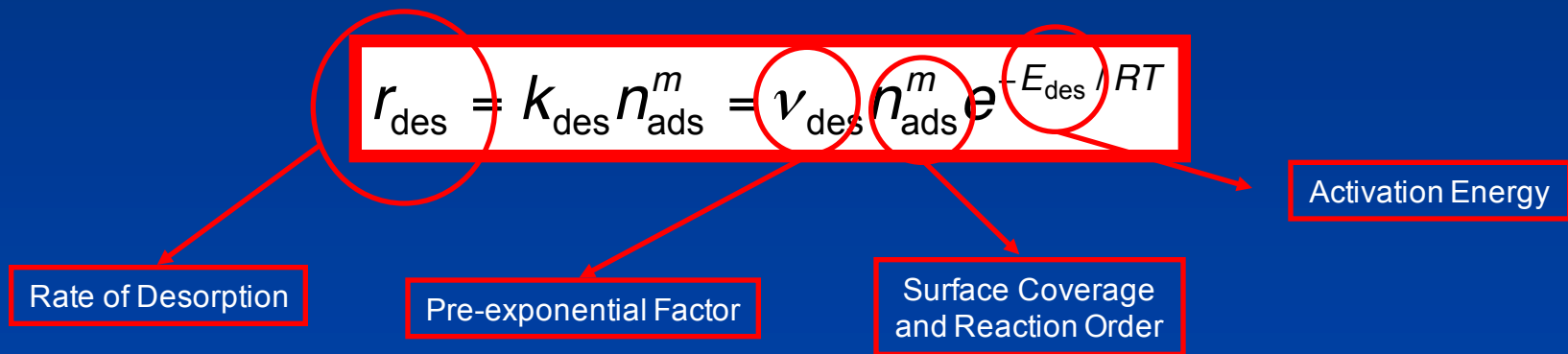
Stuff Leaves the Surface…

☞ Desorption…

☞ Getting stuff off the surface can be achieved thermally and non-thermally

☞ Kinetic measurement… where the rate of desorption is dependent on three factors

- Activation Energy
- Frequency Factor
- Desorption Order (generally limited to 1 for monolayers and 0 for thicker films)
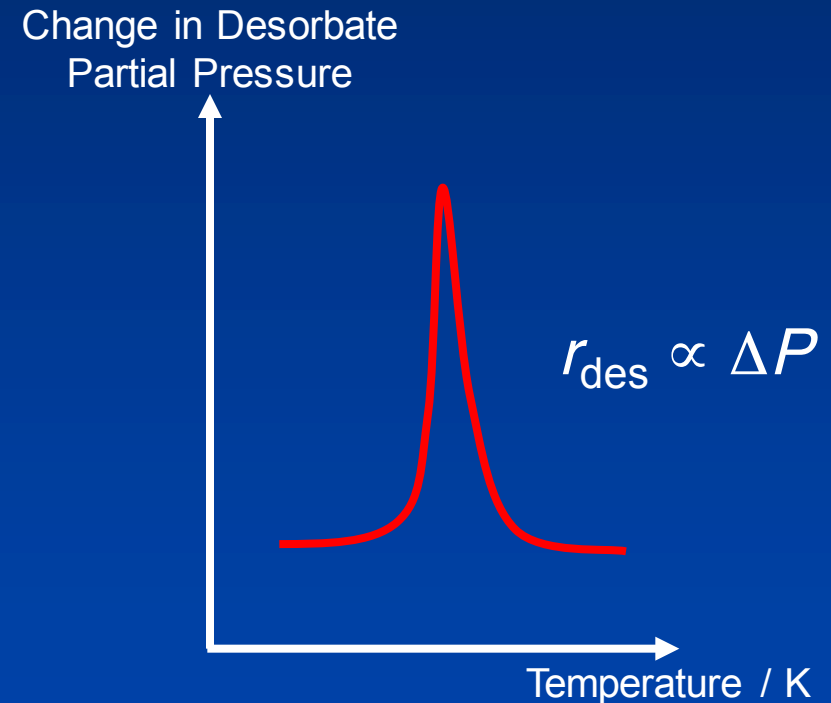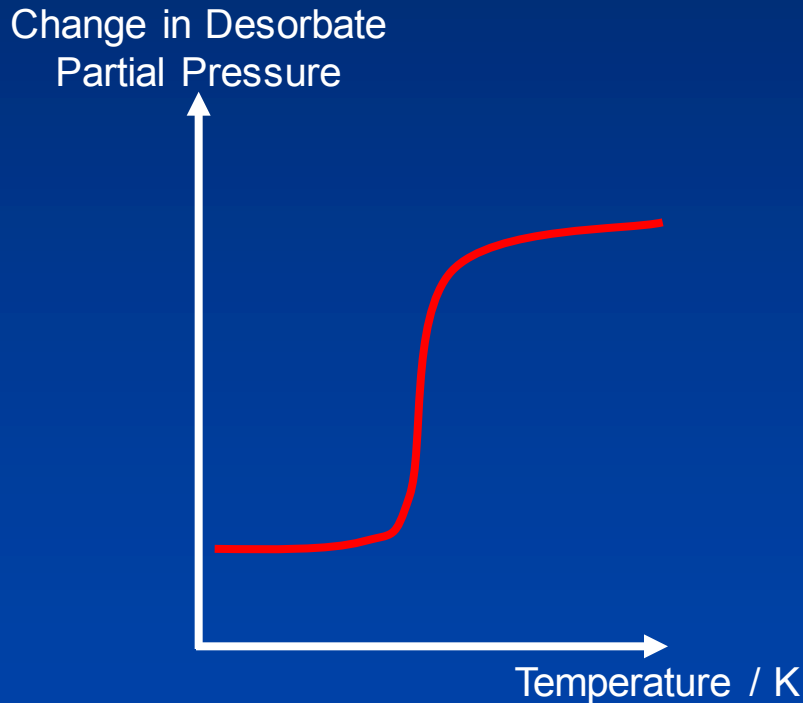

