

α = 4^h 14^m 28^s

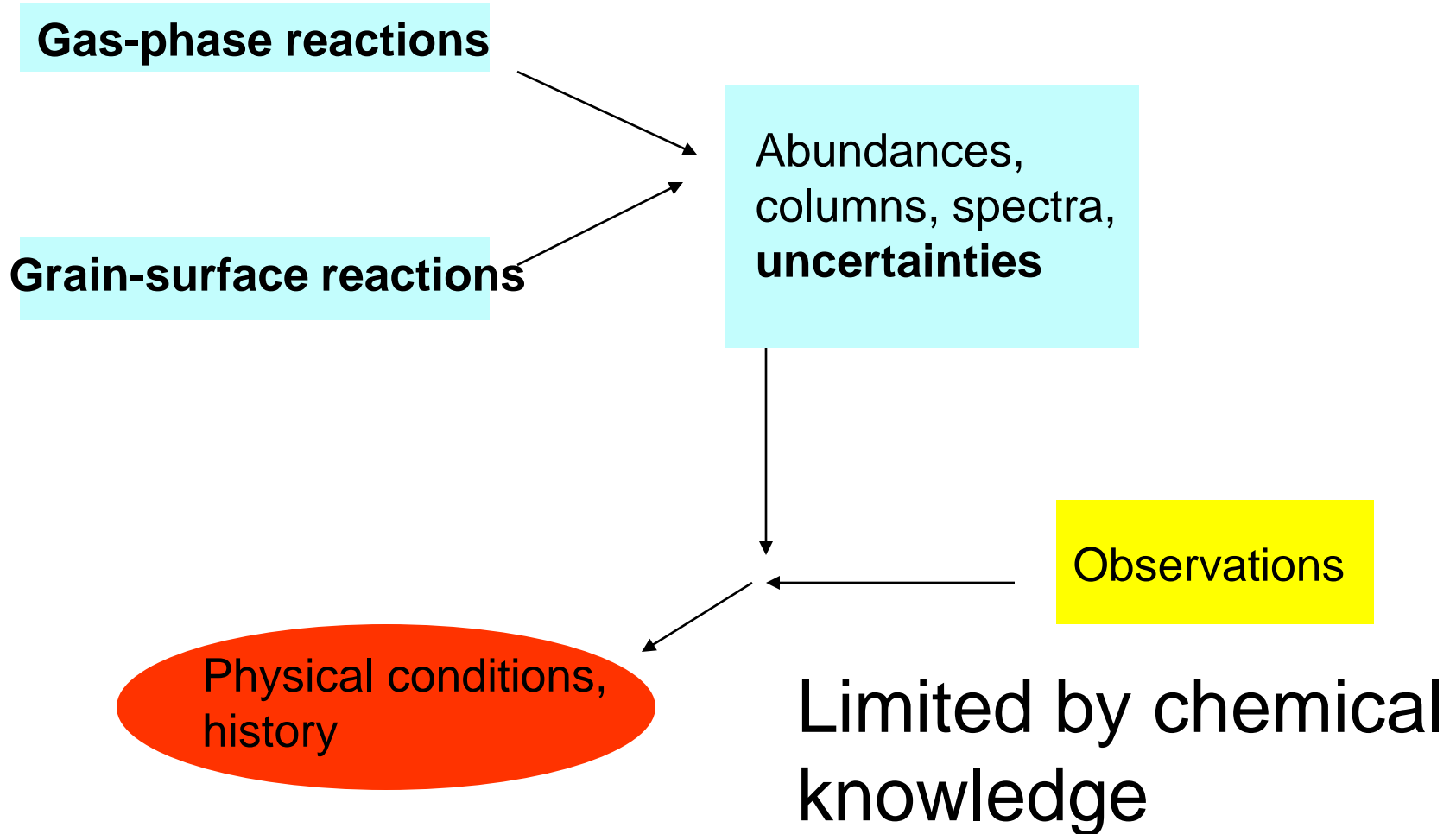
The Role of Surface Chemistry in the Synthesis of Interstellar Molecules

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Gaseous interstellar molecules (151)

