Kinetic modelling of interstellar chemistry

Herma Cuppen

Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University

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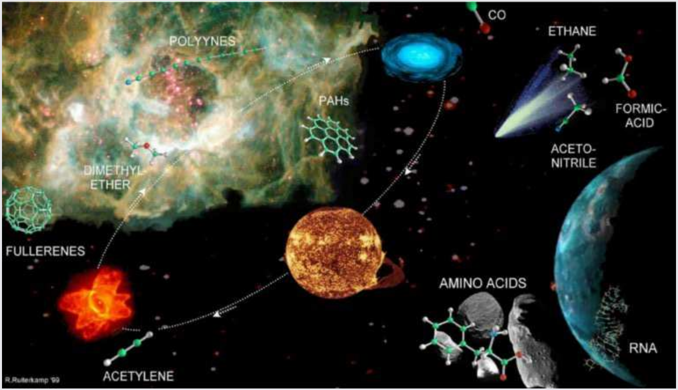
Introduction

- Regions of space between stars not empty but filled with very dilute gas
- Molecules are found in the cold, neutral component of the interstellar medium (ISM)

Introduction

- Interstellar clouds are birthplaces of new stars
  - Evolution abundances molecules: **astrochemistry**
  - Molecules as physical diagnostics: **astrophysics**
- Progress strongly driven by observations: **technology and spectroscopy**

Lifecycle of gas and dust



What are building blocks for life elsewhere in the Universe? How have they formed?

Interstellar Clouds

	Diffuse	Dense	Sea level
UV photon flux	High	Low	
Gas composition	Atomic	Molecular	Molecular
Gas Temperature (K)	$\sim$ 50-100	~ 10	~ 300
Grain Temperature (K)	~ 20	~ 10	
Densities (cm^{-3})	$\sim 10^2$	$\sim 10^4$	$\sim 3\ 10^{19}$

Timescales

- Collision time: $\sim$ 1 month at 10^4 cm^{-3}
- Chemical time: $\sim 10^5$ yr ($\sim$ 100 collisions/particle)
- Star formation: $\sim 10^6$ yr
- Lifetime cloud: $\sim 10^7$ yr

$\longrightarrow$ Not expected to find molecules since reactions are slow

Surprise: many complex interstellar molecules!!

Molecular clouds

Star formation in the Rho Ophiuchi Cloud

In blue 2800 cm^{-1}, green 1250 cm^{-1} and red 410 cm^{-1} (PAH's)

Molecular clouds

Diffuse cloud
$n_H = 10^{2-3}$ cm^{-3}
T_{gas} = 20 K
T_{dust} = 50–100 K

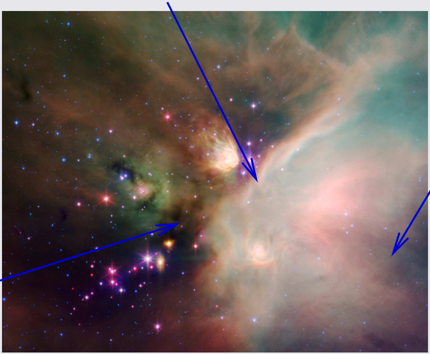
Dense cloud
$n_H = 10^{4-5}$ cm^{-3}
T_{gas} = 10 K
T_{dust} = 10 K

Star formation in the Rho Ophiuchi Cloud

In blue 2800 cm^{-1}, green 1250 cm^{-1} and red 410 cm^{-1} (PAH's)

Large range in temperatures and densities

Molecular clouds



Photon Dominated Regions (PDR's)
$n_H = 10^{3-5}$ cm^{-3}
T_{gas} = 20−400 K
T_{dust} = 100−2000 K

Diffuse cloud
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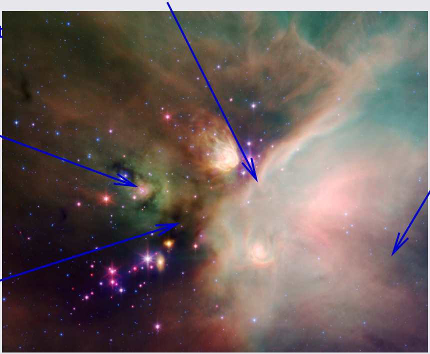

Photon Dominated Regions (PDR's)
$n_H = 10^{3-5}$ cm^{-3}
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T_{dust} = 100−2000 K

Young Stellar Object
$n_H = 10^{4-5}$ cm^{-3}
T_{gas} = 10−300 K
T_{dust} = 10−1000 K

Diffuse cloud
$n_H = 10^{2-3}$ cm^{-3}
T_{gas} = 20 K
T_{dust} = 50−100 K

Dense cloud
$n_H = 10^{4-5}$ cm^{-3}
T_{gas} = 10 K
T_{dust} = 10 K

Star formation in the Rho Ophiuchi Cloud

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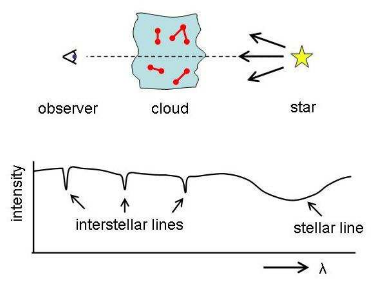
Observations of diffuse clouds

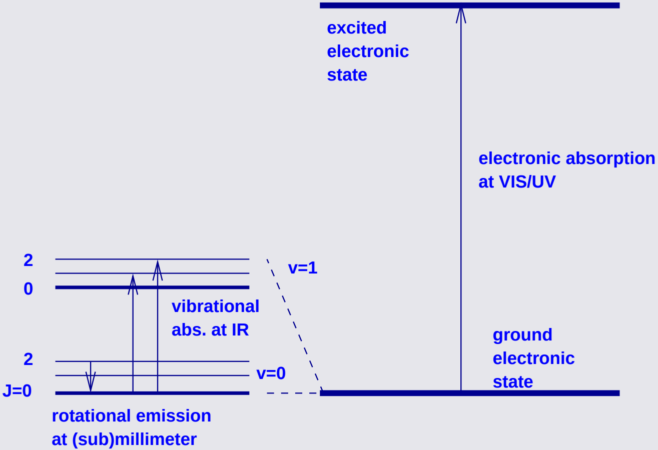
Mostly atomic gas in diffuse clouds

- Observed primarily by absorption lines at visible (since 1900's) and UV wavelengths (since 1970's)
- Spectra show sharp interstellar lines super-imposed on broad spectral lines



Molecular Spectroscopy

$$E = E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}}$$

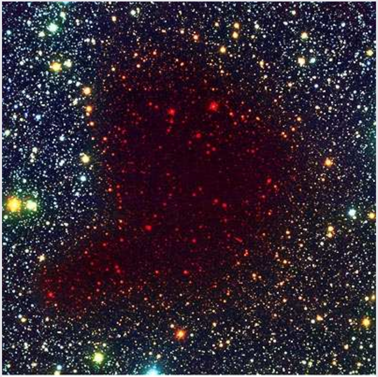


Dense interstellar cloud cores

The "Black Cloud" B68
(VLT ANTU + FORS1)

ESO PR Photo 20a/99 (30 April 1999)

Dense interstellar cloud cores



Seeing Through the Pre-Collapse Black Cloud B68
(VLT ANTU + FORS 1 - NTT + SOFI)

ESO PR Photo 02b/01 (10 January 2001)

Observations of dense clouds

- Opaque at visible and UV wavelength → molecules shielded from dissociating UV radiation
- Millimeter emission: **rotational** transitions

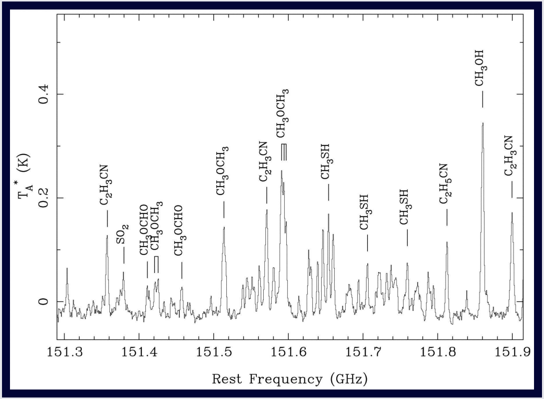
  Limitation: molecule must have permanent dipole moment → cannot observe H_2, C_2, CH_4, C_2H_2, ...

  Advantage: many molecules down to low abundances; lines in emission → map
- Infrared absorption: **vibrational** transitions

  Limitation: need background IR source → only info along line of sight

  Advantage: symmetric molecules + solid state
- Earth's atmosphere prevents observations of key molecules: H_2O, O_2, CO_2

Gas phase: sub-mm observations

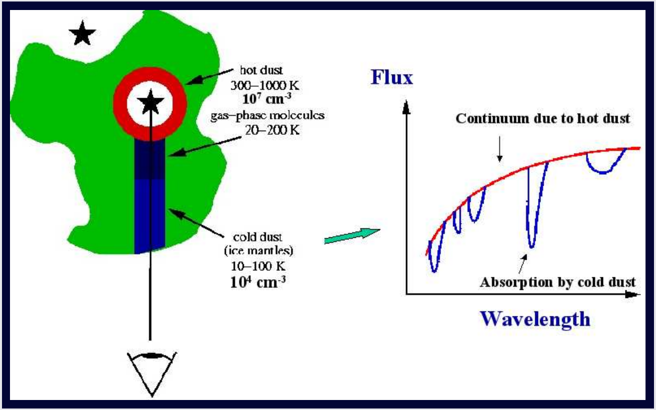


Gibb et al. (2000)

Hot Core G327.3-0.6 (Swedish-ESO Submillimetre Telescope)

- Doppler shift: measured with respect to CO
- Not all lines identified

Infrared absorption



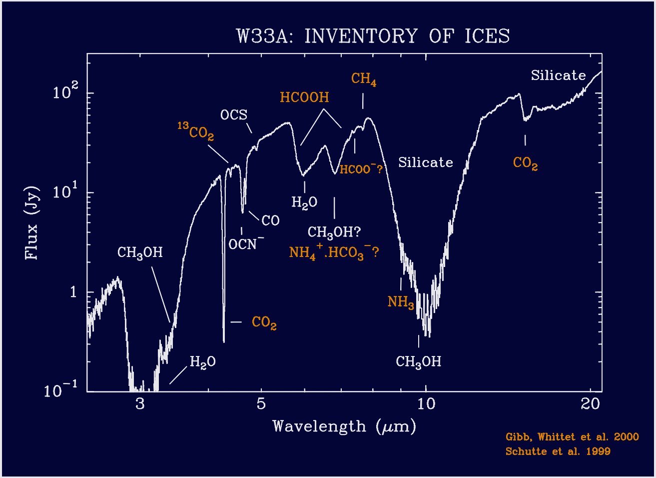
Vibrational transitions of gases *and* solids
Mostly spacebased → lower resolution, higher detection limit

Importance of molecules

- Exotic chemistry: unique laboratory
- Astrochemical evolution
- Molecules as diagnostics of temperature $T_{\rm kin}$, density $n_{\rm H}$, velocity, ?
- Molecules as coolants
  Radiation escapes from cloud $\longrightarrow$ net kinetic energy lost $\longrightarrow$ cloud cools down

Ice mantles on interstellar grains

IR observations



Gibb, Whittet et al. 2000
Schutte et al. 1999

Identified interstellar species

2	3	4	5	6	7	8	9
H_2	H_3^+	CH_3	CH_4	C_2H_4	CH_3NH_2	CH_3CH_3	C_2H_5OH
CH	CH_2	NH_3	NH_4^+	CH_3OH	CH_3CCH	C_3H_4O	CH_3OCH_3
CH^+	NH_2	H_3O^+	CH_2NH	CH_3CN	c-C_2H_4O	CH_2OHCHO	CH_3CH_2CN
NH	H_2O	C_2H_2	H_3CO^+	CH_3NC	CH_3CHO	CH_3COOH	CH_3CONH_2
OH	H_2O^+	H_2CO	SiH_4	NH_2CHO	CH_2CHCN	$HCOOCH_3$	CH_3C_4H
OH^+	C_2H	$HCNH^+$	c-C_3H_2	CH_3SH	C_6H	CH_2CCHCN	C_8H
HF	HCN	H_2CN	H_2CCC	H_2C_4	C_6H^-	CH_3C_3N	C_8H^-
C_2	HNC	c-C_3H	CH_2CN	HC_4H	HC_5N	C_6H_2	HC_7N
CN	HCO	l-C_3H	H_2CCO	c-H_2C_3O		HC_6H	
CN^+	HCO^+	$HCCN$	NH_2CN	HC_2CHO		C_7H	
CO	HN_2^+	$HNCO$	$HCOOH$	C_5H			
CO^+	HOC^+	$HNCO^-$	C_4H	C_5N			
N_2^+	HNO	$HOCO^+$	C_4H^-	$H_2C_3N^+$			
SiH	H_2S	H_2CS	HC_3H	HC_4N			
NO	H_2S^+	C_3N	$HCCNC$				
CF^+	C_3	C_3O	$HNCCC$				
HS	C_2O	$HNCS$	C_5				
HS^+	CO_2	SiC_3	SiC_4				
HCl	CO_2^+	C_3S					
SiC	N_2O						
SiN	HCS^+						
CP	$NaCN$						
CS	$MgCN$						
SiO	$MgNC$						
PN	c-SiC_2						
AlF	$AlNC$						
NS	$SiCN$						
SO	$SiNC$						
SO^+	C_2S						
SiS	OCS						
$AlCl$	SO_2						
S_2							
FeO							
KCl							
$NaCl$							

10	11	13
CH_3CH_2CHO	CH_3C_6H	$HC_{11}N$
CH_3COCH_3	HC_9N	
$HOCH_2CH_2OH$		
NH_2CH_2COOH ??		

