Faculty of Mathematics
University of Belgrade

Atomic and Molecular Data - Application on Formation of Molecules in Dark Clouds

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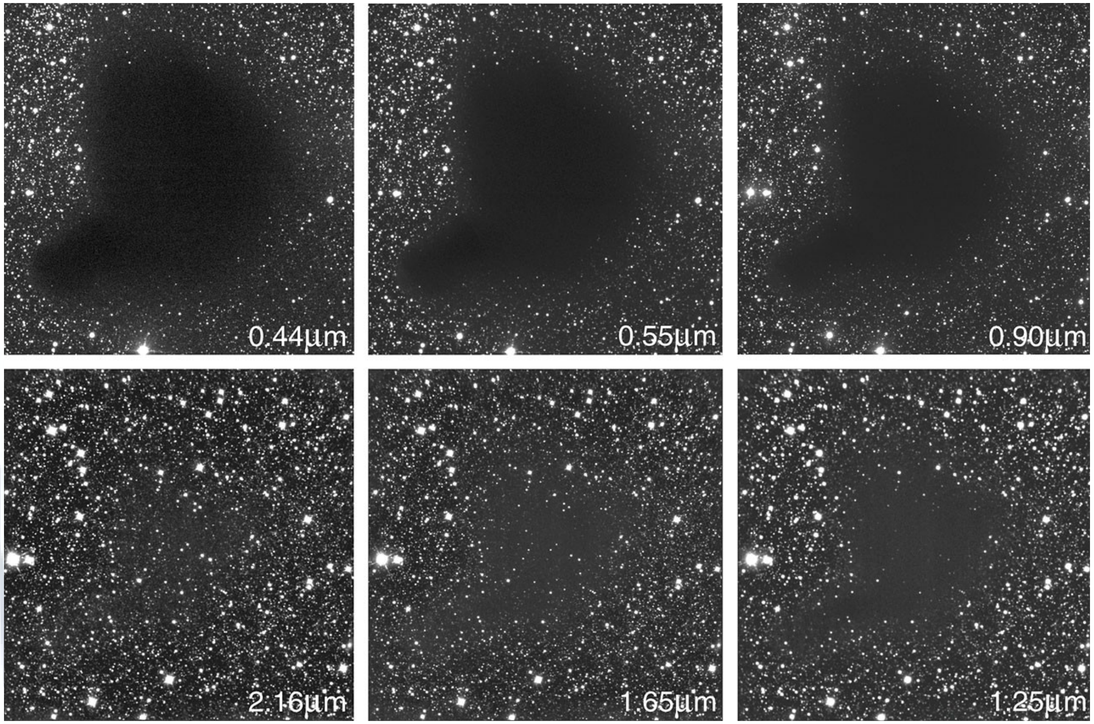
Astrochemistry

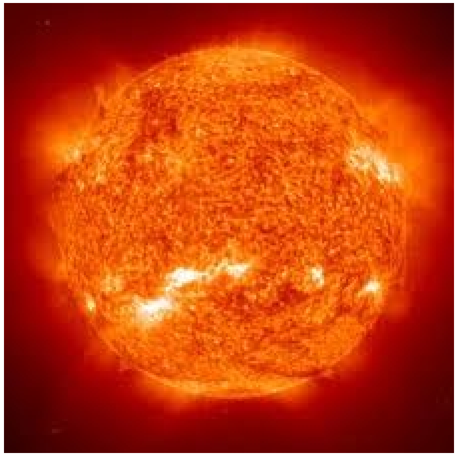
- The study of the synthesis of molecules in space and their role in determining properties of Interstellar Medium.



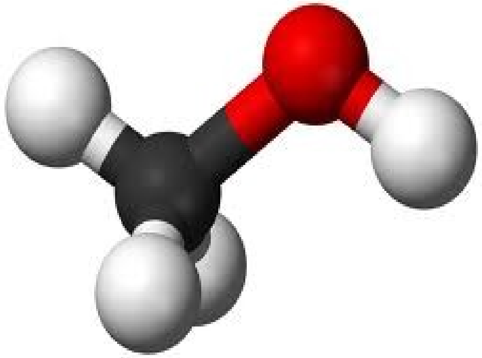
Top row – optical images of B68

Bottom row – IR images of B68
(Dust extinction is less efficient at longer wavelengths)

Interstellar medium (ISM)

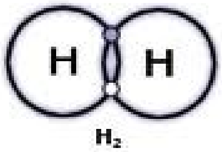


- 20 – 30 % of our Galaxy
- $T = 10 – 10^4$ K (Sun temperature - 5778 K)
- $\rho = 100 – 10^8$ H atoms cm^{-3}
- H is most abundant; He ~ 10%; C,N,O ~ 0.1%
- 1% of ISM mass is in grains
- Organic and inorganic molecules
- Complex chemistry



Dark clouds

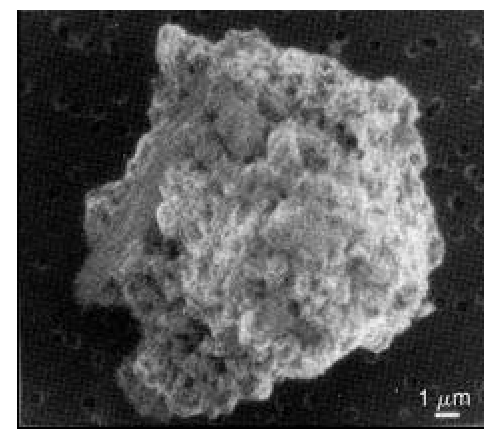
- T ~ 10 K
- $\rho = 10^{10-12}$ H atoms m^{-3}
- Cold gas chemistry+ grain chemistry
- Not penetrated by optical and UV photons
- Little ionisation
- Interesting because material is mostly molecular, dominant species is H_2 .