N=2		N=3		N=4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
H ₂	AlCl	CH ₂	C ₂ S	NH ₃	CH ₄	CH ₃ OH	CH ₃ NH ₂	HCOOCH ₃	(CH ₃) ₂ O	(CH ₃) ₂ CO
CH	PN	H ₂ S	OCS	H ₂ CO	SiH ₄	CH ₃ SH	CH ₃ CCH	CH ₃ C ₂ CN	C ₂ H ₅ OH	CH ₃ C ₄ CN
NH	SiN	NH ₂	MgCN	H ₂ CS	CH ₂ NH	C ₂ H ₄	CH ₃ CHO	HC ₆ H	C ₂ H ₅ CN	CH ₃ CH ₂ CHO
OH	SiO	H ₂ O	MgNC	H ₂ CN	C ₅	H ₂ C ₄	c-CH ₂ OCH ₂	C ₇ H	CH ₃ C ₄ H	(CH ₂ OH) ₂
O ₂ (?)	SiS	HNO	NaCN	I-C ₃ H	I-C ₃ H ₂	CH ₃ CN	CH ₂ CHCN	HOCH ₂ CHO	C ₈ H	
HF	PO	C ₂ H	SO ₂	c-C ₃ H	c-C ₃ H ₂	CH ₃ NC	HC ₄ CN	CH ₃ COOH	HC ₆ CN	
C ₂	SH	HCN	N ₂ O	HCCH	H ₂ CCN	NH ₂ CHO	C ₆ H	H ₂ CCCHCN	CH ₃ CONH ₂	N = 11
CN	AlF	HNC	SiCN	HNCO	H ₂ NCN	H ₂ CCHO	H ₂ CCHOH	H ₂ C ₆	CH ₂ CHCH ₃	HC ₈ CN
CO	FeO	HCO	SiNC	HNCS	CH ₂ CO	C ₅ H		CH ₂ CHCHO		CH ₃ C ₆ H
CS	SiC	c-SiC ₂	CCP	HCCN	HCOOH	C ₅ N				
CP		MgCN		C ₂ CN	C ₄ H	HC ₄ N				
NO		MgNC		C ₃ O	HC ₂ CN	C ₅ S(?)				N = 12
NS		AlNC		C ₃ S	HC ₂ NC	HC ₄ H				C ₆ H ₆
SO		HCP	H ₃ ⁺	c-SiC ₃	C ₄ Si	CH ₂ CNH				
HCl	CH ⁺	C ₃	HCO ⁺	C ₃ N ⁻	HNCCC	HC ₂ CHO				
NaCl	CO ⁺	C ₂ O	HOC ⁺	H ₃ O ⁺	CNCHO	c-C ₃ H ₂ O				N = 13
KCl	SO ⁺	CO ₂	N ₂ H ⁺	HCNH ⁺	H ₂ COH ⁺					HC ₁₀ CN
N ₂ (?)	CF ⁺		HCS ⁺	HOCO ⁺	C ₄ H ⁻	HC ₃ NH ⁺	C ₆ H ⁻		C ₈ H ⁻	

Chemical Simulations



Sources Modeled

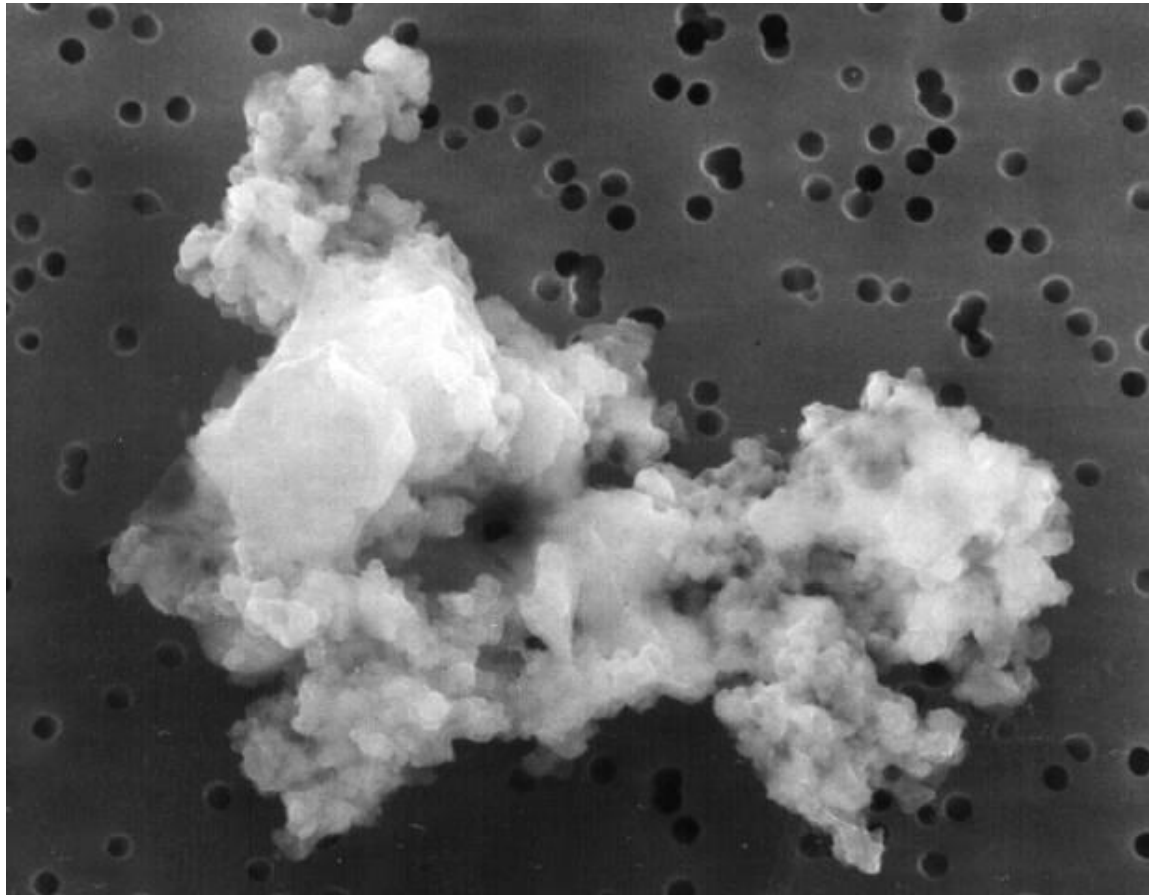
- Diffuse clouds
- Cold cores (10 K)
- Pre-stellar cores
- Hot Cores (100 K)
- Outflows
- Shocks
- Protoplanetary disks
- PDR's; XDR's
- IRDC's
- Circumstellar envelopes
- Protoplanetary nebulae
- Planetary nebulae
- AGN disks
- Earliest clouds
- Exo-planetary atmospheres