Diversity of molecules

- More than 150 different molecules found
- Ordinary molecules (NH_3, H_2O, H_2CO, CH_3OH, ...)
- Exotic molecules (HCO^+, N_2H^+, HCCCCCCCN, ...)
- Many unsaturated molecules → no thermodynamic equilibrium

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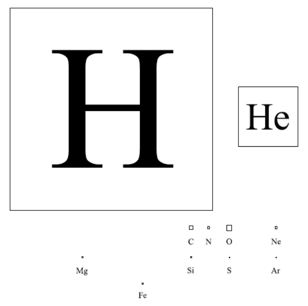
Astronomers' Periodic Table



B. McCall 2001

Types of chemical reactions

- Formation of bonds
  - Radiative association: $X + Y \rightarrow XY + h\nu$
  - Grain surface: $X + Y\text{:grain} \rightarrow XY + \text{grain}$
  - Associative detachment: $X^- + Y \rightarrow XY + e$
- Destruction of bonds
  - Photo-dissociation: $XY + h\nu \rightarrow X + Y$
  - Dissociative recombination: $X^+ + e \rightarrow X + Y$
  - Collisional dissociation: $XY + M \rightarrow X + Y + M$
- Rearrangement of bonds
  - Ion-molecule reaction: $X^+ + YZ \rightarrow XY^+ + Z$
  - Charge-transfer reaction: $X^+ + YZ \rightarrow X + YZ^+$
  - Neutral-neutral reaction: $X + YZ \rightarrow XY + Z$

Basic molecular processes

gas phase

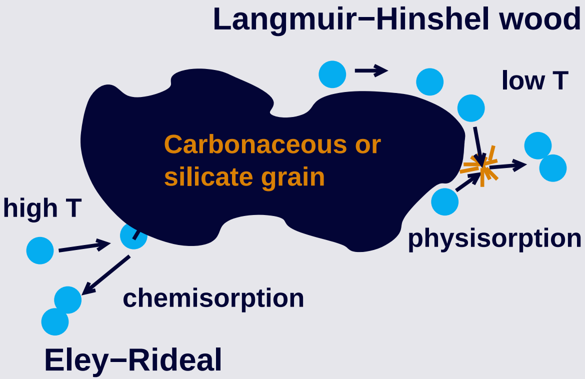
- Because of low temperatures and densities in clouds, chemistry is **not** in thermodynamic equilibrium but controlled by two body reactions → abundances depend on physical conditions (T, n, radiation field), history,...
- Three body reactions do not become important until $n > 10^{12}$ cm^{-3}
- Although models contain thousands of reactions, only few different types of processes are important
- How would you model these reactions?

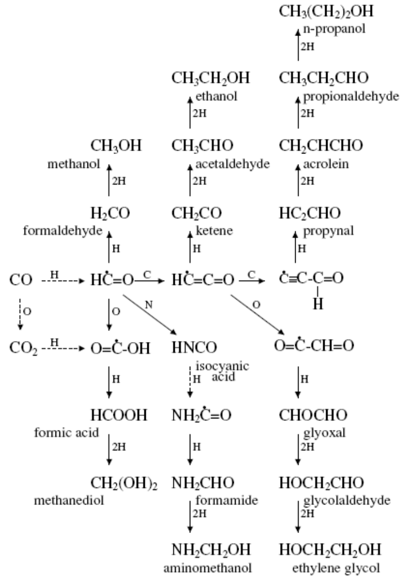
Basic molecular processes

gas phase

- Typical gas phase network contains over 4000 reactions
- Few reactions are studied in the laboratory
    - Obtaining unstable species
    - Low temperature regime (sticking of reactants)
    - Three body reactions
- Some reactions studied theoretically
- Other rates determined by analogy

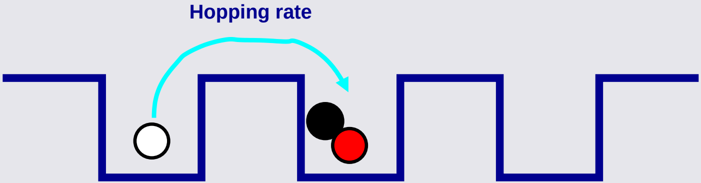
Grain surface chemistry





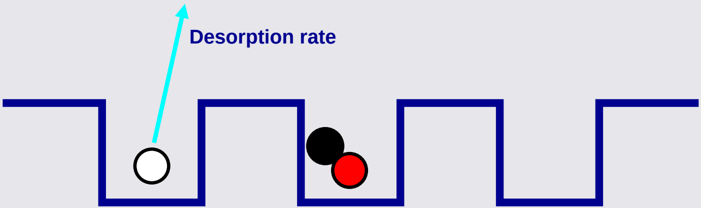
- Mostly addition reactions
- Photodissociation plays important role
- Only handful of reactions are studied

What determines formation rate?



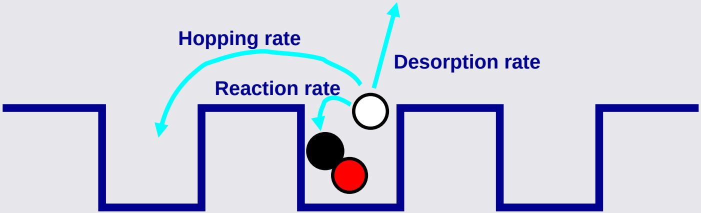
Diffusion for two reactants to meet

What determines formation rate?



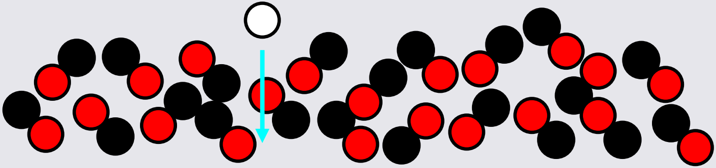
Diffusion	for two reactants to meet
Desorption	for residence time of reactants
Flux	for surface abundance of reactants

What determines formation rate?



Diffusion	for two reactants to meet
Desorption	for residence time of reactants
Flux	for surface abundance of reactants
Competition	of diffusion, desorption and reaction

What determines formation rate?



Diffusion	for two reactants to meet
Desorption	for residence time of reactants
Flux	for surface abundance of reactants
Competition	of diffusion, desorption and reaction

Penetration depth : how many layers are affected

Types of surface reactions

Reactants: Mainly mobile atoms and radicals

$$\mathbf{A + B \rightarrow AB}$$

$$\mathbf{H + X \rightarrow XH (X = H, O, C, N, CO, etc)}$$

which converts

$$\mathbf{H \rightarrow H_2}$$

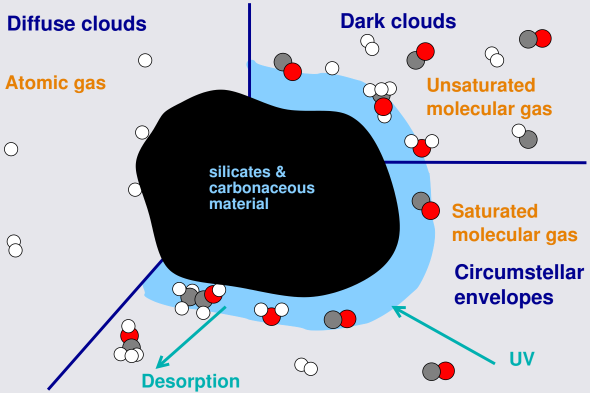
$$\mathbf{O \rightarrow OH \rightarrow H_2O}$$

$$\mathbf{C \rightarrow CH \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_4}$$

$$\mathbf{N \rightarrow NH \rightarrow NH_2 \rightarrow NH_3}$$

$$\mathbf{CO \rightarrow HCO \rightarrow H_2CO \rightarrow H_3CO \rightarrow CH_3OH}$$

Grain surface chemistry



- Surface chemistry important for simple molecules (H_2, H_2O, CH_3OH)
- Different processes important in different regimes
- Different modelling problems in different regimes

Different regimes

Small grains in diffuse clouds
Number densities can become very small and mean field methods cannot be applied. Diffusion is not the rate limiting step for reaction. (accretion limit) (Tielens (1982))

Icy mantles
Ice layers start to build-up. Due to layered structure some processes are blocked. (UV processing/accesibility of accreting species)

Modelling surface reactions

- Rate equations

  Pickles & Williams (1977) ApJSS, 52, 443
- Macroscopic Monte Carlo simulations

  Stantcheva, Shematovich & Herbst. (2002) A&A, 391, 1069, Charnley (1998) ApJ, 509, L121
- Master equation

  Biham et al. (2001) ApJ, 553, 595, Green et al. (2001) A&A, 375, 1111
- Microscopic Monte Carlo simulations

  Chang, Cuppen & Herbst (2005) A&A,434, 599

Rate equations

$$\begin{aligned}\frac{\mathrm{d}n_s(A)}{\mathrm{d}t} &= \sum_i \sum_j k_{\mathrm{react},i,j}\left(k_{\mathrm{hop},i} + k_{\mathrm{hop},j}\right) n_s(i) n_s(j) \\ &- n_s(A) \sum_j k_{\mathrm{react},A,j}\left(k_{\mathrm{hop},j} + k_{\mathrm{hop},A}\right) n_s(j) \\ &+ k_{\mathrm{acc}} n(A) - [k_{\mathrm{evap},A} + k_{\mathrm{nonthermal},A}] n_s(A)\end{aligned}$$

- Second order reactions
- First order desorptions
- Mean field method
- Deterministic

Rate equations

Advantages:

- Fast
- Easy to couple with gas phase rate equations

Disadvantages:

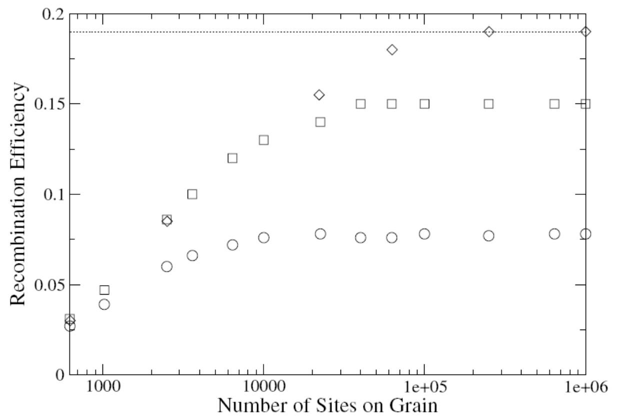
- No layering or positional information (intrinsic of mean field)
- Problem in accretion limit → could be circumvented with modified rate method

Rate equations

Example: H$_2$ formation

$$\begin{aligned}\frac{\mathrm{d}n_s(H)}{\mathrm{d}t} &= -\frac{2\cdot 2}{2}k_{\mathrm{hop},j}n_s(H)^2\\ &+ k_{\mathrm{acc}}n(H) - [k_{\mathrm{evap}} + k_{\mathrm{nonthermal}}]n_s(H)\\ \frac{\mathrm{d}n(H_2)}{\mathrm{d}t} &= \frac{2}{2}k_{\mathrm{hop},j}n_s(H)^2\end{aligned}$$

Rate equations



Chang, Cuppen & Herbst (2005) A&A,434, 599

Rate equations break down when

$$< n(\mathrm{X}) n(\mathrm{Y}) > \neq < n(\mathrm{X}) > < n(\mathrm{Y}) >$$

Master equations

$$\begin{aligned}\frac{\mathrm{d}P_{m,n}}{\mathrm{d}t} &= k_{\mathrm{react},A,B}\left(k_{\mathrm{hop},A}+k_{\mathrm{hop},B}\right)[(m+1)(n+1)P_{m+1,n+1}\\ &\quad -mnP_{m,n}]\\ &+ k_{\mathrm{acc},A}n(A)[P_{m-1,n}-P_{m,n}]\\ &+ k_{\mathrm{acc},B}n(B)[P_{m,n-1}-P_{m,n}]\\ &- [k_{\mathrm{evap},A}+k_{\mathrm{nonthermal},A}][(m+1)P_{m+1,n}-mP_{m,n}]\\ &- [k_{\mathrm{evap},B}+k_{\mathrm{nonthermal},A}][(n+1)P_{m,n+1}-nP_{m,n}]\end{aligned}$$

- Second order reactions
- First order desorptions
- Mean field method
- Stochasitic

How to solve the master equation?

1. Write down equations for all combinations necessary ($P_{0,0}$, $P_{1,0}$, $P_{0,1}$, $P_{1,1}$, etc.)
2. Integrate all equations numerically

For two species system: $P_{n,m}$
For three species system: $P_{n,m,o}$
For four species system: $P_{n,m,o,p}$
etc.

How to solve the master equation?

Integrate all equations numerically

Advantages:

- Treats low surface densities correctly (uses $< n(\mathrm{X}) n(\mathrm{Y}) >$ instead of $< n(\mathrm{X}) >< n(\mathrm{Y}) >$)
- Relatively easy to couple with gas phase rate equations

Disadvantages:

- Number of equations increases rapidly with abundance → smart cut-off, moment equations (Lipshtat & Biham (2003) A&A 400, 585)
- Large changes in density are not straightforward

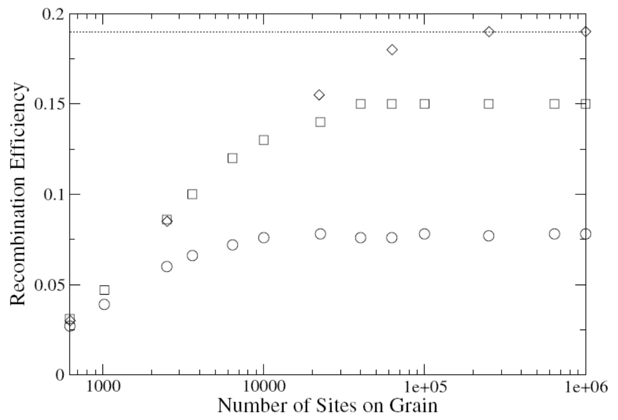
Master equations

Example: H_2 formation

$$
\begin{aligned}
\frac{\mathrm{d}P_0}{\mathrm{d}t} &= 2k_{\mathrm{hop}}P_2 - k_{\mathrm{acc}}n(H)P_0 \\
&- [k_{\mathrm{evap}} + k_{\mathrm{nonthermal}}]P_1 \\
\frac{\mathrm{d}P_1}{\mathrm{d}t} &= 6k_{\mathrm{hop}}P_3 + k_{\mathrm{acc}}n(H)[P_0 - P_1] \\
&+ [k_{\mathrm{evap}} + k_{\mathrm{nonthermal}}][2P_2 - P_1] \\
\frac{\mathrm{d}P_2}{\mathrm{d}t} &= 2k_{\mathrm{hop}}[12P_4 - P_2] + k_{\mathrm{acc}}n(H)[P_1 - P_2] \\
&+ [k_{\mathrm{evap}} + k_{\mathrm{nonthermal}}][3P_3 - 2P_2]
\end{aligned}
\tag{1}
$$

$$
\frac{\mathrm{dH_2}}{\mathrm{d}t} = 2k_{\mathrm{hop}}[P_2 + 12P_4 + \ldots]
$$

Rate equations



Chang, Cuppen & Herbst (2005) A&A,434, 599

Rate equations break down when

$$< n(\mathrm{X})n(\mathrm{Y}) > \neq < n(\mathrm{X}) >< n(\mathrm{Y}) >$$

Summary

Interstellar chemistry

- Very extreme conditions (temperature, pressure, timescales)
- Gas phase: mostly unsaturated molecules
- Solid phase: mostly saturated molecules

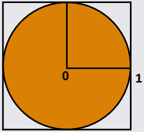
Modelling techniques

- Rate equations: deterministic, easy
- Master equations: stochastic, requires many equations for simple systems

How to solve the master equation?

Integration by Monte Carlo

Monte Carlo started and is mostly seen as a numerical way to calculate integrals



If we draw pairs of random numbers (x_i, y_i) where the x_i and the y_i are uniformly distributed in $[0, 1]$ the probability for the point to lie within the circle is equal to $\pi/4$.

How to solve the master equation?