FRESH PRODUCE

Stuff Leaves the Surface…

☞ The kinetics is governed by the *Polyani-Wigner Equation*

$$r_{\text{des}} = k_{\text{des}} n_{\text{ads}}^m = \nu_{\text{des}} n_{\text{ads}}^m e^{-E_{\text{des}}/RT}$$

Rate of Desorption

Pre-exponential Factor

Surface Coverage and Reaction Order

Activation Energy

Stuff Leaves the Surface…

☞ Two limiting behaviours

Change in Desorbate
Partial Pressure

Temperature / K

Change in Desorbate
Partial Pressure

$$r_{\text{des}} \propto \Delta P$$
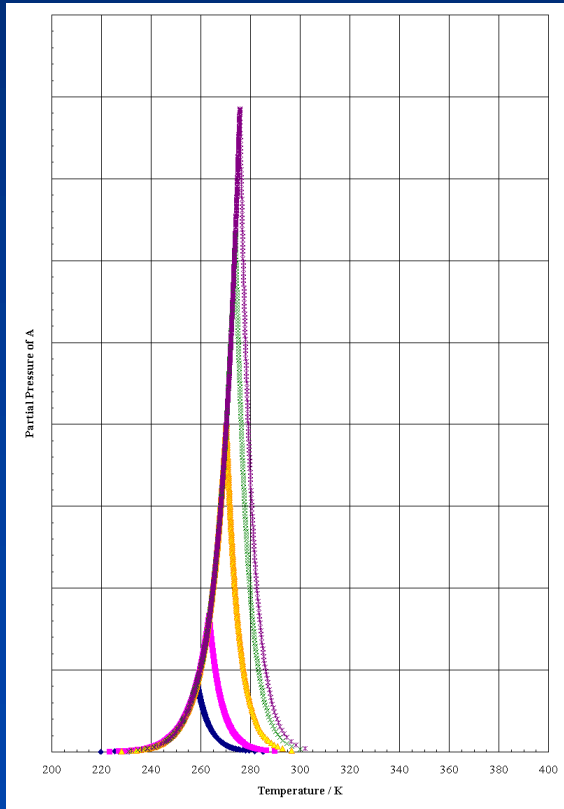
Temperature / K