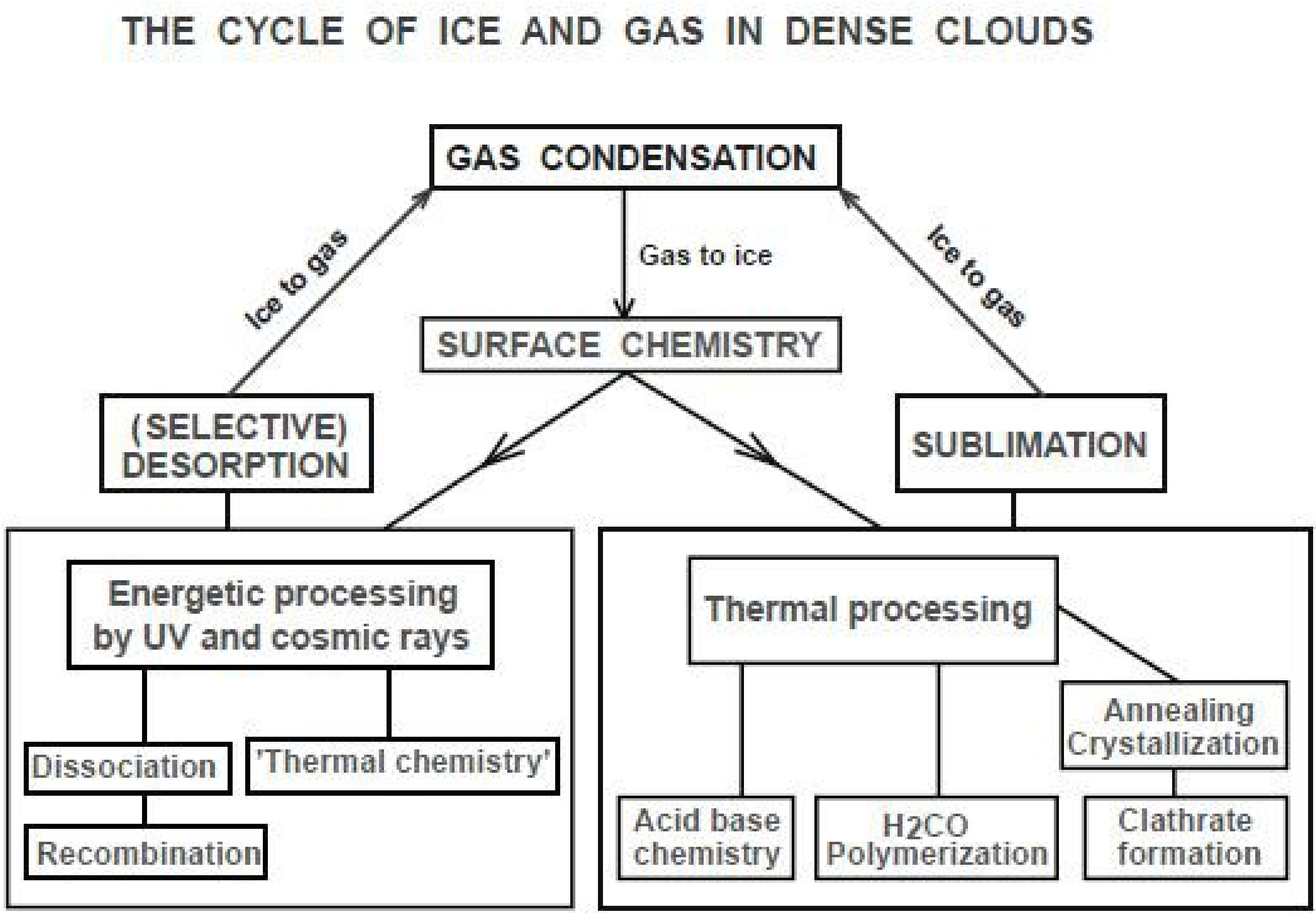


- Over 60 detected molecules; radio astronomy

Dark clouds

- Cold gas and grain chemistry
- CO, N_2, O_2, C_2H_2, HCN, simple carbon chains
- Grain chemistry – H_2, CO_2, CH_3OH
- Largest detected molecule $HC_{11}N$
- 1-500 solar masses
- 1-5 pc (distance to Proxima Centauri - 1.3 pc)
- Can form one or a couple of low-mass stars




THE CYCLE OF ICE AND GAS IN DENSE CLOUDS
GAS CONDENSATION
Ice to gas
Gas to ice
Ice to gas
SURFACE CHEMISTRY
(SELECTIVE) DESORPTION
SUBLIMATION
Energetic processing by UV and cosmic rays
Dissociation
'Thermal chemistry'
Recombination
Thermal processing
Annealing Crystallization
Acid base chemistry
H2CO Polymerization
Clathrate formation