Strengths/**Failures** of Gas-Phase Networks

- Exotic and unsaturated gaseous species (carbon chains, ions, radicals, isomers) in cold dense cores (ion-molecule chemistry; no barriers)
- Carbon-rich stellar envelopes
- Early universe chemistry (H and He)

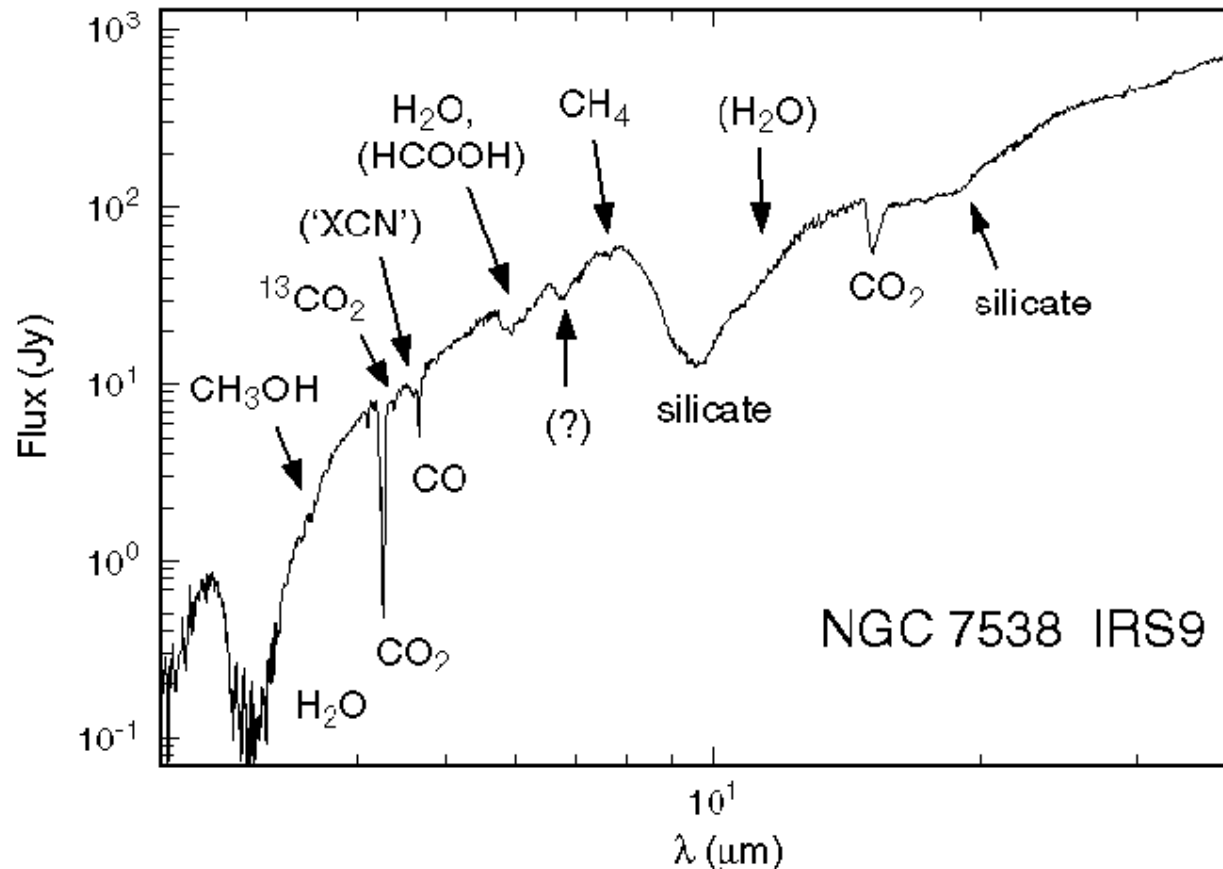
- **Formation of molecular hydrogen in the ISM**
- **Explanation of ices in cold cores**
- **Existence of saturated species in gas of cold cores (methanol, propylene)**
- **High abundances of complex organic molecules in hot cores**

An Interplanetary Dust Particle



Size of interstellar dust ranges from 1-1000 nm;
Mainly silicates and carbonaceous material