Integration by Monte Carlo

We would like to know average distribution of species at t

1. Start with initial grain abundance (no species, same as for master equation)
2. Propagate in time by using transition probablities and random numbers (same probabilities as in master equation)
3. Repeat for many different initial seeds and average

Follow one grain's populations instead of integrating **all** possibilities

Macroscopic Monte Carlo

Sampling

Two ways of sampling:

1. At each time interval, evaluate if/which process will happen (slow if probablities changes significantly over time)
2. Propagate time with $\Delta t = 1/\sum(R)$ and evaluate which process will happen ($P_i = R_i/\sum(R)$)
3. Propagate time with $\Delta t = \ln(X)/\sum(R)$ and evaluate which process will happen ($P_i = R_i/\sum(R)$)

Macroscopic Monte Carlo

Compared to numerical integration

Advantages:

- Works for both low and high surface coverage

Disadvantages:

- Hard to couple to gas phase rate equations (gas phase MC)
- Hard to get enough resolution (sample over many trajectories)

Let's return to our integral problem

Random sampling

$$I = \int_{x_1}^{x_2} f(x)\mathrm{d}x$$

Random sampling

1. Randomly choose x on interval $[x_1, x_2]$
2. Evaluate $f(x)$
3. Average over many iterations (M)

Is correct for $M \rightarrow \infty$

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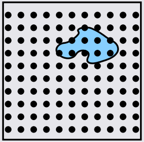


Many samples 'wasted' on parameter space that does not contributed to I. Becomes worse with increasing dimensions.

Importance sampling

$$I = \int_0^1 w(x) \frac{f(x)}{w(x)} \mathrm{d}x$$

$$\frac{\mathrm{d}u(x)}{\mathrm{d}x} \equiv w(x)$$

$$I = \int_0^1 \frac{f(x(u))}{w(x(u))} \mathrm{d}u$$

Importance sampling

1. Randomly choose u on interval $[0, 1]$
2. Find matching x
3. Evaluate $\frac{f(x)}{w(x)}$
4. Average over many iterations (M)

What do we gain by this?

$$\sigma^2 = \frac{1}{M^2}\sum_{i=1}^{M}\sum_{j=1}^{M}\left\langle\left(\frac{f(x(u_i))}{w(x(u_i))} - < f/w >\right)\left(\frac{f(x(u_j))}{w(x(u_j))} - < f/w >\right)\right\rangle$$

if i and j are independent

$$\sigma^2 = \frac{1}{M^2}\sum_{i=1}^{M}\left\langle\left(\frac{f(x(u_i))}{w(x(u_i))} - < f/w >\right)^2\right\rangle$$

$$\sigma^2 = \frac{1}{M}\left[< (f/w)^2 > - < f/w >^2\right]$$

What do we gain by this?

Metropolis importance sampling

In statistical physics often

$$< A >= \frac{\int A(\mathbf{r}^N)\exp(-U(\mathbf{r}^N)/kT)\mathrm{d}\mathbf{r}^N}{Q}$$

Let's choose

$$u(\mathbf{r}^N) = \frac{\exp(-U(\mathbf{r}^N)/kT)}{Q}$$

then

$$< A >\approx \frac{1}{M}\sum_{i}^{M} A(\mathbf{r}_i)$$

Metropolis algorithm

Metropolis algorithm (JCP 21 (1953) 1087)

1. Choose initial condition
2. Make small displacement to obtain new configuration
3. Evaluate E for new configuration
4. If $\Delta E < 0$, accept new configuration, else accept with $exp(-\Delta E/kT)$ probability
5. Repeat from step 2

This algorithm only works if the system is **ergodic**, i. e. there is a finite probability to reach any point in configuration space

Markov Chain

$$\begin{aligned} P_n(x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_1, t_1) &= P_{1|n-1}(x_n, t_n; \\ &\quad \ldots x_{n-1}, t_{n-1}; \ldots; x_1, t_1) \\ &\quad P_{n-1}(x_{n-1}, t_{n-1}; \ldots; x_1, t_1) \end{aligned}$$

Let us assume a **Markov Chain**, which means that **given the present state, future states are independent of the past states**.

$$\begin{aligned} P_n(x_n, t_n; x_{n-1}, t_{n-1}; \ldots; x_1, t_1) &= P_{1|1}(x_n, t_n; x_{n-1}, t_{n-1}) \\ &\quad P_{n-1}(x_{n-1}, t_{n-1}; \ldots; x_1, t_1) \end{aligned}$$

$$P_{1|1}(x_3, t_3|x_1, t_1) = \sum_{x_2} P_{1|1}(x_3, t_3|x_2, t_2) P_{1|1}(x_2, t_2|x_1, t_1)$$

For a stationary Markov process, we can write

$$P_{1|1}(x_2, t_2|x_1, t_1) = P_t(x_2, x_1), t = t_2 - t_1,$$

where we want P_t to denote a transition probability within the time interval t from state x_1 to state x_2.

$$P_{t+t'}(x_3|x_1) = \sum_{x_2} P_t(x_3|x_2) P_{t'}(x_2|x_1)$$

$$\begin{aligned} P_{t+t'}(x_3|x_1) - P_t(x_3|x_1) &= \sum_{x_2} P_{t'}(x_3|x_2) P_t(x_2|x_1) \\ &\quad - \sum_{x_2} P_{t'}(x_2|x_3) P_t(x_3|x_1) \end{aligned}$$

$$\begin{aligned} P_{t+t'}(x_3|x_1) - P_t(x_3|x_1) &= \sum_{x_2} \omega(x_3|x_2) t' P_t(x_2|x_1) \\ &\quad - \sum_{x_2} \omega(x_2|x_3) t' P_t(x_3|x_1) \end{aligned}$$

Master equation

Here we are at the general master equation

$$\frac{P_{t+\Delta t}(\alpha) - P_t(\alpha)}{\Delta t} = \sum_i P_t(i)\omega_{i\to\alpha}\Delta t - \sum_j P_t(\alpha)\omega_{\alpha\to j}\Delta t$$

$$\frac{\mathrm{d}P(\alpha)}{\mathrm{d}t} = \sum_i P(i)\omega_{i\to\alpha} - \sum_j P(\alpha)\omega_{\alpha\to j}$$

ω is independent of history of events
In the case of a **continuous-time Markov Chain** times can be described by a **Poisson Process**

$$P(t_k - t_{k-1} < t) = \exp(-\omega t) \tag{2}$$

Equilibrium conditions

In equilibrium, **detailed balance** or **microscopic reversibility**

$$P_i^{\mathrm{eq}} \omega_{i \to j} = P_j^{\mathrm{eq}} \omega_{j \to i}$$

and the states are distributed according to

$$P_\alpha^{\mathrm{eq}} = \frac{\exp(-U(\alpha)/kT)}{Q}$$

which leads to

$$\frac{\omega_{i \to j}}{\omega_{j \to i}} = \frac{P_j^{\mathrm{eq}}}{P_i^{\mathrm{eq}}} = \exp(-(U(j) - U(i))/kT)$$

Freedom to choose transition scheme

$$\frac{\omega_{i\rightarrow j}}{\omega_{j\rightarrow i}} = \frac{P_j^{\mathrm{eq}}}{P_i^{\mathrm{eq}}} = \exp(-(U(j) - U(i))/kT)$$

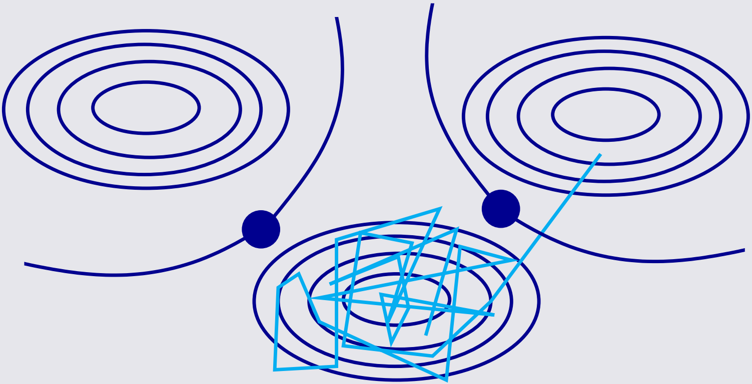
Metropolis: $\omega_{i\rightarrow j} = \omega_0 \min(1, \exp\left[-(U(j) - U(i))/kT\right])$
Glauber: $\omega_{i\rightarrow j} = \omega_0 \frac{1}{2}(1 - \tanh\left[-(U(j) - U(i))/kT\right])$

In **equilibrium** is the end result independent of the choice of the transition scheme.
Monte Carlo method is used to obtain $< A >$.

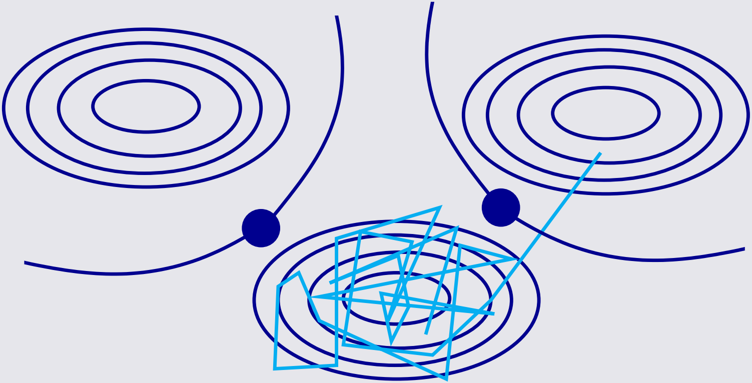
Outside equilibrium the result depends on the transition scheme → **kinetic regime**
Monte Carlo method is mostly used to obtain **evolution of the system**

Kinetic/Dynamic Monte Carlo use rates that describe this regime

Outside equilibrium still Markov Chain

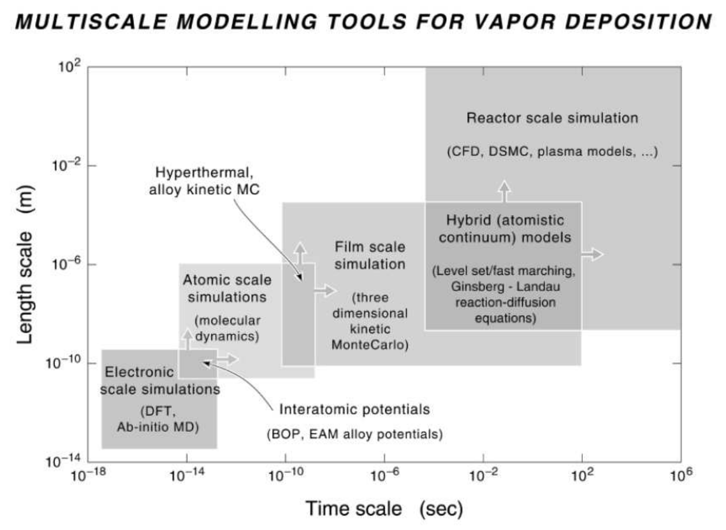


Outside equilibrium still Markov Chain



Vibrations help losing the history of the trajectory between states.

Monte Carlo simulations vs. Molecular Dynamics



Wadley et al. Prog. Mater. Sci. 46 (2001) 329

How to obtain the transition probabilities?

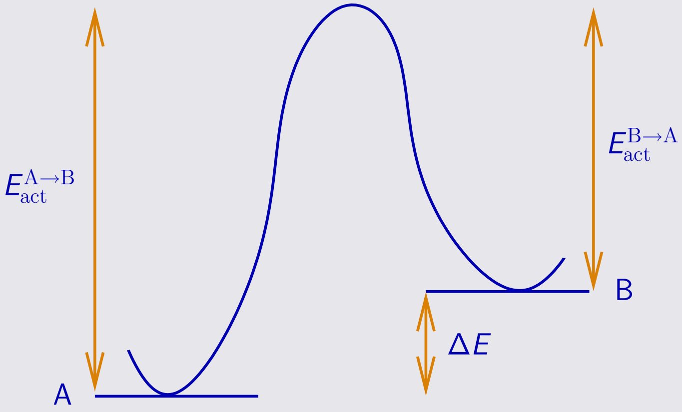
Lattice-gas assumption

Often (Q)TST is used.

Approximation using Harmonic TST:

$$\omega_{i\to j} = \frac{\Pi_i^{3N}\nu_{R,i}}{\Pi_i^{3N-1}\nu_{\dagger,i}} \exp(-(E_{\mathrm{SP}} - E_{\mathrm{min}})/kT)$$

Kinetic Monte Carlo



$$\frac{\omega_{\mathrm{A}\rightarrow\mathrm{B}}}{\omega_{\mathrm{B}\rightarrow\mathrm{A}}} = \exp\left(-\frac{\Delta E}{kT}\right) = \frac{\exp\left(-E_{\mathrm{act}}^{\mathrm{A}\rightarrow\mathrm{B}}/kT\right)}{\exp\left(-E_{\mathrm{act}}^{\mathrm{B}\rightarrow\mathrm{A}}/kT\right)}$$

How to determine transition probabilities?

Ideal case:
Use very accurate PES to determine rates using QTST or TST.

Unfortunately,

- interstellar surfaces not well defined (material)
- amorphous/mixed ice layers
- high degree of roughness

we have to use different methods.

Laboratory experiments

Temperature Programmed Desorption

Standard technique for desorption temperature determination

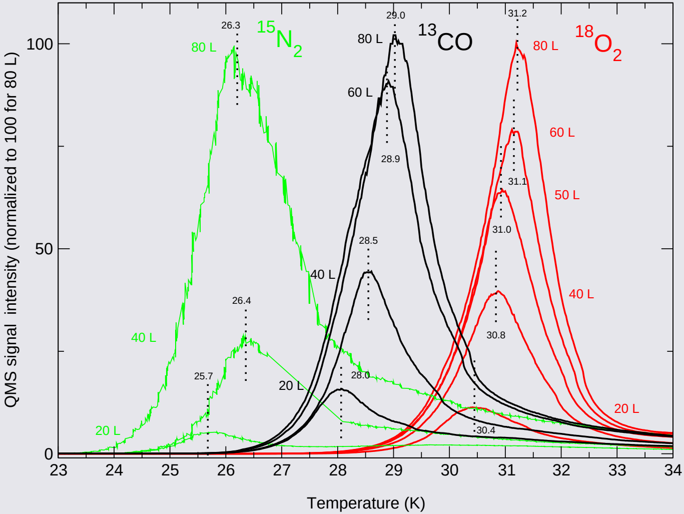
Phase 1

Deposition of interesting species at constant low temperature on the substrate of interest

Phase 2

Linear increase of the temperature as a function of time. Measuring desorption using QMS.