Chemical Kinetics

(**first order** - rate of formation and
loss proportional to the concentration of one reactant)

$$A + h\nu \rightarrow C + D \qquad \beta \ \text{(units } s^{-1}\text{)}$$

- Loss of A per unit volume per unit second is:

$$dn(A)/dt = -\beta n(A) \quad m^{-3}\ s^{-1}$$

where β is photodissotiation rate of A

Chemical Kinetics

(**second order** - rate of formation and loss proportional to the concentration of two reactants)

$$A + B \rightarrow C + D \qquad\qquad k = \langle \sigma v \rangle \quad m^3\ s^{-1}$$

- Loss of A and B per unit volume per unit second is:

$$dn(A)/dt = -\ kn(A)n(B) \qquad m^{-3}\ s^{-1}$$

where $n(A)$ is number of molecules of A per unit volume k and is rate constant

- Formation of C (and D) per unit volume per unit second is:

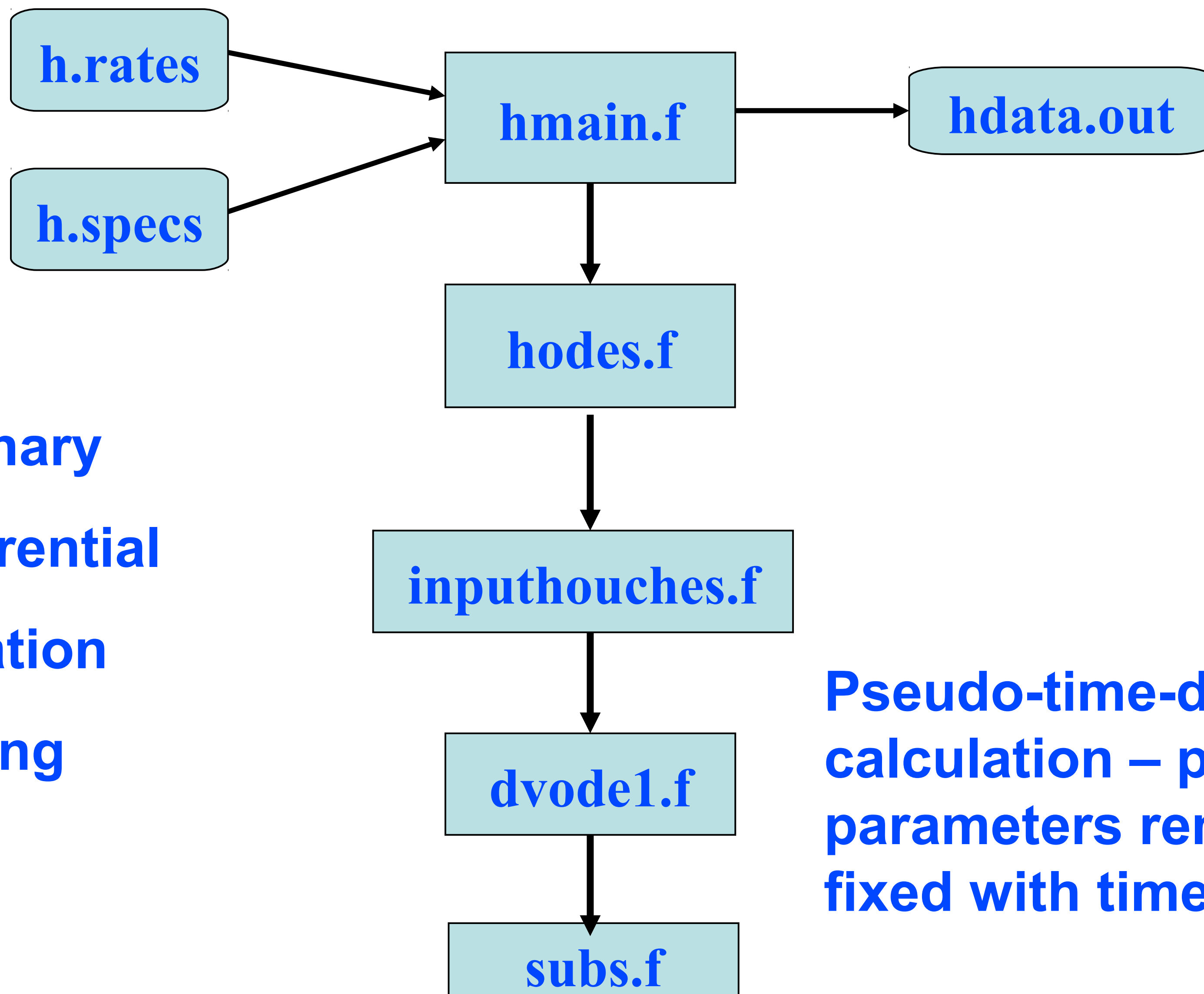
$$dn(C)/dt = +\ kn(A)n(B) \qquad m^{-3}\ s^{-1}$$