IR Absorption Spectroscopy

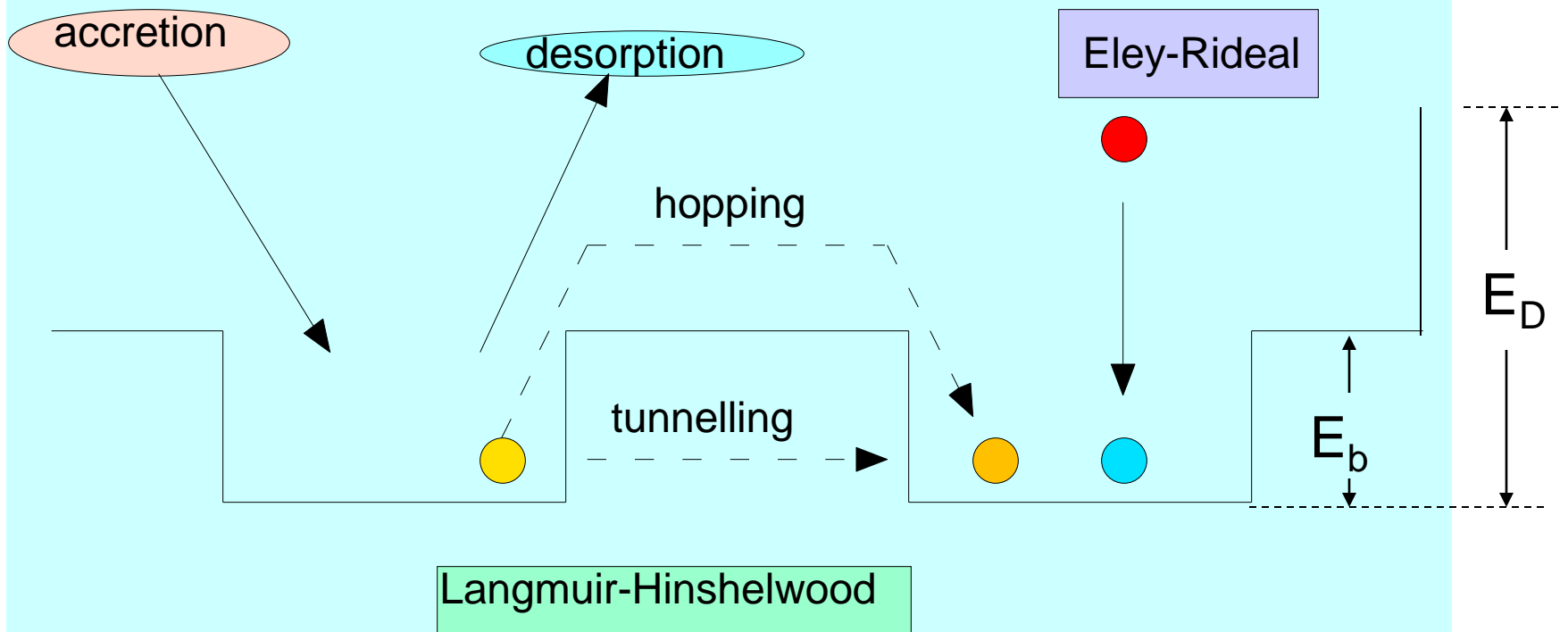


IR absorption showing a silicate core and ice mantle, mainly water. Not sensitive enough to find larger species.

Granular Processes

1. Bare surface chemistry (silicates, carbon)
2. Thermal chemistry on and possibly in ices
3. Photochemistry
4. Other non-thermal mechanisms (hot atoms, cosmic rays, X-rays, energetic electrons)
5. Thermal desorption
6. Non-thermal desorption (photodesorption; reactive desorption)

Reactive Mechanisms

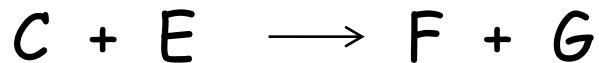
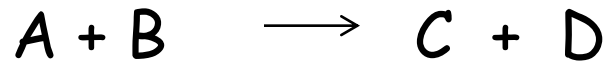


“flat” corrugated surface in 1D

Mathematical Methods for Model Including Surface Chemistry

- Rate equations: used for most calculations.
- Stochastic methods (master equation, method of moments, Monte Carlo).
- Monte Carlo: Random numbers determine process in time interval based on relative rates.
- Macroscopic MC: Vasyunin et al.
- Microscopic MC (CTRW, KMC): soon!

Coupled Rate Equations: gas or grain



$$d[C]/dt = k_1[A][B] - k_2[C][E]$$

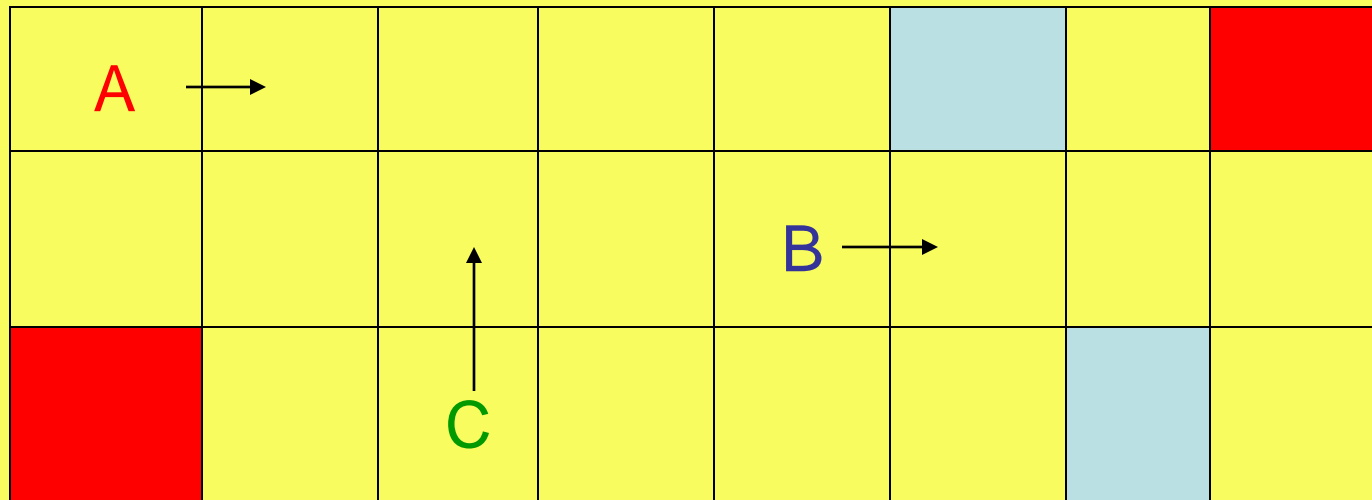
Master Equation: $dP_n(C)/dt = \dots, n = 0, 1, 2, 3, \dots$