TPD experiments



Analysis of TPD experiments

- Fitted to Polanyi-Wigner equation:

$$r = \frac{\mathrm{d}\theta}{\mathrm{d}t} = v\theta^n exp(-E/RT) \tag{3}$$

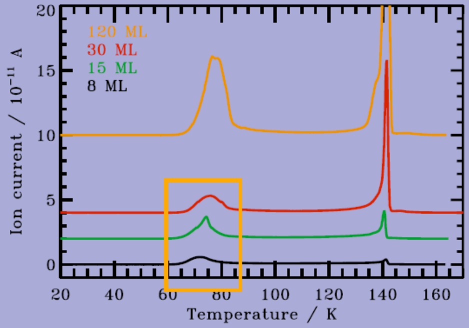
- Fit to rate equation model
- Fit using MC program

Points to consider:

- The influence of lateral interactions
- The order of the process
- Use of the model: what do you put in?

TPD experiments

Surface segregation during desorption



Desorption pattern explained by surface segregation before or during desorption for H_2O:CO_2 4:1 ices

Analysis of TPD experiments

How to handle time dependent rates?

Remember for time-independent rates:

$$P(t_k - t_{k-1} < t) = \exp(-\omega t) \tag{4}$$

$$\Delta t = -\ln(X)/\omega \tag{5}$$

Rate is generally of the form:

$$\omega = \nu \exp(-E/kT) \tag{6}$$

For TPD, T changes in known manner → ω becomes temperature dependent.
Way to handle this suggested by A. P. J. Jansen, Comp. Phys. Comm. 86 (1995) 1

How to handle time dependent rates?

$$P(t_k - t_{k-1} < t) = \exp(-\int_0^t \omega(t')\mathrm{d}t') \tag{7}$$

Assume a constant ramp of $T = T_0 + Bt$

$$-\ln(X) = \int_0^t \nu \exp\left(-\frac{E}{k(T_0 + Bt')}\right)\mathrm{d}t' = \Omega(t) - \Omega(0) \tag{8}$$

with

$$\Omega(t) = \frac{\nu}{B}(T_0 + Bt')E_2\left[\frac{E}{k(T_0 + Bt')}\right] \tag{9}$$

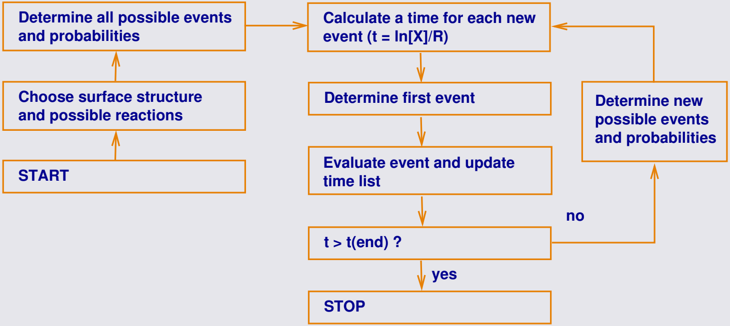
A. P. J. Jansen, Comp. Phys. Comm. 86 (1995) 1

How to handle time dependent rates?

Different $T(t)$ function possible as well.
Numerical effort depends on the integration of
$\int_0^t \nu \exp\left(-\frac{E}{kT(t)}\right) \mathrm{d}t'$
Example:

- thermalization of species on the surface
- different temperature ramps for TPD (thermal conductance)

Continous-time, random-walk Monte Carlo



Determine all possible events and probabilities

Choose surface structure and possible reactions

START

Calculate a time for each new event (t = ln[X]/R)

Determine first event

Evaluate event and update time list

t > t(end) ?

yes

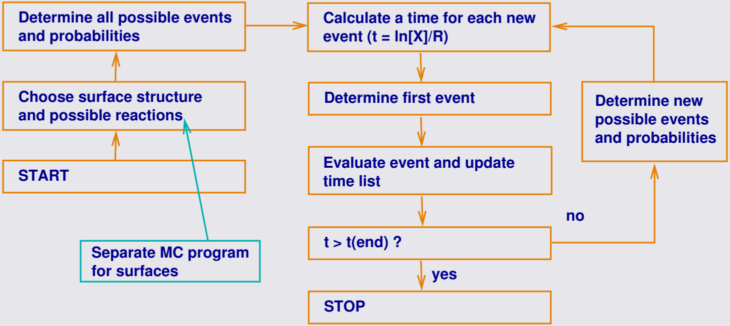
STOP

no

Determine new possible events and probabilities

- Ranks atoms by event time
- Montroll & Weiss, J. Math. Phys., 6 (1965) 167

Continous-time, random-walk Monte Carlo



START

Choose surface structure and possible reactions

Determine all possible events and probabilities

Separate MC program for surfaces

Calculate a time for each new event (t = ln[X]/R)

Determine first event

Evaluate event and update time list

t > t(end) ?

yes

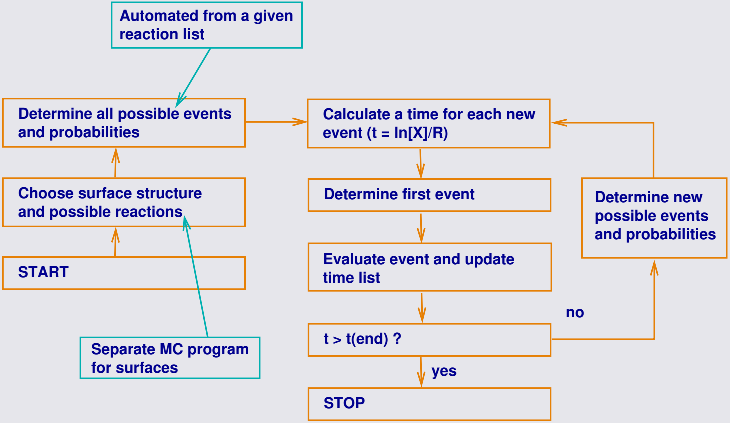
STOP

no

Determine new possible events and probabilities

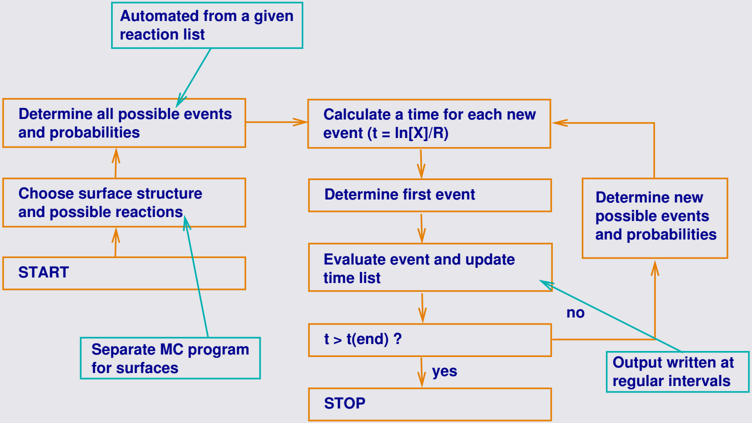
- Ranks atoms by event time
- Montroll & Weiss, J. Math. Phys., 6 (1965) 167

Continous-time, random-walk Monte Carlo



- Ranks atoms by event time
- Montroll & Weiss, J. Math. Phys., 6 (1965) 167

Continous-time, random-walk Monte Carlo



Automated from a given reaction list

Determine all possible events and probabilities

Calculate a time for each new event (t = ln[X]/R)

Choose surface structure and possible reactions

Determine first event

Determine new possible events and probabilities

START

Evaluate event and update time list

no

t > t(end) ?

Separate MC program for surfaces

Output written at regular intervals

yes

STOP

- Ranks atoms by event time
- Montroll & Weiss, J. Math. Phys., 6 (1965) 167

Continous-time, random-walk Monte Carlo

Advantages:

- Treats low surface densities correctly
- Correct treatment of backdiffusion
- Can handle both low and high densities
- Can include surface specific processes
- Layering

Disadvantages:

- Hard to couple to gas phase rate equations
- Computationally expensive
- Not easy to use for large reaction network

Monte Carlo simulations

Sequence of processes is chosen using random numbers according to transition probabilities

Free parameters

- temperature
- flux
- surface
- energy barriers

▨ **Grain**

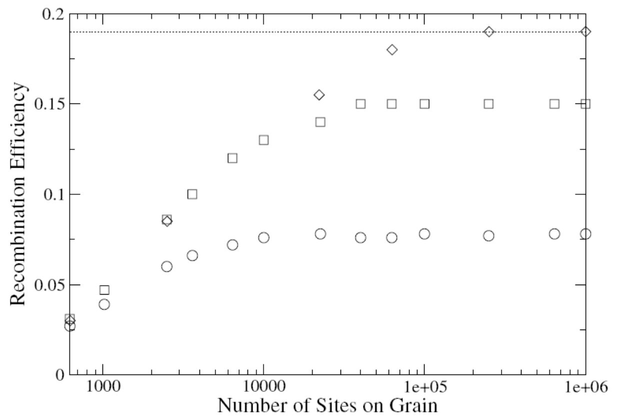
🟩 **Hydrogen**

🟥 **Oxygen**

Top view of the surface (50 × 50 sites)

∼1 day

Comparison with other techniques



Chang, Cuppen & Herbst (2005) A&A,434, 599

Difference due to backdiffusion

n-fold way

Bortz, Kalos & Lebowitz, J. Comp. Phys. 17 (1975) 10

1. Construct list with all possible events that can occur
2. Choose event according to relative occurance
3. Propagate time with $\ln(X)/R_{\mathrm{tot}}$
4. Update list

Advantage: Very fast
Disadvantage: Need to know all possible events (lattice-gas)

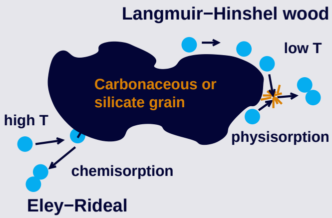
Summary

Monte Carlo technique

- Detailed balance for transition probabilities
- Transition probabilities very important in kinetic regime
- Different sampling techniques can reduce the error and increase the running speed

H_2 formation in diffuse clouds

- atomic H abundance ($\approx 100\ \mathrm{cm}^{-3} \approx 3 \times 10^6\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$)
- gas temperature (60-100 K)
- grain temperature (≈ 20 K)
- energies of evaporation
- hopping barriers



Laboratory experiments

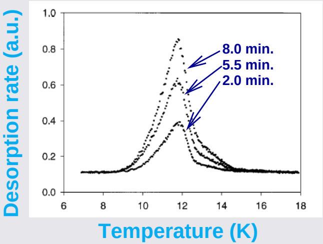
Temperature Programmed Desorption

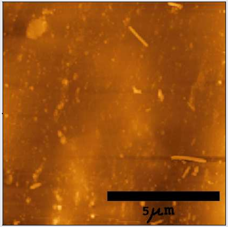
Phase 1

Phase 2

TPD experiments

$$\mathrm{H} + \mathrm{D} \rightarrow \mathrm{HD}$$





Pirronello et al., ApJ. 483 (1997) L131

Desorption under laboratory conditions

Analysis of TPD experiments

- Fitted with simple rate equations
- Translated to interstellar conditions (very low fluxes)

Analysis of TPD experiments

- Fitted with simple rate equations
- Translated to interstellar conditions (very low fluxes)

$\longrightarrow$ Only efficient for 6-10 K

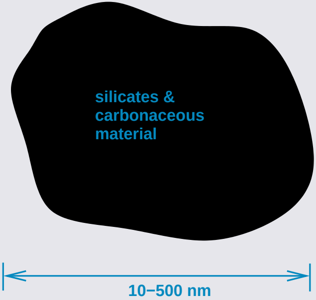
Analysis of TPD experiments

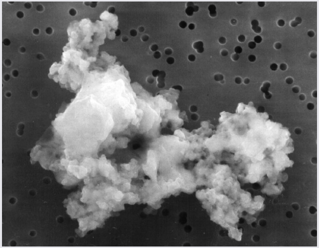
- Fitted with simple rate equations
- Translated to interstellar conditions (very low fluxes)

→ Only efficient for 6-10 K
→ Not a possible formation route

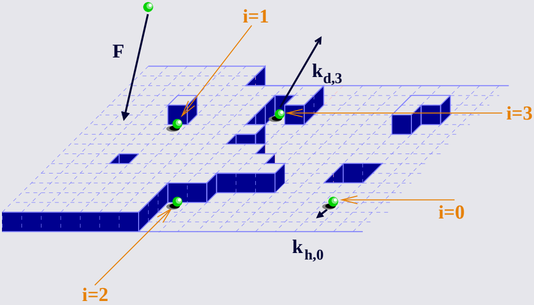
Interstellar grains

- have a "fluffy" shape
- are bare in these conditions





Surfaces



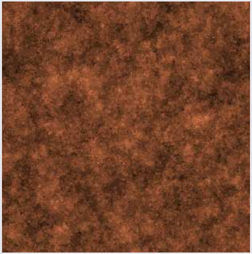
$$k_{hop} = \nu \exp\left(-\frac{E_h + iE_l}{kT}\right)$$

$$k_{des} = \nu \exp\left(-\frac{E_D + iE_l}{kT}\right)$$

Surfaces

flat

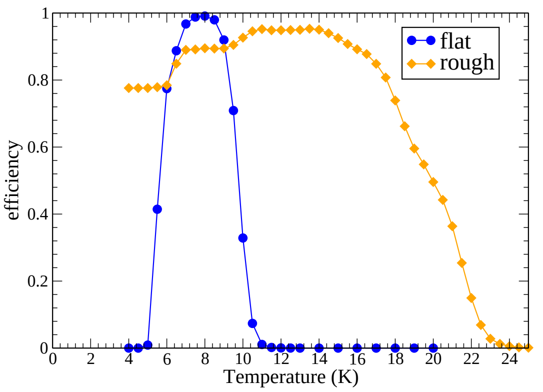
rough



$$k_{hop} = \nu \exp\left(-\frac{\mathbf{E_h} + i\mathbf{E_l}}{kT}\right)$$

$$k_{des} = \nu \exp\left(-\frac{\mathbf{E_D} + i\mathbf{E_l}}{kT}\right)$$

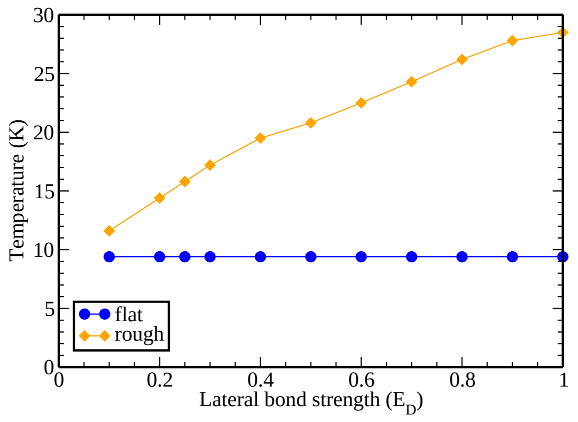
Results at constant temperature



- Efficient H_2 formation for rough surface

Cuppen & Herbst, MNRAS (2005), 361, 565-576

Influence of the lateral bond

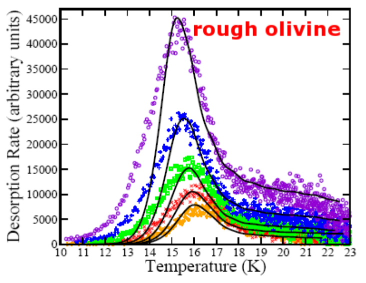


- Strong dependence of temperature range on lateral bond
- For small lateral bond still increase in temperature range