Kinetic Calculation

Millar *et. al.* 1991.
Astron. Astrophys. Suppl. Ser. 87

Rate file

Species file



Ordinary Differential Equation solving

Pseudo-time-dependent calculation – physical parameters remain fixed with time

69 species

1	H+	0.00e+00	1.0
2	H	0.00e+00	1.0
3	H2+	0.00e+00	2.0
4	H3+	0.00e+00	3.0
5	He+	0.00e+00	4.0
6	C+	0.00e+00	12.0
7	C	0.00e+00	12.0
8	CH	0.00e+00	13.0
9	CH+	0.00e+00	13.0
10	CH2	0.00e+00	14.0
11	CH2+	0.00e+00	14.0
12	N	0.00e+00	14.0
13	N+	0.00e+00	14.0
14	NH	0.00e+00	15.0
15	CH3	0.00e+00	15.0
16	CH3+	0.00e+00	15.0
17	NH+	0.00e+00	15.0
18	CH4+	0.00e+00	16.0
19	NH2+	0.00e+00	16.0
20	NH2	0.00e+00	16.0
21	O+	0.00e+00	16.0
22	CH4	0.00e+00	16.0
23	O	0.00e+00	16.0
24	OH+	0.00e+00	17.0
25	NH3+	0.00e+00	17.0
26	NH3	0.00e+00	17.0
27	OH	0.00e+00	17.0
28	CH5+	0.00e+00	17.0
29	NH4+	0.00e+00	18.0
30	H2O	0.00e+00	18.0
31	H2O+	0.00e+00	18.0
32	H3O+	0.00e+00	19.0

1199 reactions

1	H	CH	C	H2	1.31E-10	0.00	80.0
2	H	CH2	CH	H2	6.64E-11	0.00	0.0
3	H	NH	N	H2	1.73E-11	0.50	2400.0
4	H	CH3	CH2	H2	1.00E-10	0.00	7600.0
5	H	NH2	NH	H2	5.25E-12	0.79	2200.0
6	H	NH2	NH	H2	1.05E-10	0.00	4450.0
7	H	CH4	CH3	H2	5.94E-13	3.00	4045.0
8	H	OH	O	H2	6.99E-14	2.80	1950.0
9	H	NH3	NH2	H2	7.80E-13	2.40	4990.0
10	H	H2O	OH	H2	1.59E-11	1.20	9610.0
11	H	C2	CH	C	4.67E-10	0.50	30450.0
12	H	C2H2	C2H	H2	3.80E-10	0.00	13634.0
13	H	HCN	CN	H2	6.20E-10	0.00	12500.0
14	H	C2H3	C2H2	H2	3.32E-11	0.00	0.0
15	H	CO	OH	C	1.10E-10	0.50	77700.0
16	H	HCO	O	CH2	6.61E-11	0.00	51598.0
17	H	HCO	CO	H2	2.00E-10	0.00	0.0
18	H	NO	O	NH	9.29E-10	-0.10	35220.0
19	H	NO	OH	N	3.60E-10	0.00	24910.0
20	H	H2CO	HCO	H2	4.85E-12	1.90	1379.0
21	H	HNO	OH	NH	2.40E-09	-0.50	9010.0
22	H	HNO	NH2	O	1.05E-09	-0.30	14730.0
23	H	HNO	NO	H2	4.50E-11	0.72	329.0
24	H	O2	OH	O	2.61E-10	0.00	8156.0
25	H2	C	CH	H	6.64E-10	0.00	11700.0
26	H2	CH	CH2	H	5.46E-10	0.00	1943.0
27	H2	N	NH	H	1.69E-09	0.00	18095.0
28	H2	CH2	CH3	H	5.18E-11	0.17	6400.0
29	H2	NH	NH2	H	5.96E-11	0.00	7782.0

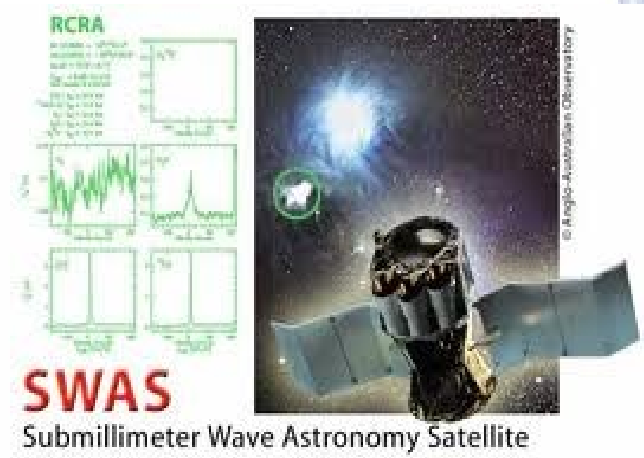
- Initial abundances: e, H_2, He, N, C, O, Mg
- Temperature, density, cosmic-rays...
- Gas-phase and grain surface chemistry
- Change some parameters to mach the observed abundances.
- SWAS satellite
  - $H_2O \approx \; 6 \times 10^{-10}$ - 1×10^{-8}