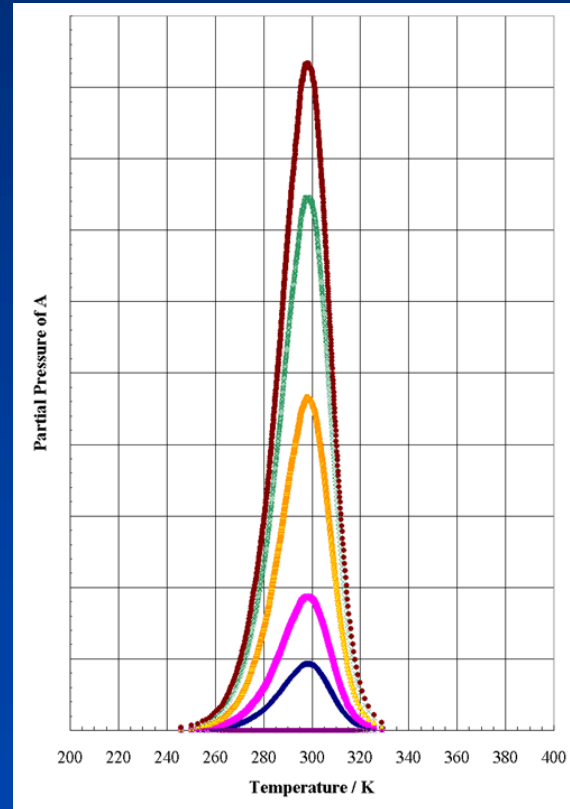Low pumping speed relative to heating rate such that desorbed material accumulates in the chamber - *Flash Desorption*

High pumping speed relative to heating rate so desorbed material rapidly removed from the chamber - *Thermal Desorption*
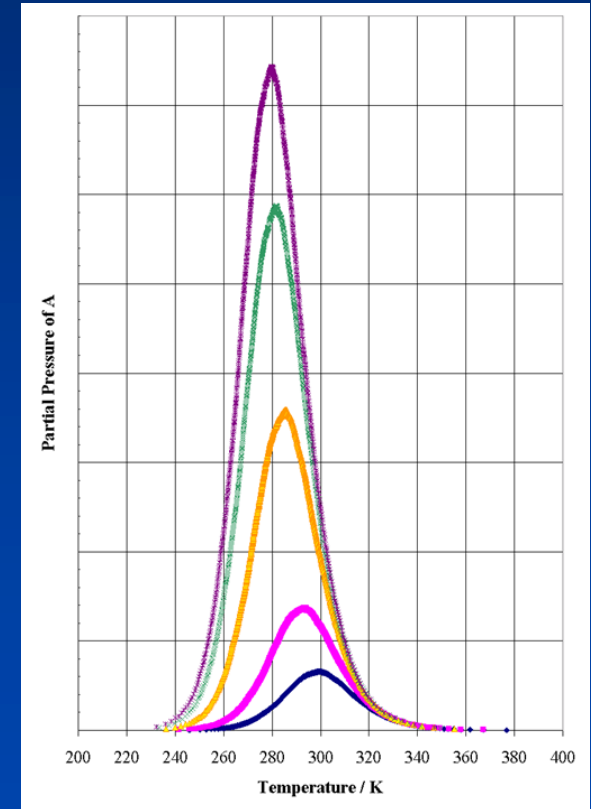
Stuff Leaves the Surface…

Zero Order Kinetics
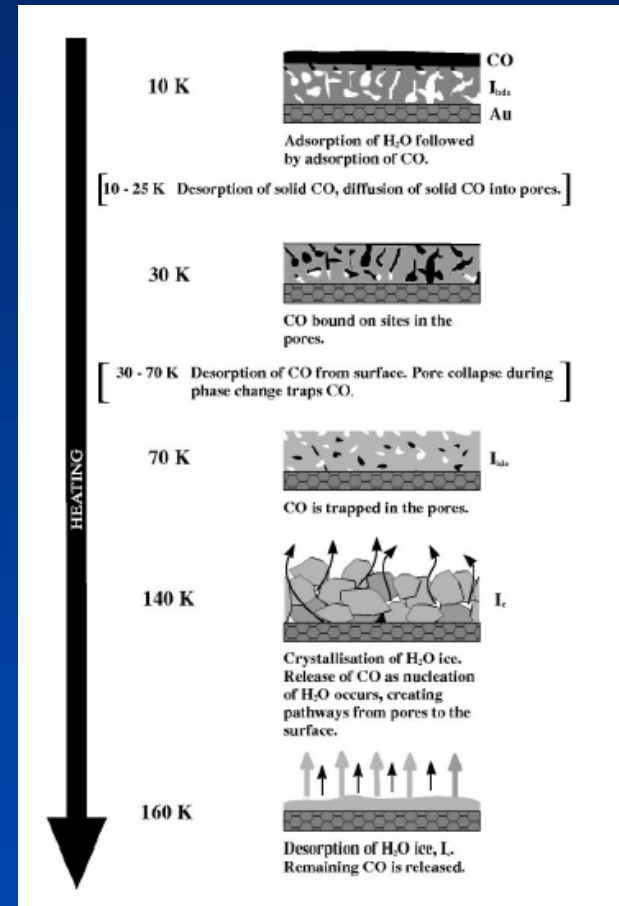
First Order Kinetics