Solve coupled differential equations vs time:
terms include accretion and desorption

CTRW (MICROSCOPIC) APPROACH

Chang, Cuppen & Herbst (2005)

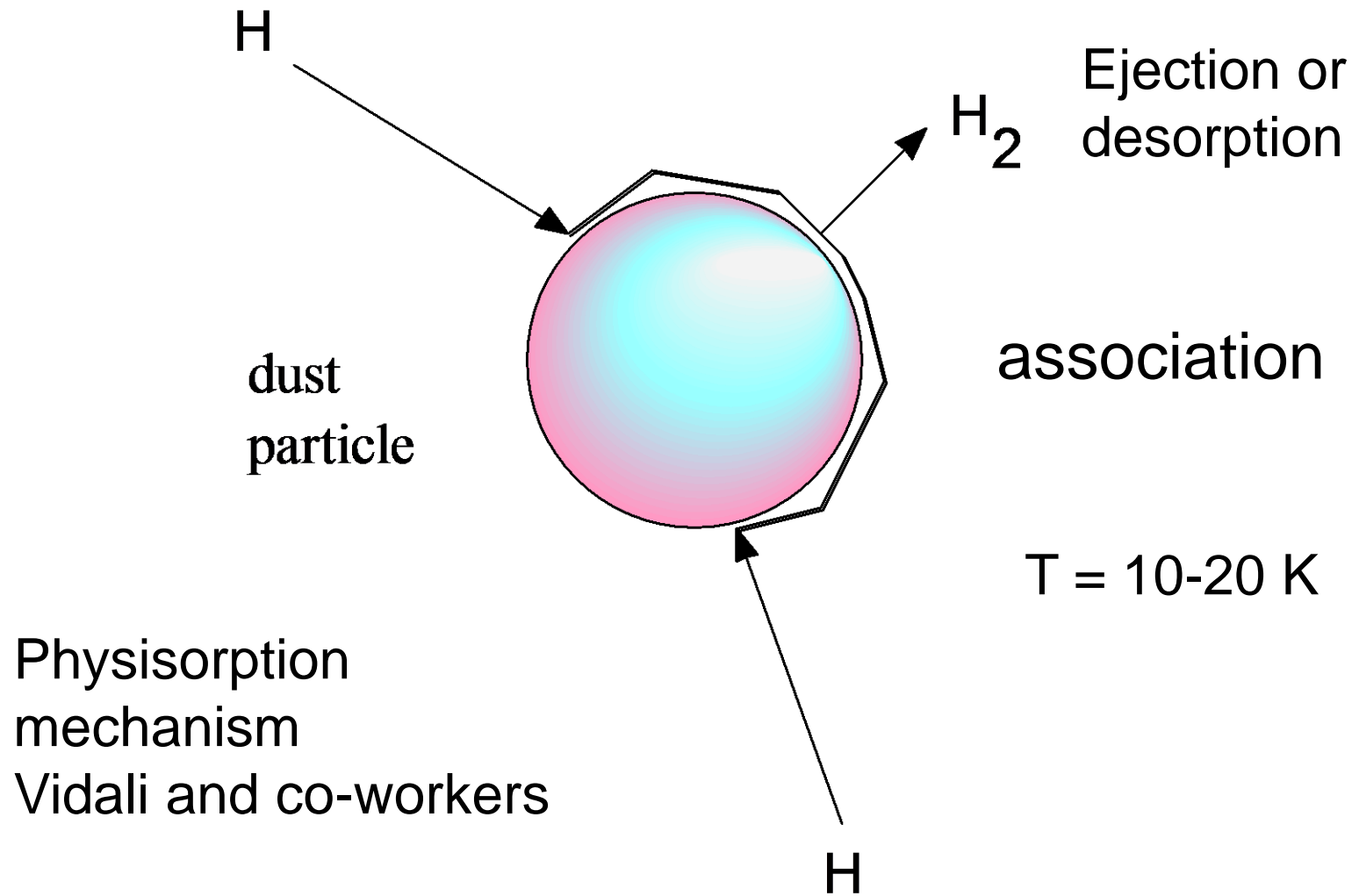
- A Monte Carlo approach in which the actual positions of individual species on a lattice are followed with time. Can use to follow reactions (LH,ER) and mantle build-up.