    sensitive to C and O abundances

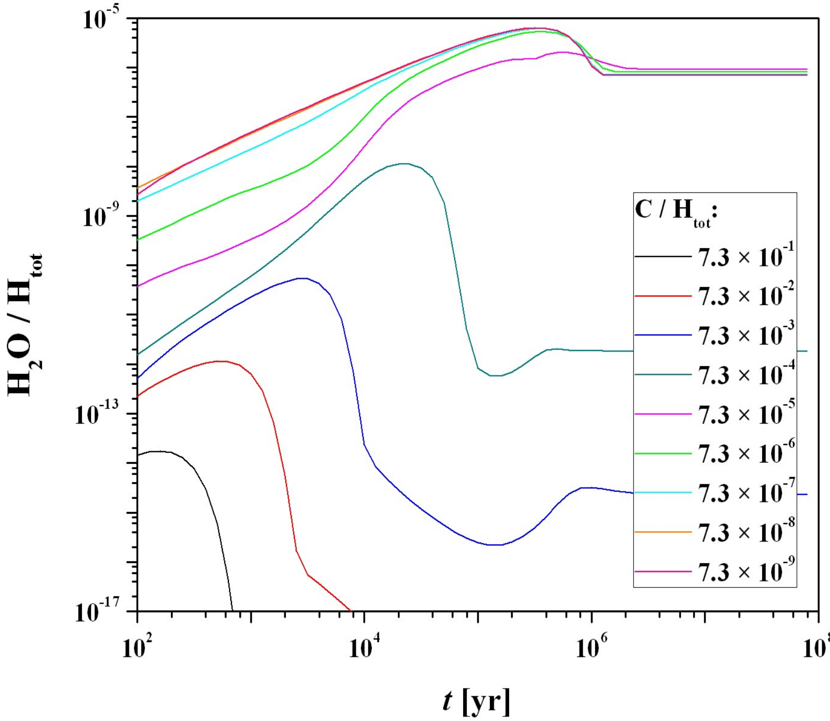
    the best match for $C \approx 10^{-5}$-10^{-4} , $O \approx 10^{-5}$
  - $O_2 \quad \lesssim \; 10^{-7}$

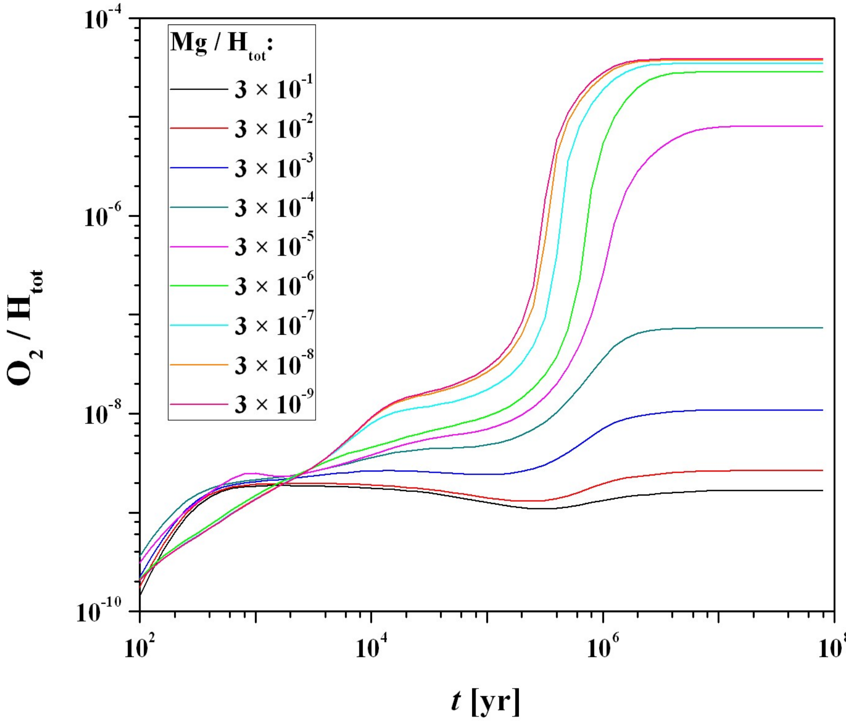
    sensitive to C, O, N and Mg abundances

    the best match for $C \approx 10^{-5}$-10^{-4} , $O \approx 10^{-5}$-10^{-4}, $Mg \approx 10^{-4}$, $N \approx 10^{-2}$