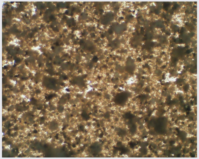
Cuppen & Herbst, MNRAS (2005), 361, 565-576

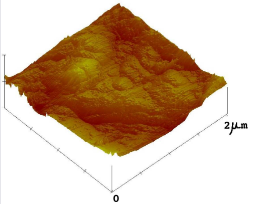
TPD experiments

$$\mathrm{H} + \mathrm{D} \rightarrow \mathrm{HD}$$



Vidali et al. J. Phys. Chem. A (2007) 111, 12611

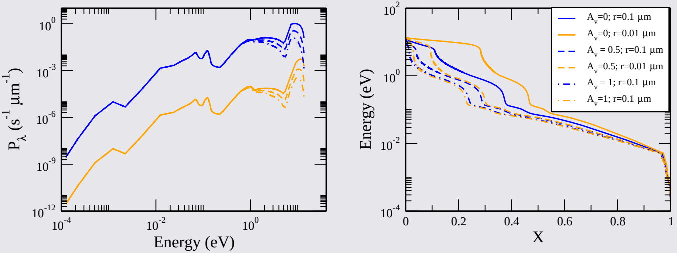




Experimental confirmation of simulation results at higher temperatures

Stochastic heating in diffuse clouds

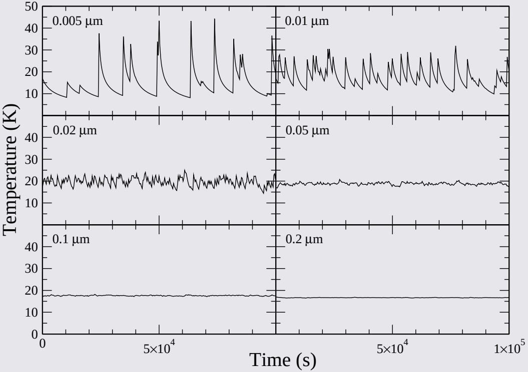
Interstellar grains are pulse heated by photons from stars in a stochastic manner



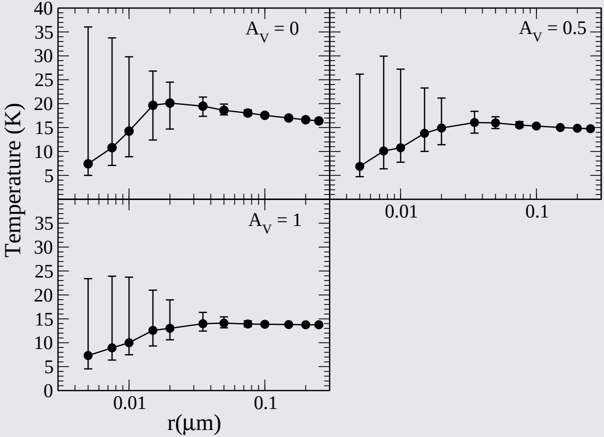
$$P_\lambda = \pi r^2 I_\lambda Q_{abs}(\lambda) D_\lambda$$

Stochastic heating in diffuse clouds

Interstellar grains are pulse heated by photons from stars (Draine, ARAA, 41 (2003) 241)

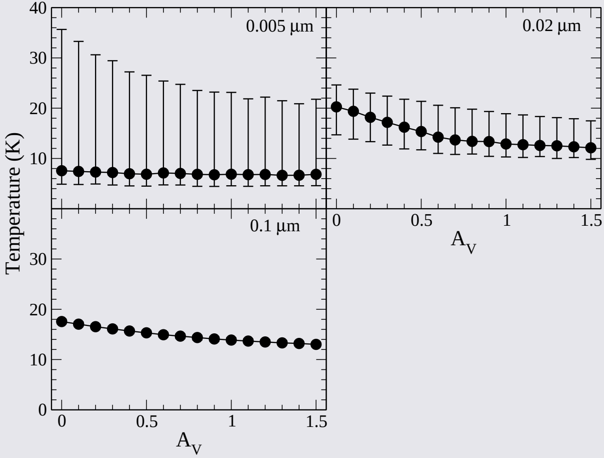


Grain temperature



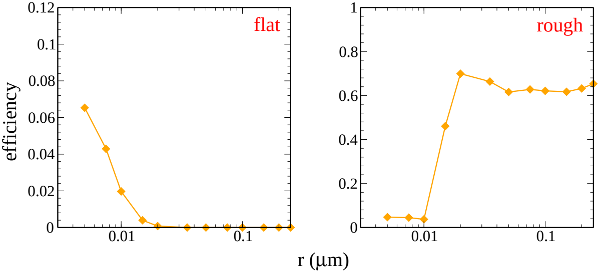
- Small grains have a lower temperature most of the time.
- Small grains have a stronger temperature fluctuations.

Grain temperature



- Small grains have a lower temperature most of the time.
- Small grains have a stronger temperature fluctuations.

Results for stochastic heating



Efficiency is highly grain size dependent

Cuppen, Morata and Herbst, MNRAS (2006), 367, 1757

Results for α

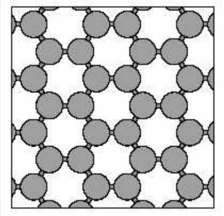
	$A_V = 0.5$	$A_V = 0.5$	$A_V = 0.5$
flat	6.50×10^{-19}	1.99×10^{-18}	2.91×10^{-18}
rough	3.12×10^{-17}	4.75×10^{-17}	5.62×10^{-17}

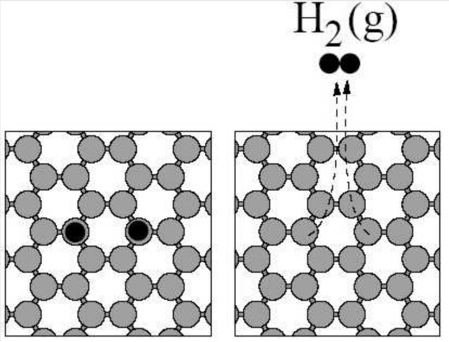
α should be 2×10^{-17} cm^3 s^{-1}

Rate is high enough for the rough surface to explain observations

Hydrogen chemistry on carbonaceous surfaces

Introduction



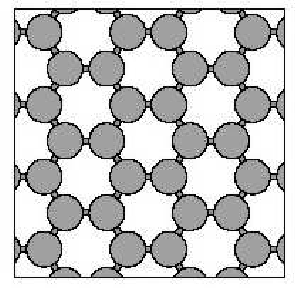


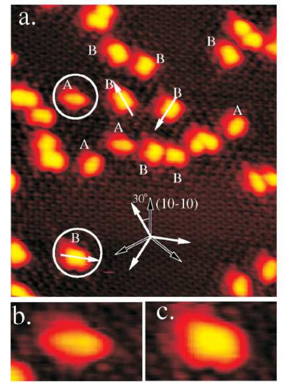
- Hydrogen storage
- Plasma-wall interaction in fusion reactors
- H_2 formation in interstellar medium

Goal

To obtain an accurate description of the H-graphite system using **Monte Carlo simulations** in order get more insight in **the H_2 formation mechanisms** by using **experimental constraints** in order to simulate H_2 formation in **warm interstellar regions**

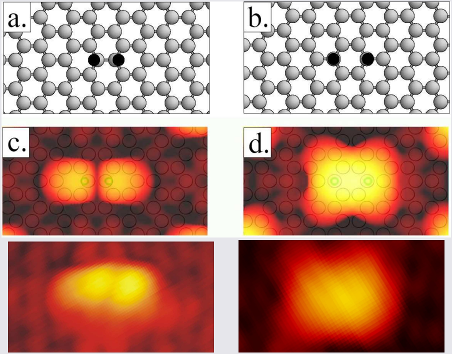
STM on graphite





Hornekær et al. PRL 96, 156104 (2006)

Hydrogen dimers

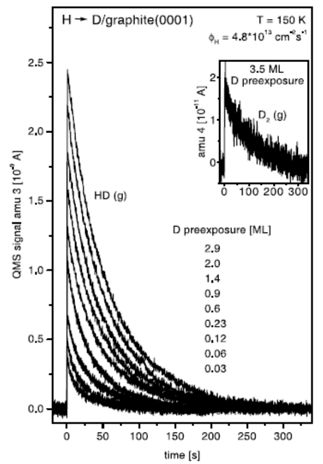


~85 % of atoms in multimer conf. at 0.01 ML

Hornekær et al. PRL 96, 156104 (2006)

Hydrogen abstraction

Known D coverage exposed to H forming HD

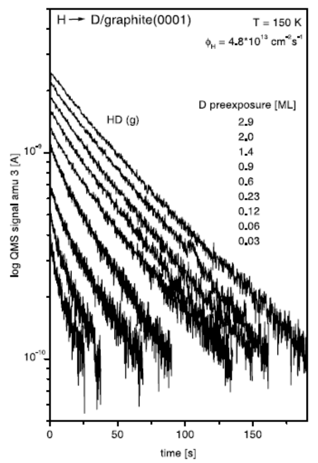


HD formation rate as a function of time

Zecho et al, Chem Phys Lett, 366 (2002) 188

Hydrogen abstraction

Known D coverage exposed to H forming HD



$$\frac{\mathrm{d[HD]}}{\mathrm{d}t} = \sigma\Phi[\mathrm{D}]_0 \exp\left(-\sigma\Phi t\right)$$

$\frac{\mathrm{d[HD]}}{\mathrm{d}t}$:HD formation rate

σ :cross section

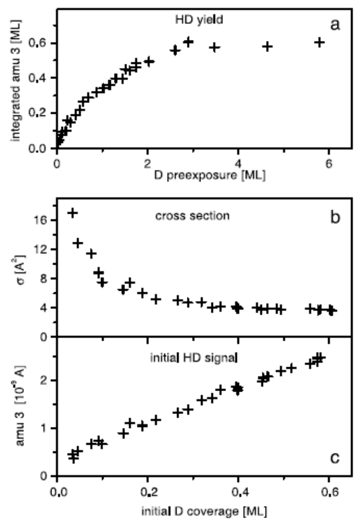
Φ :flux

$[\mathrm{D}]_0$:initial D coverage

HD formation rate as a function of time

Zecho et al, Chem Phys Lett, 366 (2002) 188

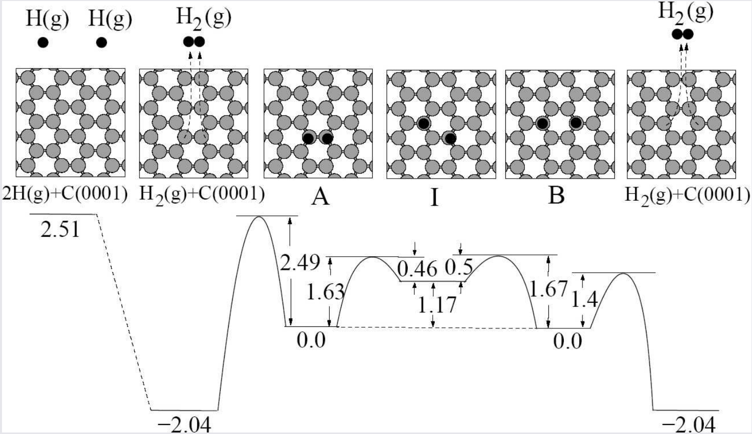
Hydrogen abstraction



Zecho et al, Chem Phys Lett, 366 (2002) 188

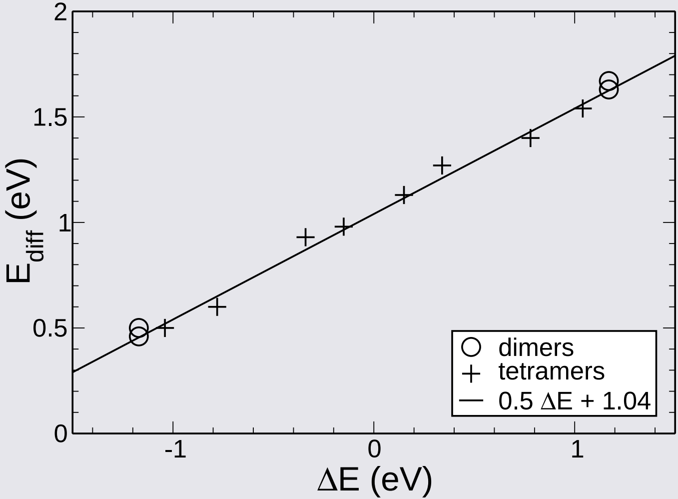
Abstraction cross section depends on coverage

Hopping rates



Hornekær et al. PRL 96, 156104 (2006)

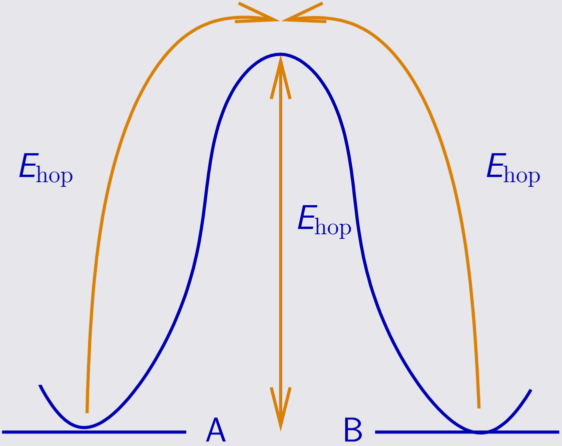
Hopping rates



Cuppen & Hornekær, JCP (2008) 128, 174707

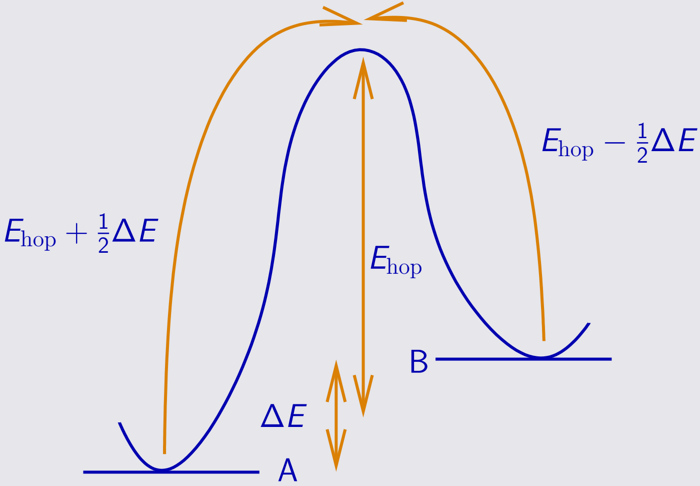
How to determine transition probabilities?

Hopping rates



How to determine transition probabilities?