Desorption Processes: Coupling Gas & Dust Chemistries

- Thermal desorption: ice mixtures very complex, as measured in TPD experiments. Trapping and volcanic effects for binary mixtures.
- Non-thermal desorption:
 - Photodesorption (appears to follow electronic spectrum; more experiments, theory needed) **competes with photodissociation**
 - Reactive Desorption: uses energy of exothermic surface reactions to blow product off surface (simple theory only)
 - Cosmic ray desorption: thermal and sputtering, rates uncertain

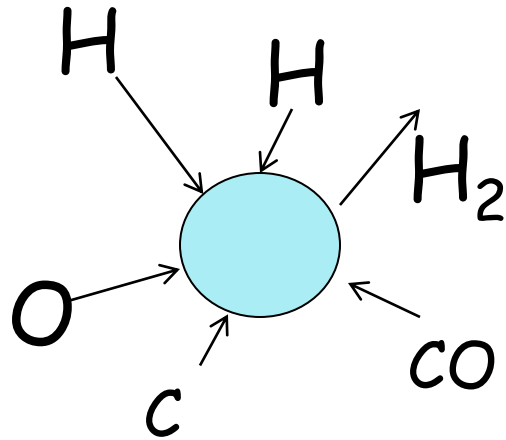
Formation of Hydrogen



H2 - More Recent Work

- Experiments
 - Rough surfaces
 - Chemisorption on graphite, PAHs
- Theory
 - Stochastic heating
 - Physisorption & chemisorption – T range
 - **Molecular dynamics**

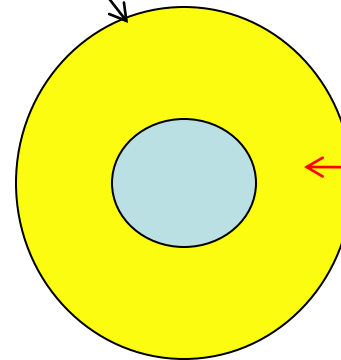
Surface/ice processes in gas-grain networks



Many studies

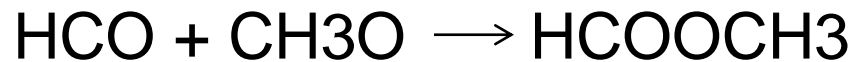
Cold core (10 K);
build up of ice
mantles
including water,
CO, CO₂, CH₄,
methanol