Second Order Kinetics

Stuff Leaves the Surface…

☞ First real surface science study of an astrophysical system… CO on H_2O… using temperature programmed desorption (TPD)

☞ Prompted further work classifying adsorbates

- Volatiles (CO, N_2 *etc.*)
- Non-volatiles (H_2S, CS_2 *etc.*)
- Hydrogen-bonding (NH_3, CH_3OH *etc.*)
- Refractories

M. P. Collings, J. W. Dever, H. J. Fraser, M. R. S. McCoustra, and D. A. Williams, *Astrophys. J.*, 2003, **58**, 1058-1062

M. P. Collings, J. W. Dever, H. J. Fraser, and M. R. S. McCoustra, *Astron. Space Sci.*, 2003, **285**, 633-659

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

Stuff Leaves the Surface…

☞ Lots of recent work from us and others looking at CO and other species binding energies on different substrates… H_2O, silica, graphite…
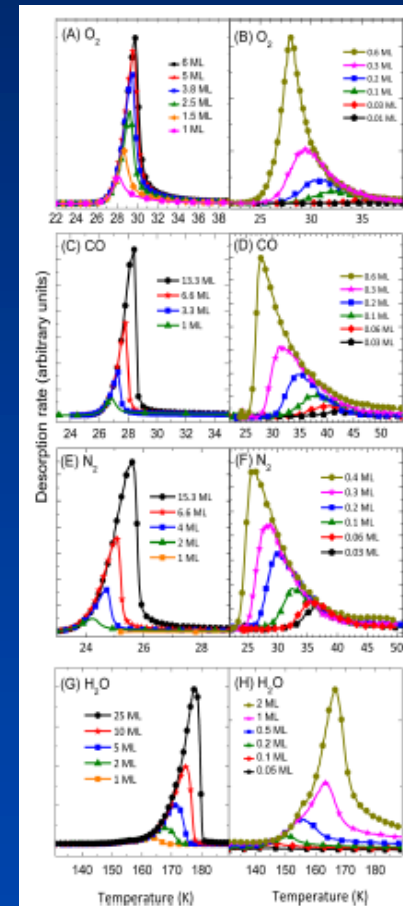
M. P. Collings, V. L. Frankland, J. Lasne, D. Marchione, A. Rosu-Finsen and M. R. S. McCoustra, *Mon. Not. R. Astron. Soc.*, 2015, **449**, 1826-1833

Stuff Leaves the Surface…

☞ Uses the inversion procedure developed by Kay and co-workers where we have a wetting monolayer

☞ Assume first order kinetics and constant pre-exponential around 10^{12} s^{-1} but can be optimized