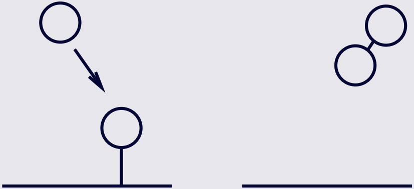
Hopping rates



Five mechanisms

Mechanism I

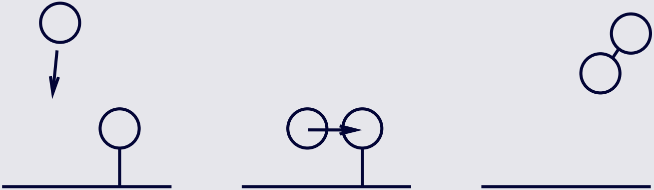
Direct Eley-Rideal



Five mechanisms

Mechanism II

Eley-Rideal with steering

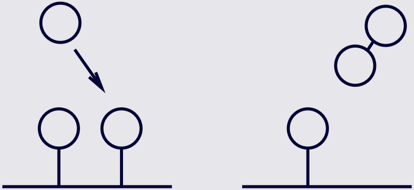


Sha & Jackson, Surf. Sci., 496 (2002) 318

Five mechanisms

Mechanism III

Dimer Eley-Rideal

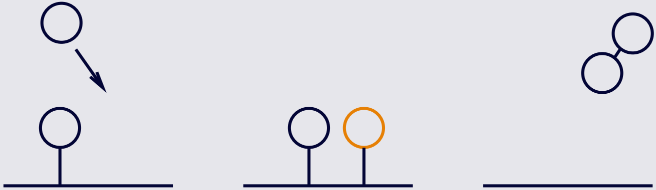


Bachellerie et al., Chem. Phys. Lett. (2007) 448, 223

Five mechanisms

Mechanism IV

Dimer mediated abstraction

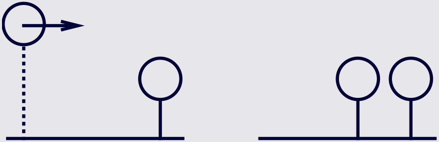


Cuppen & Hornekær, JCP (2008) 128, 174707

Five mechanisms

Mechanism V

Fast diffusion of physisorbed atoms



Bonfanti et al., JPC C (2007) 111, 5825

Monte Carlo simulations

- All mechanisms
- Combinations of mechanisms (up to three)
- Different input parameters (unknown or uncertain)

movie surface: 50 × 60 Å^2
typical sizes: 800 × 920 Å^2

colour coding: multimers

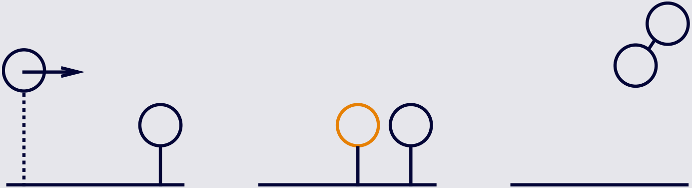
Can reproduce experiments only for specific combinations

Combination mechanism

Mechanism IV + V

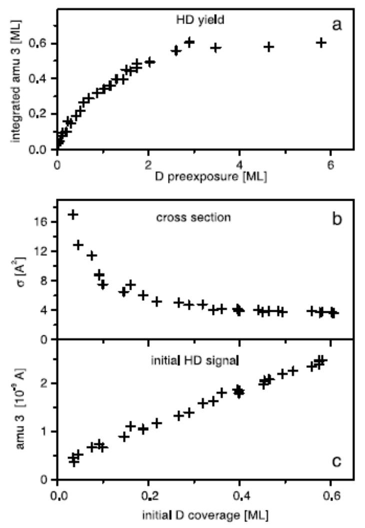
Dimer mediated abstraction → cross section

Fast diffusion of physisorbed atoms → dimer ratio

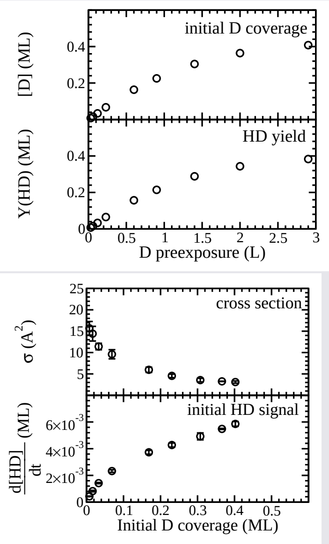


Cuppen & Hornekær, JCP (2008) 128, 174707

Cross section

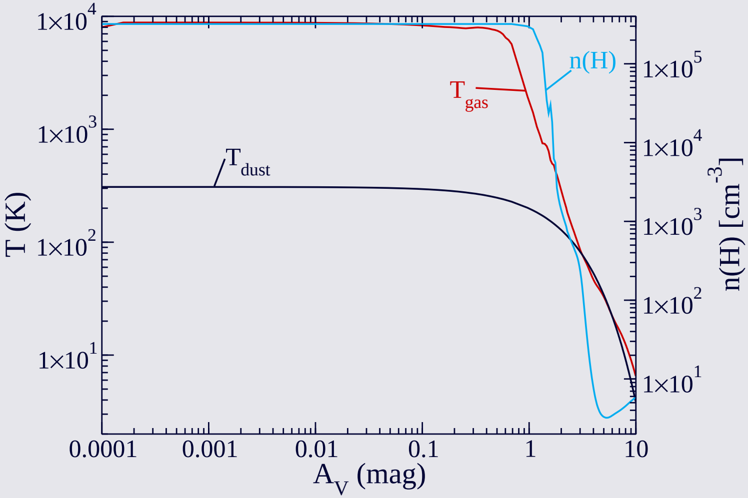


Zecho et al, Chem Phys Lett (2002) 366, 188



Simulated
Cuppen & Hornekær, JCP (2008) 128, 174707

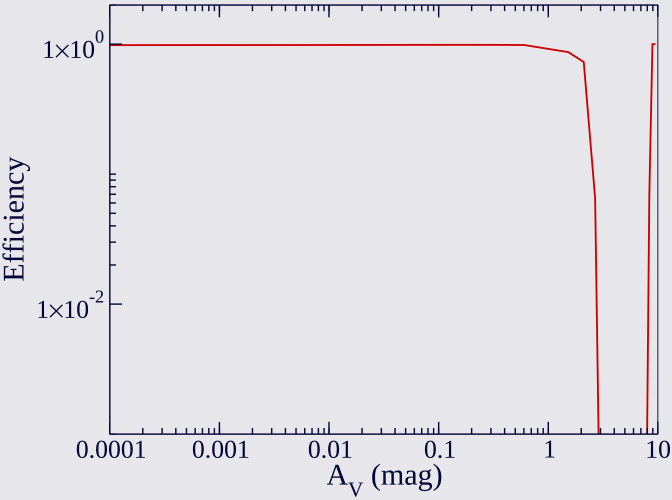
PDR physical conditions



Leiden model from Röllig et al, A. & A. 467 (2007) 187

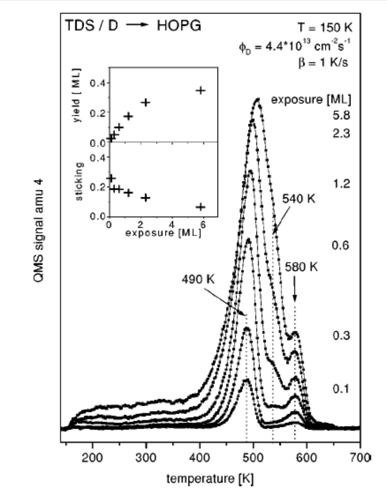
V4 conditions; $n_{\mathrm{H}} = 10^{5.5}$ cm^{-3}; $\chi = 10^5$;

Efficiency



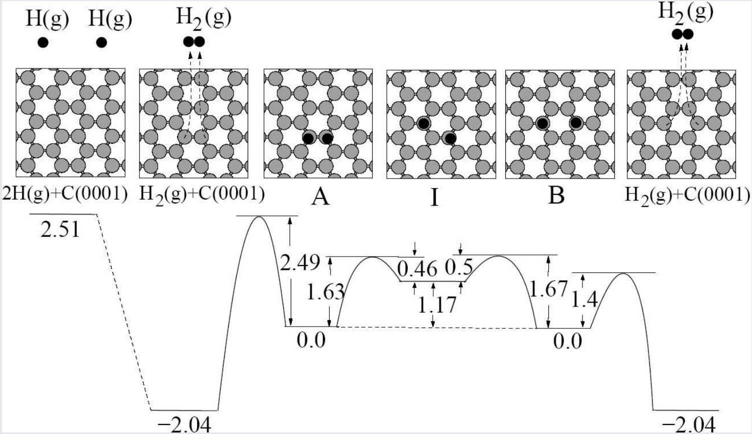
V4 conditions; $n_{\mathrm{H}} = 10^{5.5}$ cm^{-3}; $\chi = 10^{5}$;

TPD experiment



Zecho et al., JCP 117 (2002) 8486

Mechanism?

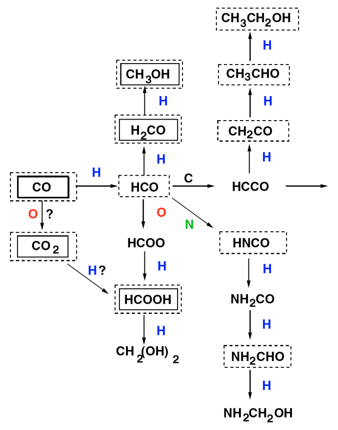


Hornekær et al. PRL 96, 156104 (2006)

Conclusions

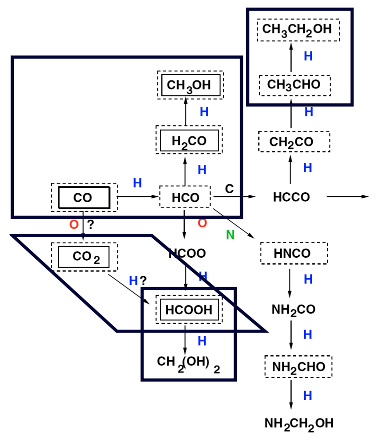
- H_2 abstraction via two mechanisms
  - Dimer mediated Eley-Rideal
  - Fast diffusion of physisorbed atom
- Efficient H_2 formation for high temperature ($T_{\mathrm{gas}} > 200$ K, $T_{\mathrm{dust}} > 100$ K)
- Surface structure can introduce a large amount of complexity → how far do we want to go?

Grain surface chemistry



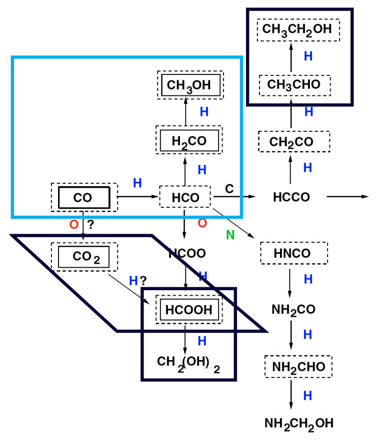
Based on Tielens and Charnley 1997, from Bisschop et al. 2007

Grain surface chemistry



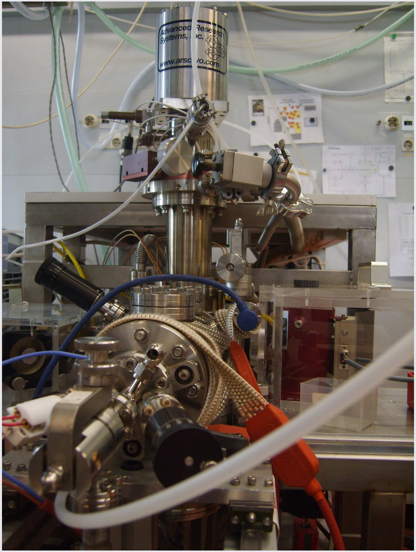
Based on Tielens and Charnley 1997, from Bisschop et al. 2007

Grain surface chemistry



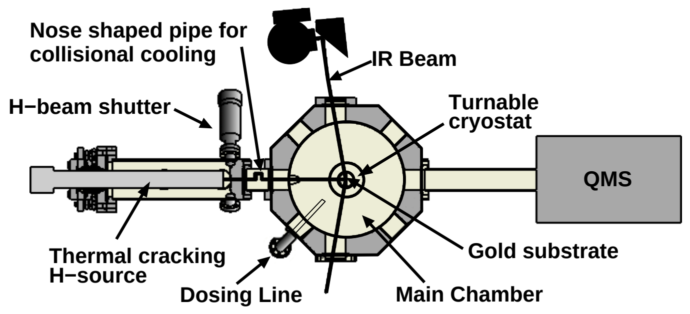
Based on Tielens and Charnley 1997, from Bisschop et al. 2007

SURFRESIDE II



- UHV system: $P < 3 \times 10^{-10}$ mbar.
- $T_{\rm surf} = 10 - 300$ K.
- H-fluxes: $10^{12} - 10^{14}$ cm^{-2} s^{-1}
- H-atoms cooled to $T_{\rm room}$ via surface collisions.