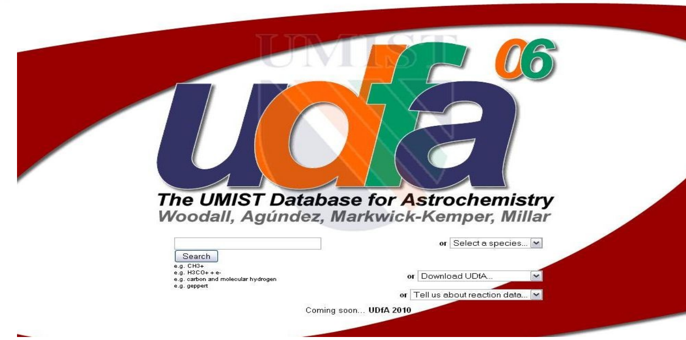


Initial abundances variation - example





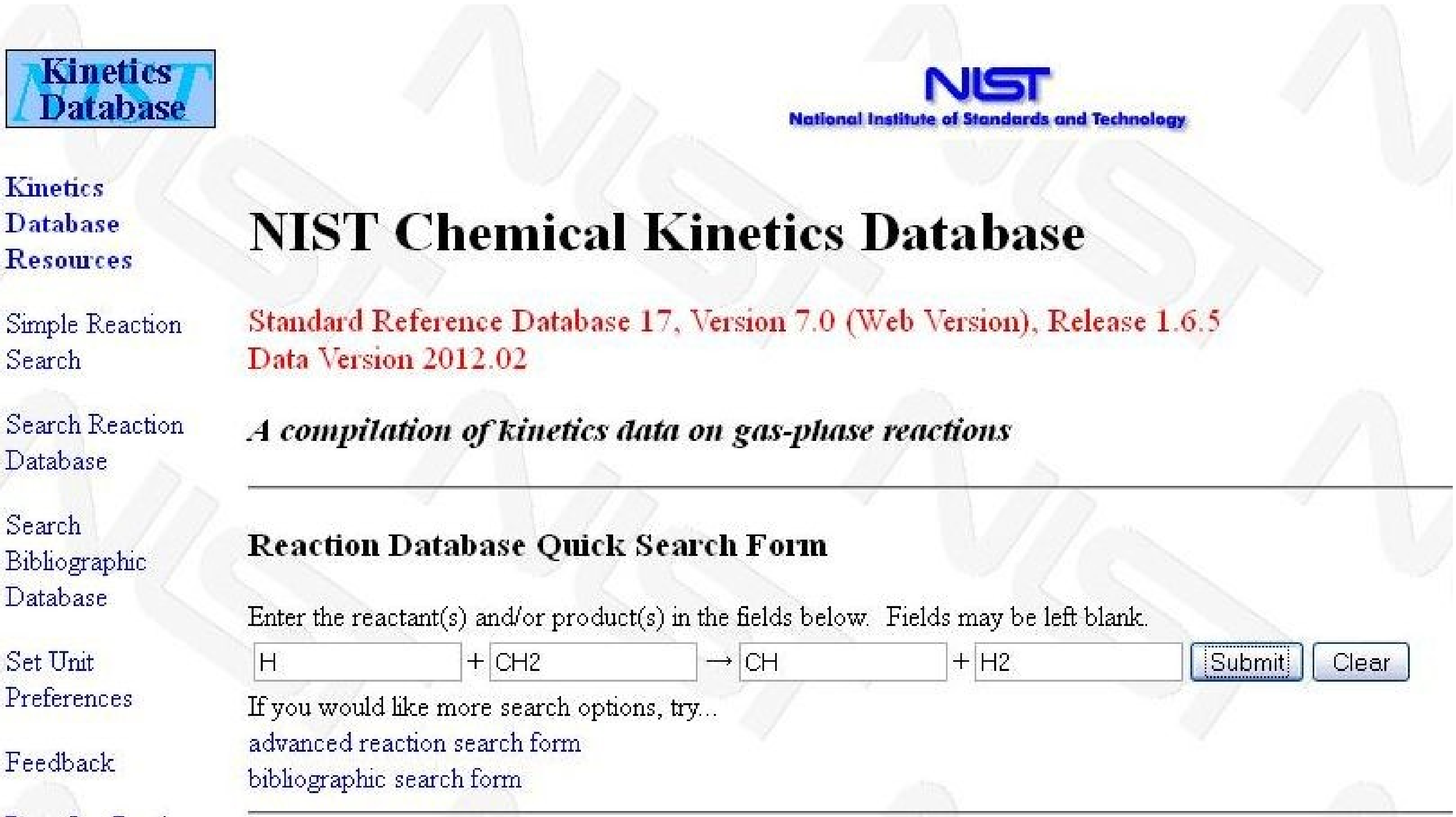
Reaction rates



- Measured in laboratory or derived from theory
- On-line databases: UMIST database for Astrochemistry, Ohio State University (OSU), JPL Anicich Database, Huebner Photo-Cross-section Database...
- NIST Chemical Kinetics Database (VAMDC external partner)

27 000 reactions, rates from experiments and theory, generates best fit

NIST



Kinetics Database

NIST
National Institute of Standards and Technology

Kinetics Database Resources

Simple Reaction Search

Search Reaction Database

Search Bibliographic Database

Set Unit Preferences

Feedback

NIST Chemical Kinetics Database

Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.5
Data Version 2012.02

A compilation of kinetics data on gas-phase reactions

Reaction Database Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

H + CH2 → CH + H2 [Submit] [Clear]

If you would like more search options, try...
advanced reaction search form
bibliographic search form

NIST

Search Results

Rate expression: $k(T) = A\,(T/298\ K)^{n}\, e^{-Ea/RT}$

Rate expression units:

First order: s^{-1}

Second order: cm^3/molecule s

Third order: cm^6/molecule^2 s

R = 8.314472E-03 kJ / mole K

Energy Units	kJ	Molecular Units	Molecule
Pressure Units	Pa	Temperature Units	K
Base Volume Unit	cm	Reference Temperature	298.0
Evaluation Temperature	298.0		

NIST

Review

1992BAU/COB411-429	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 3000	1.00E-11	-7.48		2
1986TSA/HAM1087	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 2500	2.71E-10			2
1984WAR197C	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 2500	6.64E-11			2