photons



Radical-radical reactions

40-100 K reactions
produce terrestrial
organics



Cold Core Chemistry

Rate equations

Macroscopic MC

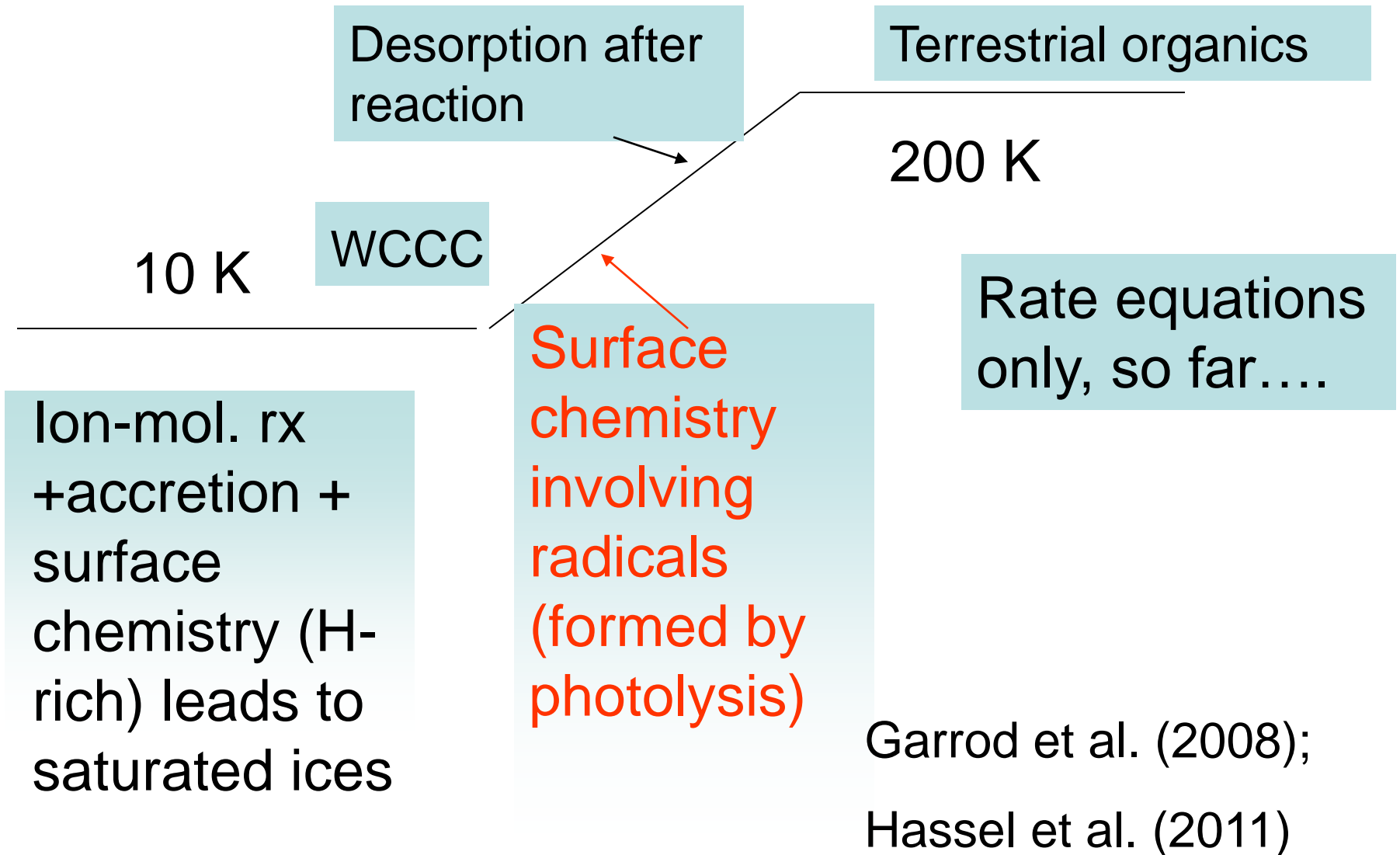
Moment equations

Modified rate method

Microscopic MC - almost



Hot Core Chemistry: gas-grain model



Recent Laboratory Success: Warm-up chemistry

- Photochemistry in warming regions: indicates that basic model of complex molecular formation OK (Oberg et al. 2009), BUT.....
- Severe problems with transferring laboratory results for multi-reaction system into space.
- Solution: Try to simulate complex chemistry occurring in the laboratory; obtain rate parameters for use in interstellar codes (Garrod, Oberg, in progress).

SUMMARY

- Current standard gas-grain model: rate equations, homogeneous ice
- Improvements on the way for surface/ice chemistry: improved laboratory simulations and more use of stochastic approaches, including microscopic ones.
- More realistic, time-dependent physical conditions.

The Real Future

As we know,

There are **known knowns**.

There are things we know we know.

We also know

There are **known unknowns**.

That is to say,

We know there are some things

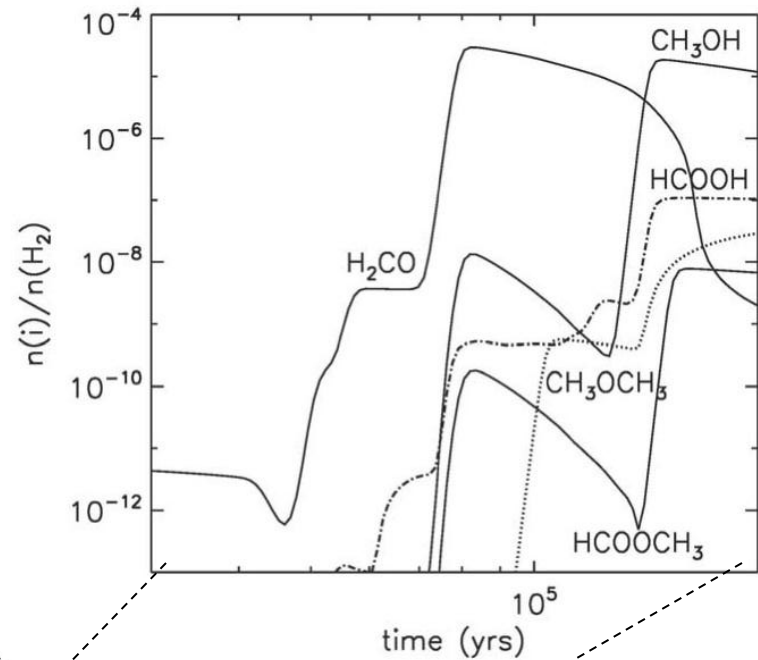
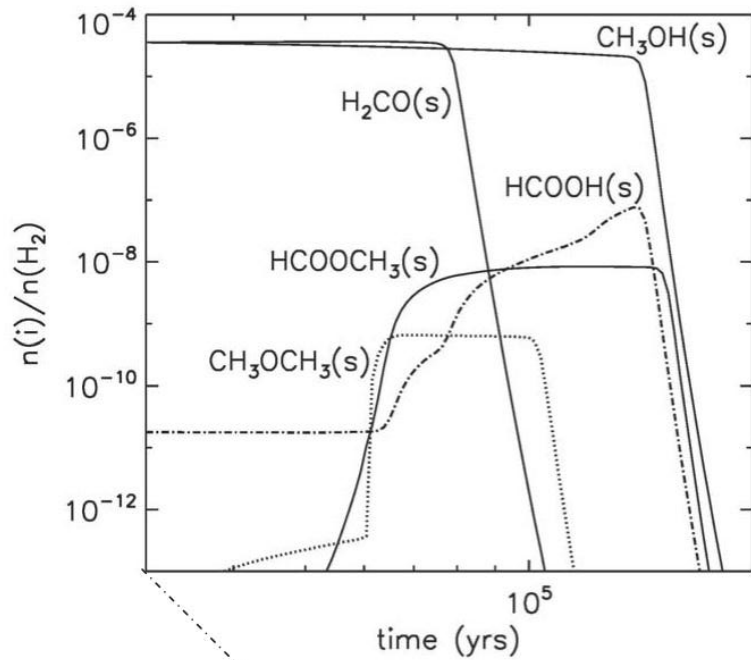
We do not know.