SURFRESIDE II



CO hydrogenation

$$\mathrm{CO} \xrightarrow{2\mathrm{H}} \mathrm{H_2CO} \xrightarrow{2\mathrm{H}} \mathrm{CH_3OH}$$

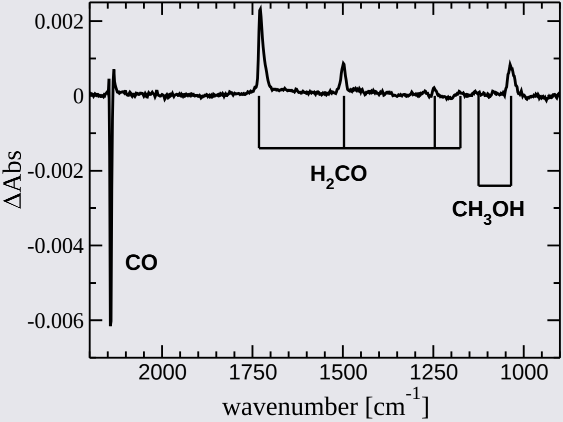
- Hiraoka et al. (1994, 2002) → efficient formaldehyde formation, no methanol
- Watanabe et al. (2002, 2003, 2004) → efficient formaldehyde and methanol formation

CO hydrogenation

$\mathrm{CO} \xrightarrow{2\mathrm{H}} \mathrm{H_2CO} \xrightarrow{2\mathrm{H}} \mathrm{CH_3OH}$

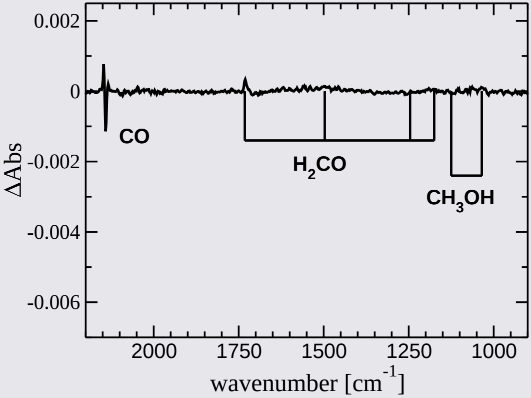
- Hiraoka et al. (1994, 2002) → efficient formaldehyde formation, no methanol
  → low flux (10^{12} cm^{-2}s^{-1}))
- Watanabe et al. (2002, 2003, 2004) → efficient formaldehyde and methanol formation
  → high flux ($10^{13} - 10^{14}$ cm^{-2}s^{-1}))

CH_3OH formation for high flux



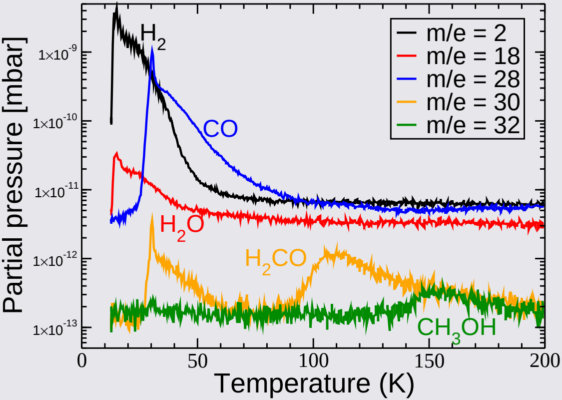
Both H_2CO and CH_3OH are formed
(5×10^{17} H atoms cm^{-2})

CH_3OH formation for low flux



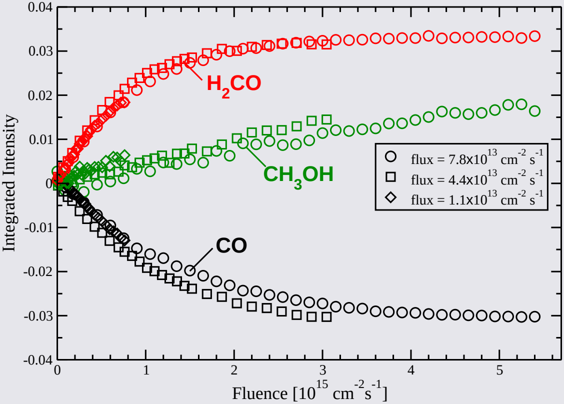
H_2CO formed, CH_3OH around detection limit
(1×10^{16} H atoms cm^{-2})

CH_3OH formation for low flux



Both H_2CO and CH_3OH are formed
(1×10^{16} H atoms cm^{-2})

CH_3OH formation

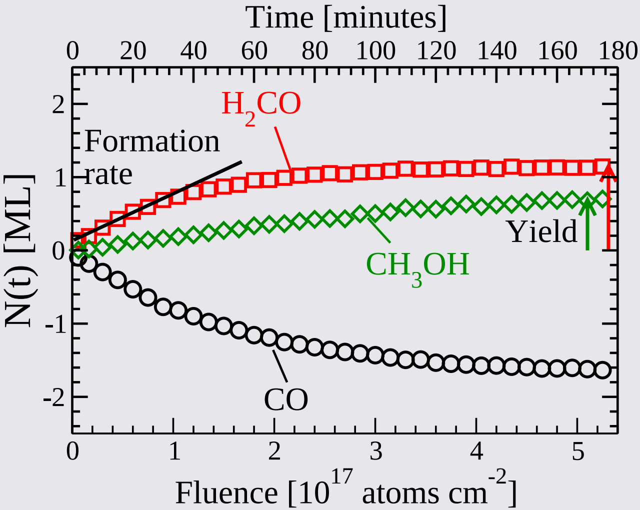


Methanol is formed for entire flux range.
For very low fluxes it is formed around the detection limit.

This suggests that there is not a change in reaction mechanism going to lower fluxes.

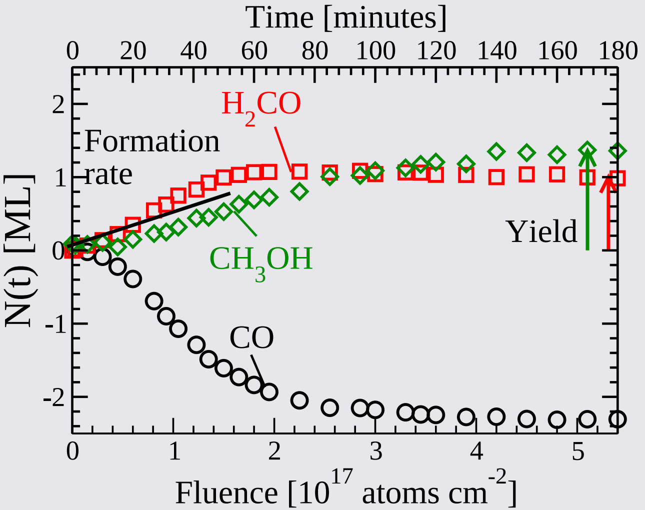
Temperature dependence

$T_{\mathrm{ice}} = 12.0$ K



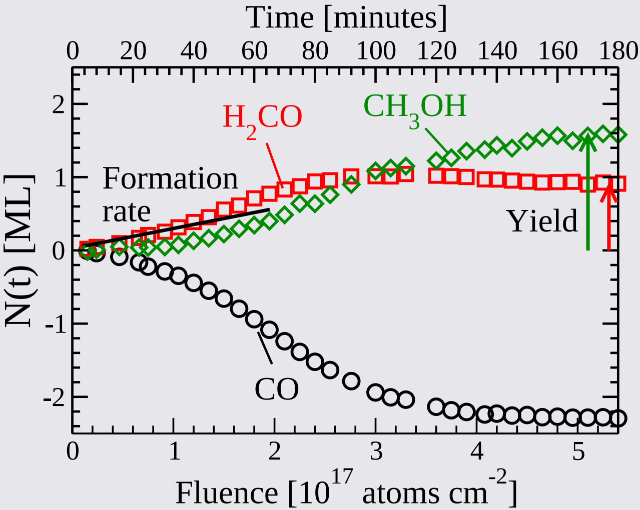
Temperature dependence

$T_{\mathrm{ice}} = 13.5$ K



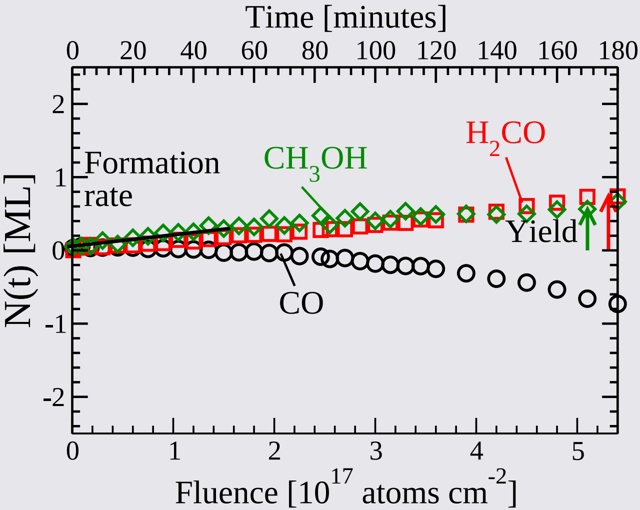
Temperature dependence

$T_{\text{ice}} = 15.0$ K

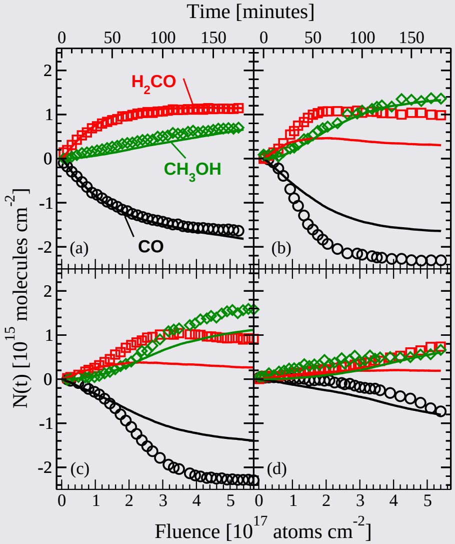


Temperature dependence

$T_{\mathrm{ice}} = 16.5$ K



Monte Carlo results



Desorption

Input parameters

$$k^{i}_{\mathrm{desorption}} = \nu \exp\left(-\frac{\mathbf{E}^{\mathbf{i}}_{\mathrm{bind}}}{kT}\right)$$

type of site	E_{bind} (meV)	(meV)*
H on flat CO (110)	27	28
H in kink site	33	
H in vacancy	38	38
CO on flat CO (110)	53	
CO in kink site	64	
CO in vacancy	75	74

* Energy minimization with accurate potential (Stefan Andersson)

Diffusion

Input parameters

$$k^{i,j}_{\mathrm{diffusion}} = \nu \exp\left(-\frac{E^{i,j}_{\mathrm{diff}}}{kT}\right)$$

$$E^{i,j}_{\mathrm{diff}} = \mathbf{E}_{\mathrm{hop}} + \frac{\mathbf{\Delta E}^{\mathbf{i,j}}_{\mathrm{bind}}}{2}$$

- For $E^{\mathrm{flat,flat}}_{\mathrm{diff}} = E_{\mathrm{hop}} = 5$ meV
- However, diffusion is limited due to presence of H_2
- Diffusion only limited effect

Flux

Input parameters

Laboratory or interstellar fluxes
(10^{12-15} cm^{-2}s^{-1} vs. 10^{7-9} cm^{-2}s^{-1})

- Different reaction channels dominate depending on H surface abundance

Reaction barriers

Fitting parameters

Varied to fit the experiments

$$k_{\mathrm{react}} = \nu \exp\left(-\frac{\mathbf{E}_{\mathrm{react}}}{kT}\right)$$

Penetration mechanism

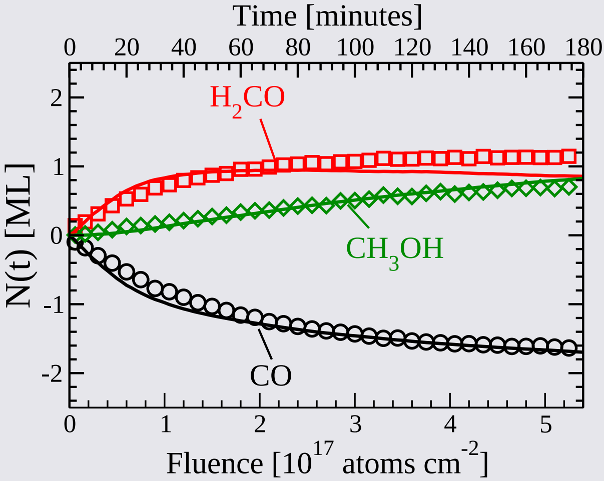
Input parameters

Minimum energy path for penetration (no thermal effects)

Temperature dependence

Monte Carlo simulations

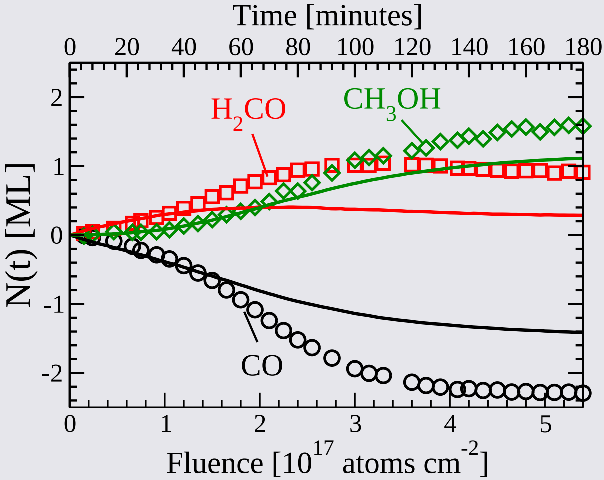
$T_{\mathrm{ice}} = 12$ K



Temperature dependence

Monte Carlo simulations

$T_{\text{ice}} = 15$ K



Reaction barriers

Fitting parameters

Varied to fit the experiments

$$k_{\mathrm{react}} = \nu \exp\left(-\frac{\mathbf{E}_{\mathrm{react}}}{kT}\right)$$

T (K)	H + CO (K)	H + H_2CO (K)
12	390 ± 20	415 ± 20
13.5	445 ± 20	445 ± 20
15	495 ± 20	490 ± 20

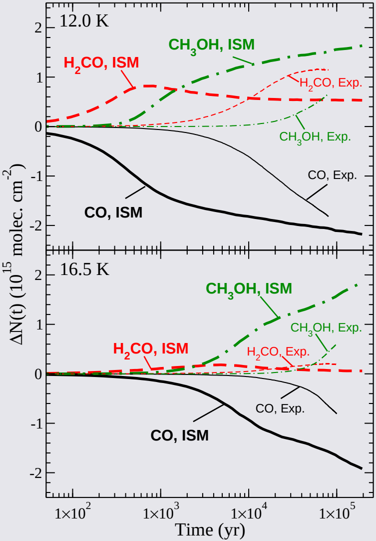
Tunneling important at these temperatures

CO hydrogenation conclusions

- Reaction rates have very little temperature dependence
- Decreasing production rate with temperature due to increasing hopping and desorption
- Larger penetration depth for higher surface temperatures

Translation to interstellar fluxes

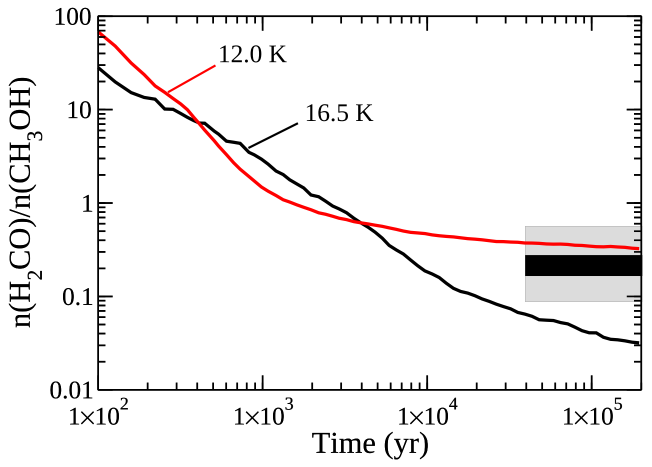
Hydrogenation of CO ice



$$n_{\rm H} = 10^5 \ {\rm cm}^{-3}$$
$$n({\rm H}) = 10^{-4} n_{\rm H}$$
$$T_{\rm gas} = 20K$$

- Fluence dependence different
- Different sticking
- CO hydrogenation becomes dominant channel (H_2 in laboratory)