Experiment

1997ROH/PET781-789	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	2200 - 2600	2.34E-10			2
1995DEV/VAN16953-16959	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 1000	5.18E-11	-5.61		2
1995DEV/VAN16953-16959	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 1000	0.40	-5.60		2
Reference reaction: $O\cdot + \cdot CH_2 \rightarrow$ Products					2	
1992BOU/PEE9810-9816	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	298	2.66E-10		2.66E-10	2
1992BOU/PEE9810-9816	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	298	2.00		2.00	2
Reference reaction: $O\cdot + \cdot CH_2 \rightarrow$ Products					2	

NIST

☐	1987BOH/TEM1205	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	298	1.83E-10				1.83E-10	2
☐	1986ZAB/FLE4373	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 2500	4.13E-11	1.54	-3.58			2
☐	1986ZAB/FLE4373	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	300 - 700	4.70E-10		3.08			2
☐	1986FRA/BHA2226	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	2000 - 2800	1.33E-11					2
☐	1986FRA422	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	1450 - 2500	1.33E-11					2
☐	1984BOH/TEM459	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	298	2.66E-10				2.66E-10	2
☐	1983HOM/WEL609	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	295 - 1000	9.13E-11				9.13E-11	2
☐	1982GRE/HOM581	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$	298	8.30E-11				8.30E-11	2

Theory

	1987BEC/CAN435-448	$H\cdot + \cdot CH_2 \rightarrow H_2 + \cdot CH$

NIST

Fit of Arrhenius parameters to set:

Temperature range: 295 - 3000 K

Two-parameter fit:

$$k(T) = A exp(-E_a/RT)$$

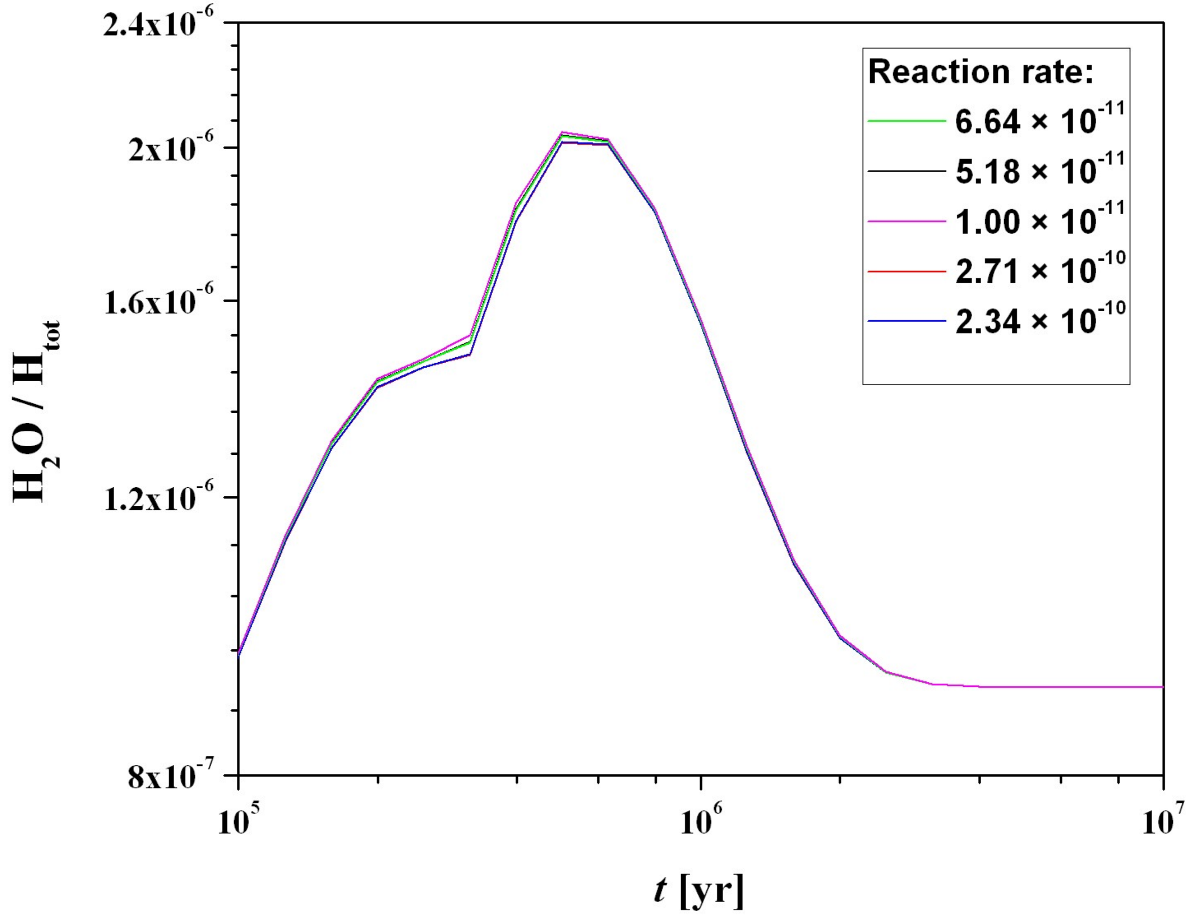
$A = 7.94\text{x}10^{-11}$ [cm^3/molecule s]
$E_a = -2.1$ [kJ]
RMSD = 1.4