☞ Doesn't work with de-wetting systems like H_2O on silica that show zero order kinetics at all coverages

$$\Delta P \propto r_{des}$$

$$r_{des} = -\frac{dn_{ads}}{dt} = \nu[n_{ads}(t)]n_{ads}(t)^n e^{-E_{ads}[n_{ads}(t)]/k_B T}$$

$$E_{ads}[n_{ads}(t)] = -k_B T \ln\left[\frac{\frac{dn_{ads}}{dt}}{\nu n_{ads}(t)}\right]$$
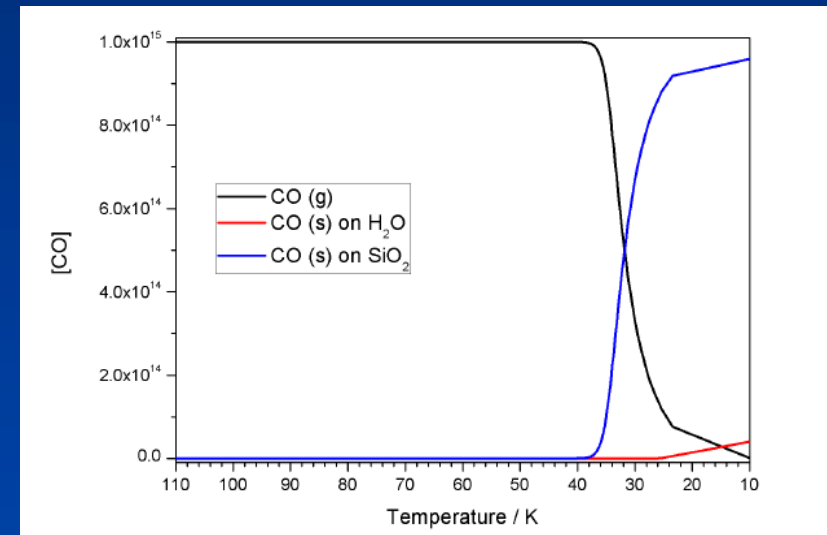
$$P(E_{des}) = -\frac{dn_{ads}}{dE_{des}}$$

S. L. Tait, Z. Dohnalek, C. T. Campbell and B. D. Kay, *J. Chem. Phys.*, 2005, **122**, 164707

R. S. Smith, R. A. May and B. D. Kay, *J. Phys. Chem. C*, 2016, **120**, 1979–1987
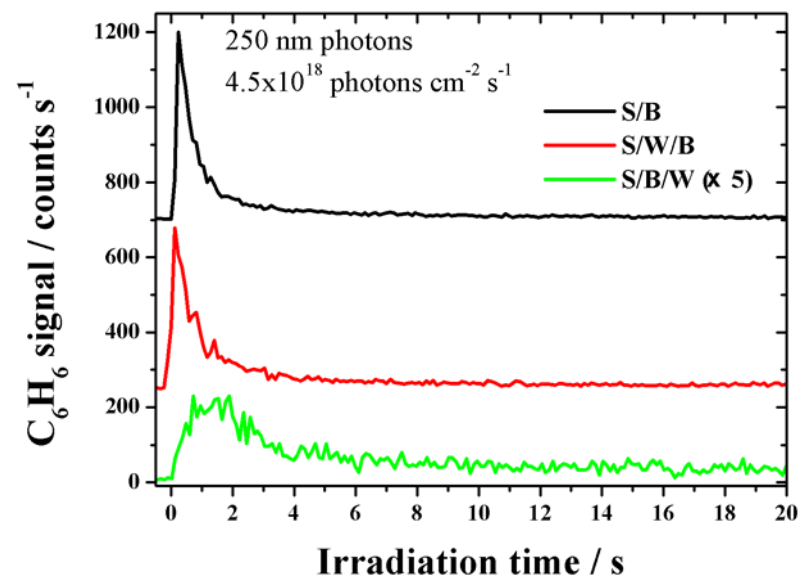
Stuff Leaves the Surface…

☞ Simple kinetic simulations show that variation of binding energies can lead to segregation of CO from H_2O in a low coverage and low temperature regime

HERIOT
WATT
UNIVERSITY

☞ **Where adsorbates can absorb optical radiation, we can see efficient desorption of the adsorbate**
- Direct (exciting the adsorbate)
- Indirect (exciting the substrate)