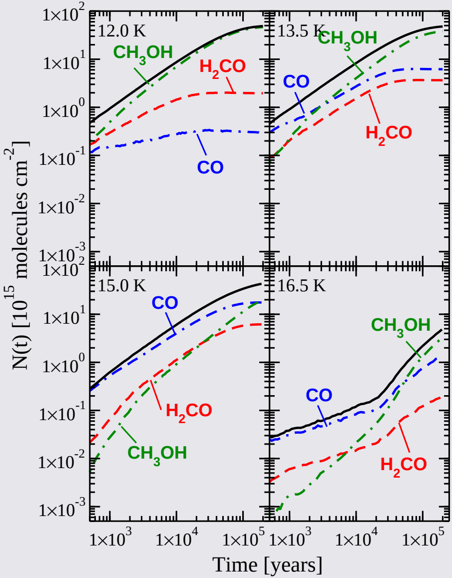
H_2CO/CH_3OH ratio



Ratio agrees with observations

Interstellar ices

Codeposition of CO and H

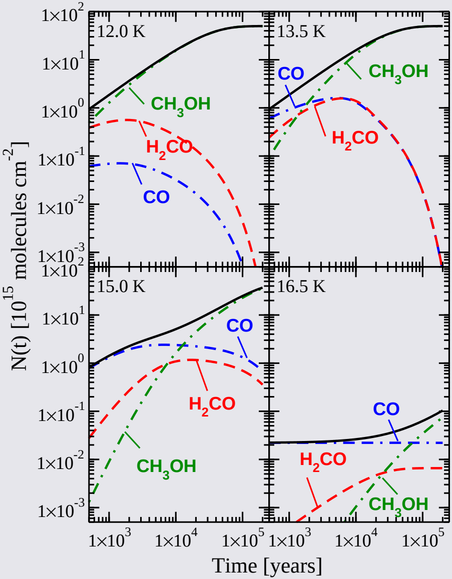


Monte Carlo simulations
$n_{\rm H} = 10^5$ cm^{-3}
$n({\rm H}) = 10^{-4} n_{\rm H}$
$n({\rm CO}) = 10^{-4} n_{\rm H}$ initial
$T_{\rm gas} = 20K$

- Sticking limited at 16.5 K
- Efficient methanol conversion for CO depletion

Interstellar ices

Comparison with rate equations



Rate equations

$n_{\mathrm{H}} = 10^5\ \mathrm{cm}^{-3}$

$n(\mathrm{H}) = 10^{-4} n_{\mathrm{H}}$

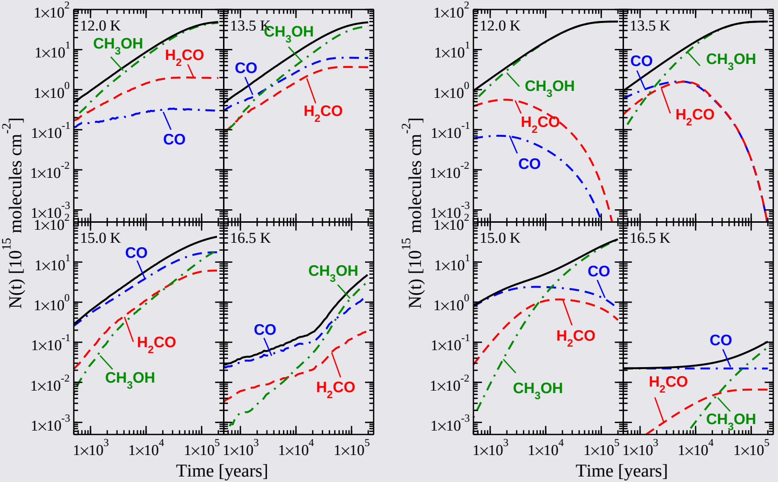
$n(\mathrm{CO}) = 10^{-4} n_{\mathrm{H}}$ initial

$T_{\mathrm{gas}} = 20K$

- CH_3OH/H_2CO ratio lower
- Large drop for CO depletion

Interstellar ices

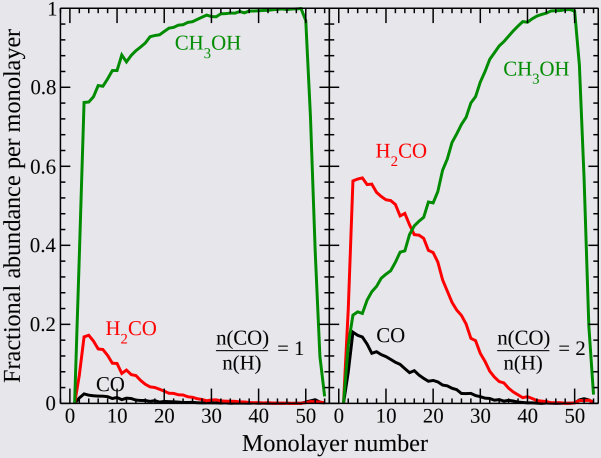
Comparison with rate equations



- Initial composition differs
- Large drop for CO depletion

Interstellar ices

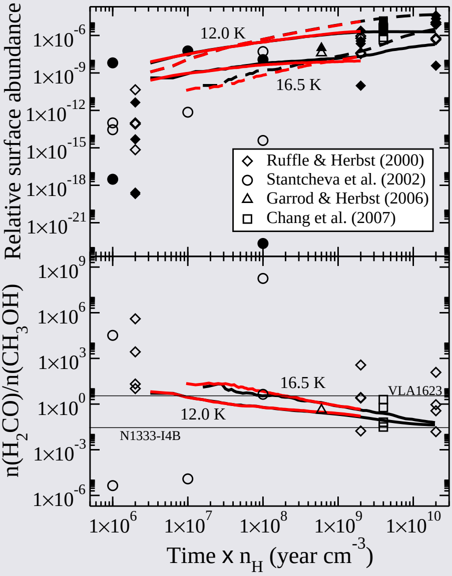
Layer composition



- H_2CO and CO locked up in lower layers
- $n(\mathrm{CO})/n(\mathrm{H})$ ratio determines CH_3OH and H_2CO formation

H_2CO/CH_3OH ratio

co-deposition



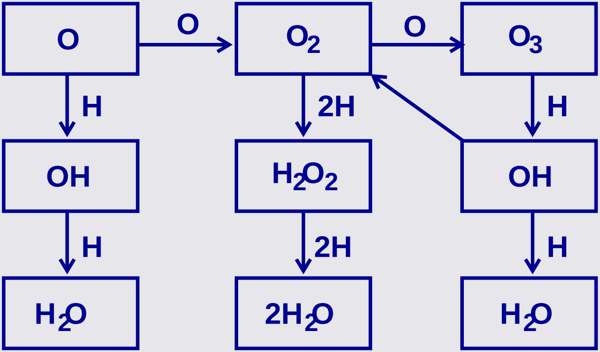
Ratio agrees with observations

Conclusions

- CH_3OH and H_2CO both efficiently formed
- Laboratory results can be explained by MC simulations.
- Layering due to changing gas phase abundance

Water reactions

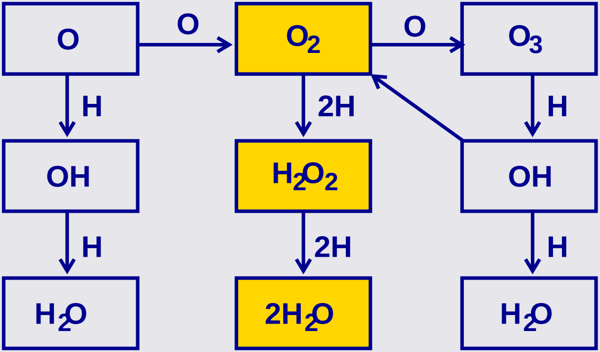
Three different formation routes have been proposed:



Tielens & Hagen, A. & A. 114 (1982) 245

Water reactions

Three different formation routes have been proposed:



O $\xrightarrow{O}$ O_2 $\xrightarrow{O}$ O_3

O $\xrightarrow{H}$ OH $\xrightarrow{H}$ H_2O

O_2 $\xrightarrow{2H}$ H_2O_2 $\xrightarrow{2H}$ $2H_2O$

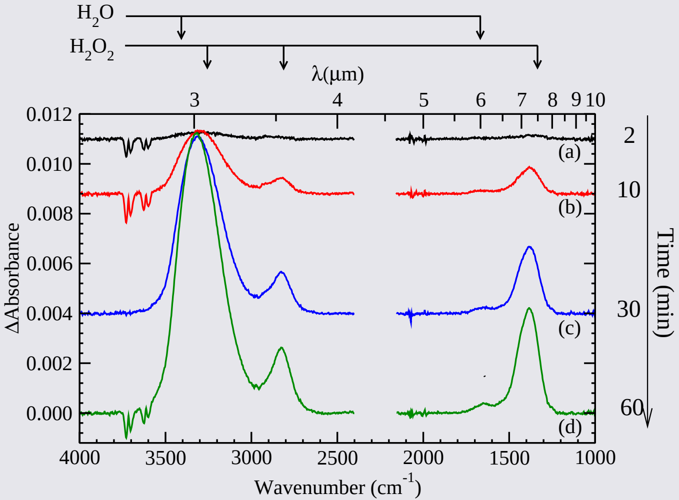
O_3 $\xrightarrow{H}$ OH $\xrightarrow{H}$ H_2O

Only separate reaction channel

Tielens & Hagen, A. & A. 114 (1982) 245

Water formation

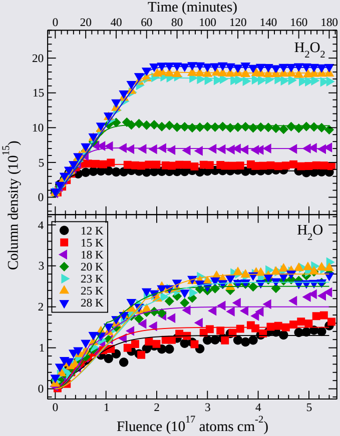
IR identification



Ioppolo et al. ApJ. 686 (2008) 1474

Water formation

$$O_2 \xrightarrow{2H} H_2O_2 \xrightarrow{2H} 2H_2O$$



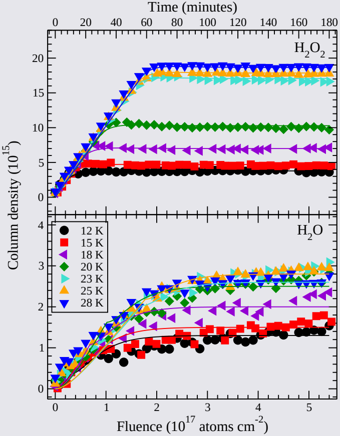
Ioppolo et al. ApJ. 686 (2008) 1474

No temperature dependence at early times

penetration depth temperature dependent

Water formation

$$O_2 \xrightarrow{2H} H_2O_2 \xrightarrow{2H} 2H_2O$$



$$\frac{d[H_2O_2](t)}{dt} = k_1[O_2][H] - k_2[H_2O_2][H]$$

$$\frac{d[H_2O_2](t)}{dt} = k_1'[O_2] - k_2'[H_2O_2]$$

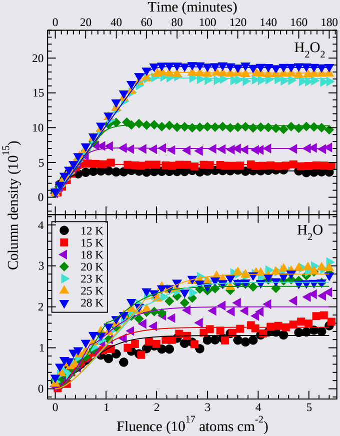
Ioppolo et al. ApJ. 686 (2008) 1474

No temperature dependence at early times

penetration depth temperature dependent

Water formation

$$\mathrm{O_2} \xrightarrow{2\mathrm{H}} \mathrm{H_2O_2} \xrightarrow{2\mathrm{H}} 2\mathrm{H_2O}$$



$$\frac{\mathrm{d}[\mathrm{H_2O_2}](t)}{\mathrm{d}t} = k_1[\mathrm{O_2}][\mathrm{H}] - k_2[\mathrm{H_2O_2}][\mathrm{H}]$$

$$\frac{\mathrm{d}[\mathrm{H_2O_2}](t)}{\mathrm{d}t} = k_1'[\mathrm{O_2}] - k_2'[\mathrm{H_2O_2}]$$

$$\frac{\mathrm{d}[\mathrm{H_2O_2}](t)}{\mathrm{d}t} = k_1'' - k_2'[\mathrm{H_2O_2}]$$

Ioppolo et al. ApJ. 686 (2008) 1474

No temperature dependence at early times

penetration depth temperature dependent

Hypothesis

Why zeroth order behaviour?

- Hydrogen trapped in ice matrix
- Trapping depends on incoming beam (no temperature dependence)
- Penetration depth depends on temperature

O_2 (001) surface

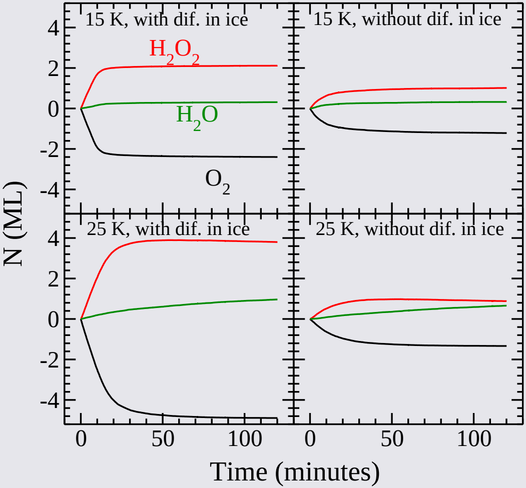
Water formation

Difference in ice structure

CO (110) surface

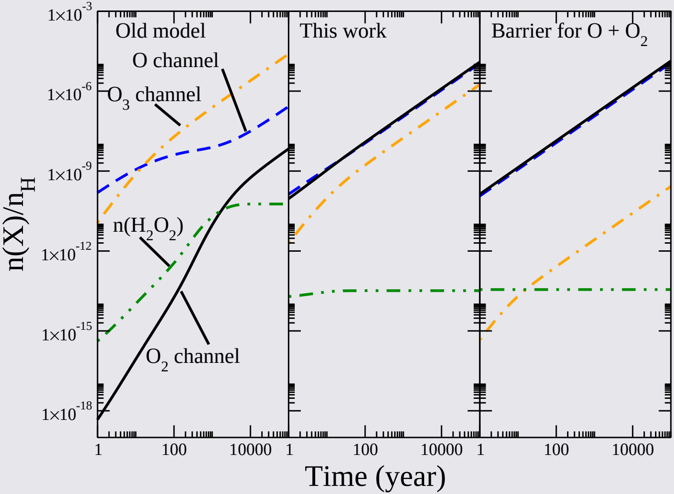
O_2 (001) surface

Monte Carlo simulations



Diffusion into ice is needed for zeroth order and penetration depth.

Monte Carlo simulations



O_2 channel more important than previously thought

Conclusions

- H_2O_2 and H_2O more efficiently formed than previously expected.
- O_2 could be a major route for H_2O formation
- Diffusion into O_2 very important process
- More data needed to fully understand how structure determines reactions (CO vs. O_2)