Three-parameter fit:

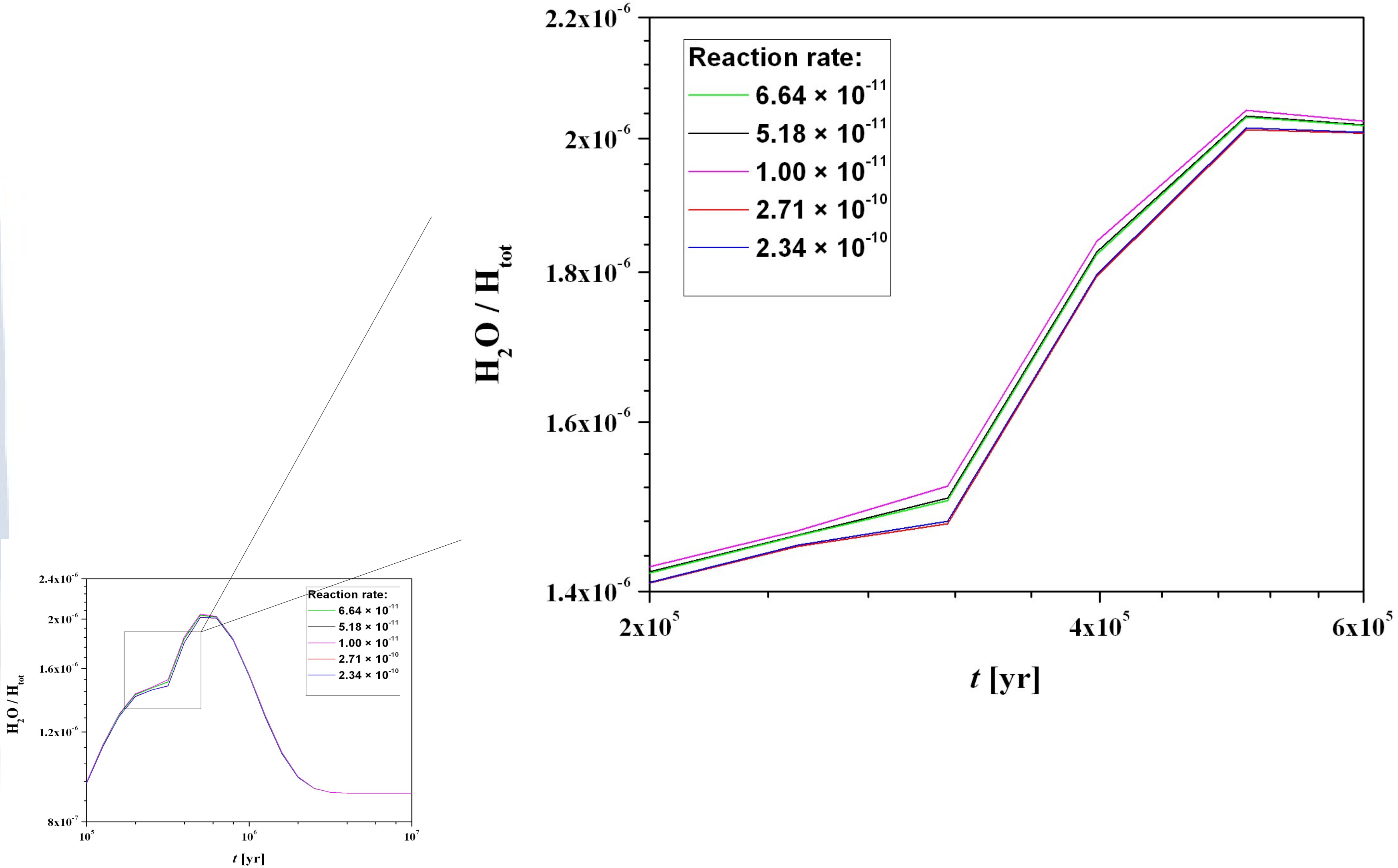
$$k(T) = A(T/T_{ref})^n exp(-E_a/RT)$$

$A = 2.26\text{x}10^{-10}$ [cm^3/molecule s]
$n = -0.6$
$T_{ref} = 298$ [K]
$E_a = 0.8$ [kJ]
RMSD = 1.3

Reaction rates - example

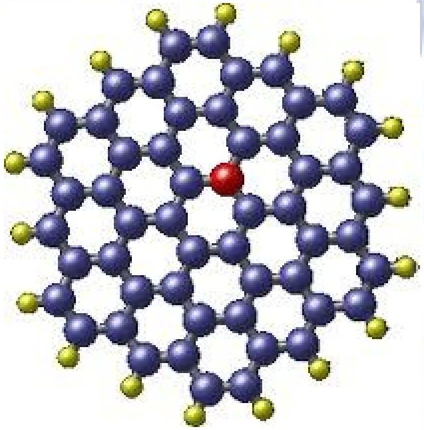


Reaction rates - example



Conclusion

- Chemical databases – very important for astrochemistry
- Modeling of chemical evolution of ISM, for example dark clouds
- Many reaction to be considered
- Data needed for calculations can be found in on-line databases
- Faster and easier search is important



Thank you for your attention!