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**, 919-924
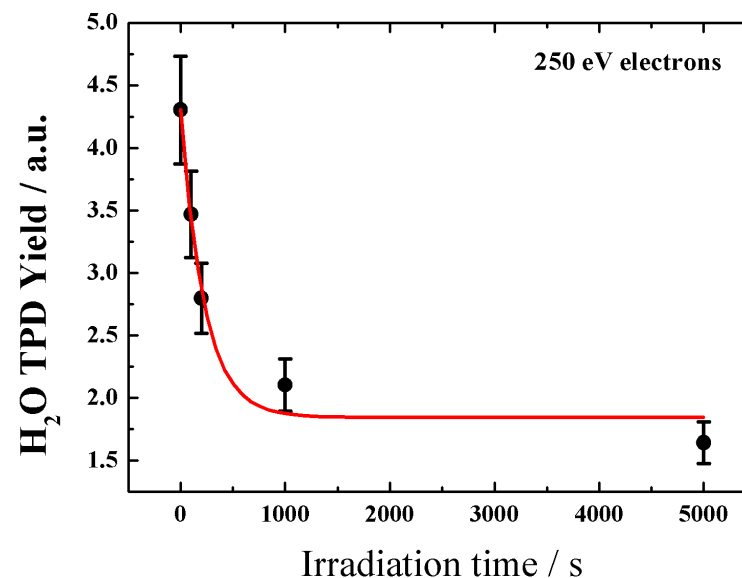
Stuff Leaves the Surface…

☞ To illustrate the indirect process, the 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 *cf.* VUV PSD which has a modest efficiency of around 5×10^{-3}
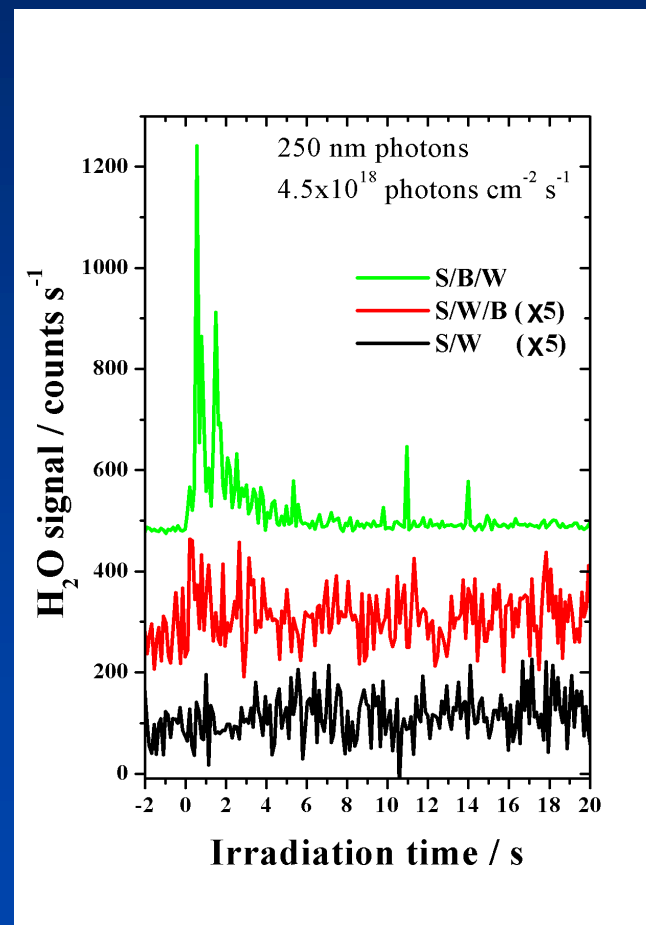
H_2O EPD was investigated a combination of TPD and RAIRS (looking only at total loss and not what's lost) and found to have a cross-section of *ca.* 5×10^{-18} cm^2

Less efficient than C_6H_6 desorption due to strong hydrogen bonding!

250 eV electrons

H$_2$O TPD Yield / a.u. vs Irradiation time / s

Stuff Leaves the Surface…

☞ Simple toy models including re-adsorption can be constructed to investigate the impact of thermal and non-thermal desorption

☞ These can be used to look at simple systems approaching equilibrium if we ignore thermal desorption

☞ Support the idea that non-thermal desorption might produce non-volatiles in low temperature environments