But there are also **unknown unknowns**,

The ones we don't know

We don't know.

Homogeneous Warm-up Model



Cold Phase

Warm-up Phase

Hot-Core Phase

Garrod et al.

Problem: lab to space conversion

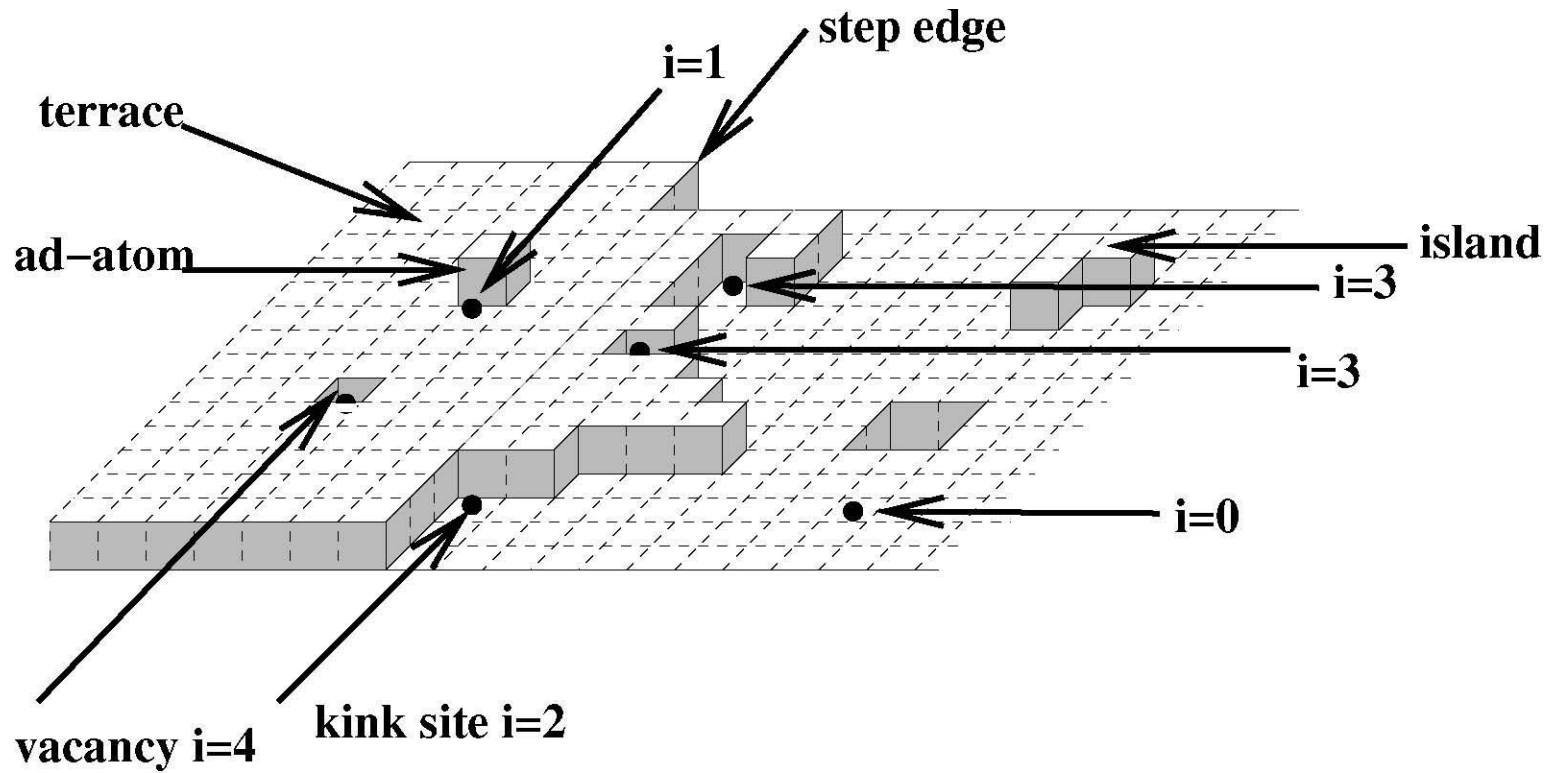
• LABORATORY

- High density/flux
- Large surface
- High radiation field
- Pure ice

• SPACE

- Low density/flux
- Nanoparticle
- Low radiation field
- Dirty ice

Irregularities on rough surface



Predictions for the Future

1. Better simulations of laboratory experiments leading to more accurate rate coefficients under interstellar conditions.
2. Inclusion of 3-D hydrodynamics into gas-grain codes for protostar formation (Aikawa)
3. Greater use of stochastic approaches for surface chemistry.
4. More detailed studies of the chemistry occurring as protoplanetary disks and planets form.
5. Greater use of high-speed computing in models

Interstellar Simulation based on Lab Simulation

Hydrogenation of CO into
methanol at temperatures of
(top to bottom) 12.0 K, 13.5
K, 15.0 K, and 16.5 K

Cuppen et al. 2009

2×10^5 yr cold core