☞ But dominant promoter is CR-generated excitons not photons!
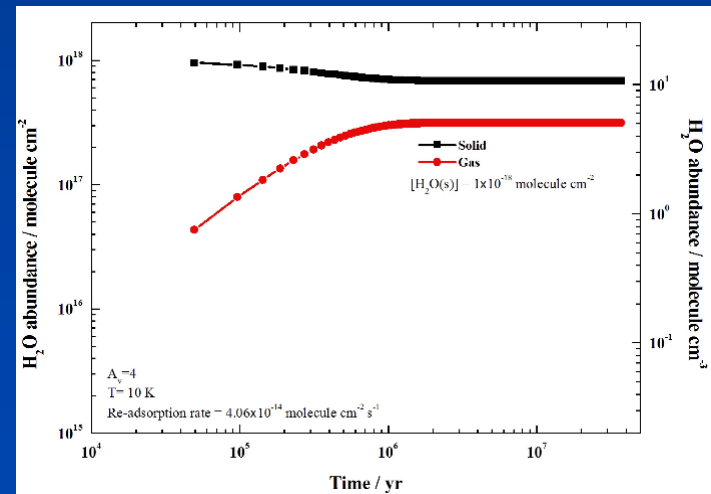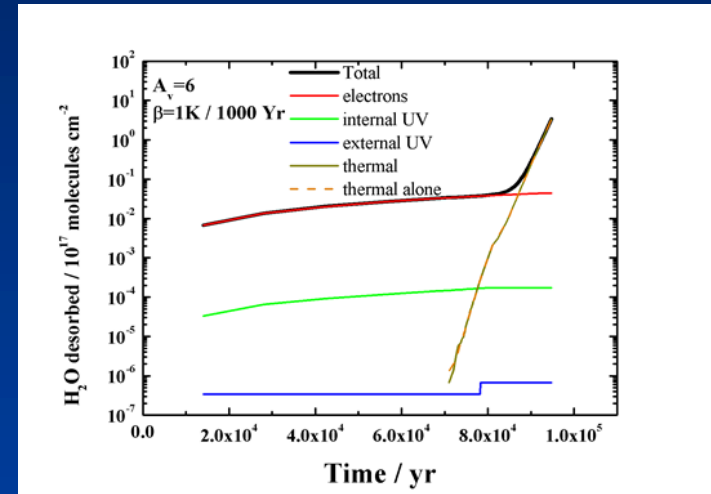
Stuff Leaves the Surface…

☞ Simulations allow us to estimate the gas phase concentration of H_2O in the core of a quiescent object like Barnard 68

☞ Value calculated is some 10^3 times too large… but why?

- Efficient routes for destruction of H_2O in the gas phase?
- CO Overlayer capping?
- What is desorbing?

J. D. Thrower, A. G. M. Abdulgalil, 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*, 2010, **28**, 799-806

Stuff Leaves the Surface…

☞ Is H_2O unique as a substrate?

☞ Comparison with CH_3OH (red) and $(CH_3CH_2)_2O$ (blue)

- Linear hydrogen bonded chains and no hydrogen bonding

☞ Fast process seen in H_2O switches off

- Though O centre in the organics may look like that in H_2O there are more relaxation pathways open to excitons due to the presence of the C atoms
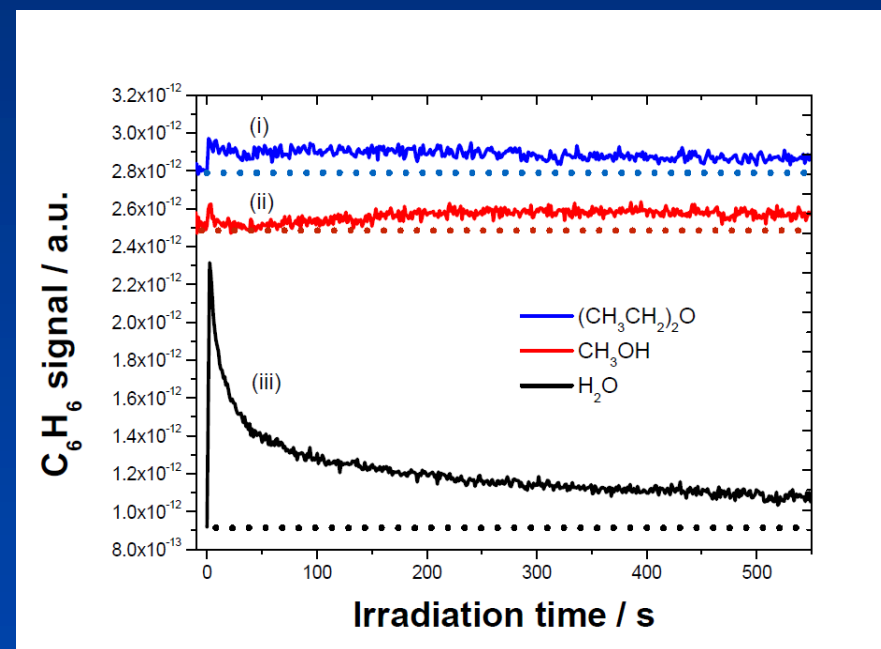
D. Marchione and M. R. S. McCoustra, *Phys. Chem. Chem. Phys.*, 2016, **18**, 29747-29755

Stuff Leaves the Surface…

👉 Care is required in these experiments to ensure we know what is desorbing

👉 We must look at the gas phase as well as the surface

👉 Not substrate desorption but H_2 desorption!
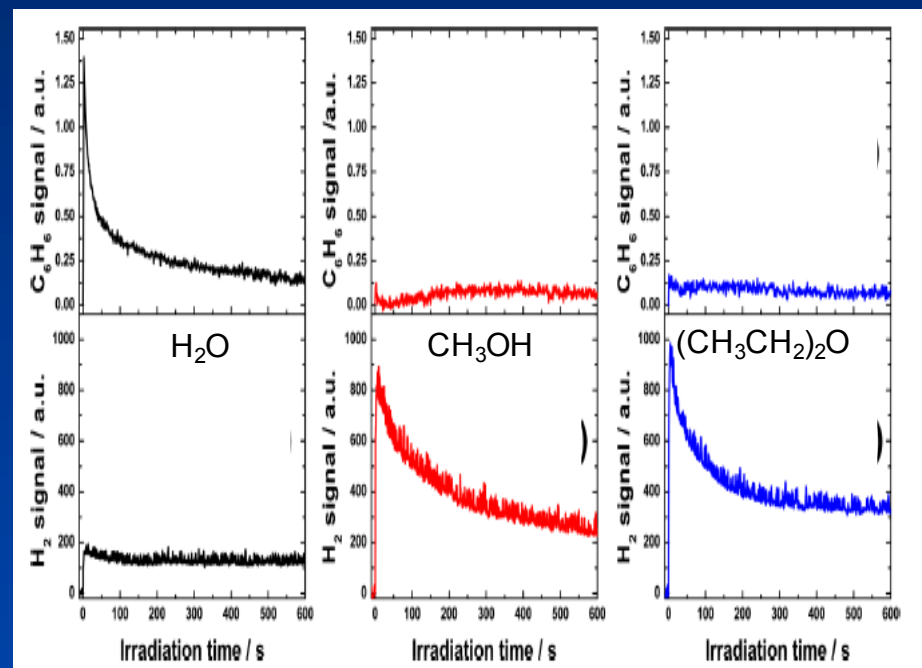
D. Marchione and M. R. S. McCoustra, *ACS Earth Space Chem.*, 2017, **1**, 310-315

Conclusions

) This tutorial lecture is but an introduction to the power of surface science is looking at gas-grain interactions

) Recent work points to

- H_2O de-wetting from silica and carbonaceous materials as it reactively accretes – Grains with "wet" and "dry" areas

- CR-induced secondary electron-promoted H_2O desorption is more efficient than VUV photodesorption and will slow H_2O ice accumulation in cooling environments

- CO accretion (and hence organic formation) on silica surfaces may be favoured compared to H_2O surfaces as CO binding energy is slightly higher (8 – 12 *versus* 8 - 10 kJ mol^{-1}) and the exciton-mediated desorption channel seen in H_2O does not operate on silica!

- Accumulation of hydrogen-rich species is tempered by exciton-promoted dehydrogenation which also means that molecular non-thermal desorption is unlikely!

Acknowledgements

Dr.'s Mark Collings and Jerome Lasne
John Dever, Simon Green, Rui Chen, John Thrower,
Vicky Frankland, Ali Abdulgalil, Demian Marchione,
Alex Rosu-Finsen, Skandar Taj and Rushdi Senevirathne

££
Leverhulme Trust
University of Nottingham
Heriot-Watt University
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Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University