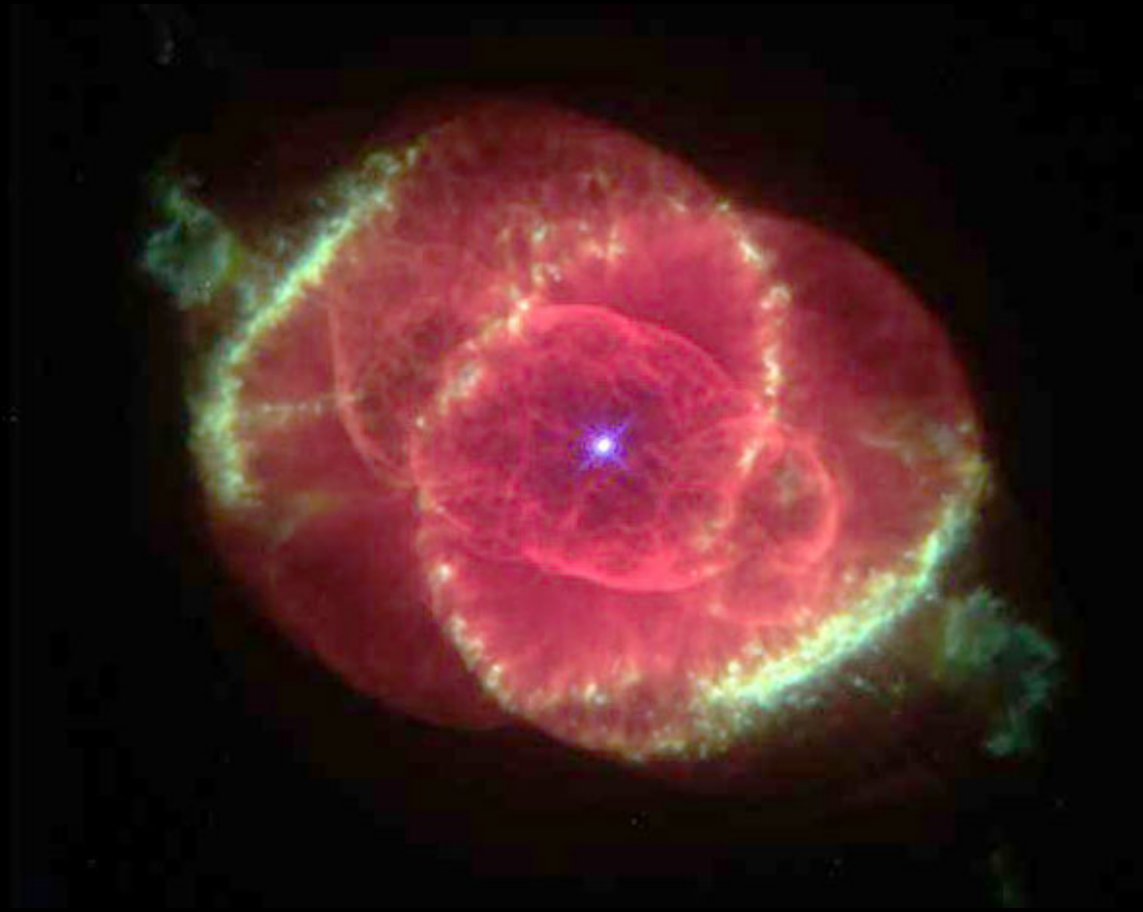
Dissociative recombination of protonated methanol



Wolf D. Geppert
ALMA Satellite Meeting
Aarhus 2006

Methanol in space

- Responsible for maser emission in star-forming regions.
- Evolution indicator in star-forming regions
- Used for determination of kinetic temperature and H_2 density simultaneously.
- From $CH_3OH_2^+/CH_3OH$ ratio electron temperature in cometary coma derived.

The Bear Claw Nebula, where a strong methanol maser was detected

Production of methanol in the ISM

Methanol production thought to happen via radiative association followed by dissociative recombination (DR):

$$CH_3^+ + H_2O \rightarrow CH_3OH_2^+$$

$$CH_3OH_2^+ + e^- \rightarrow CH_3OH + H$$

With a high rate of DR, the radiative association rate should be about 1.2×10^{-10} cm^3s^{-1} at 50 K.

(Herbst et al. 1985)

But...

Ion trap experiments yielded a an upper limit of
2×10^{-12} cm^3s^{-1} at dark cloud temperatures (Luca et al. 2002).

a factor of 60 too low !

However...

- CH_3^+ not detected so far, densities only estimates from models.
- Uncertainties in water densities.
- If the DR of $CH_3OH_2^+$ leads to methanol with a branching ratio of close to 100 %.....

Challenges for measurements of DR branching ratios

- Ample information on reaction rates (afterglow), little on branching ratios.
- Reactive ions must be clearly identified and selected.
- Low collision energies in the interstellar medium must be matched.
- All reaction products should be identified.

Theoretical prediction of DR branching ratios

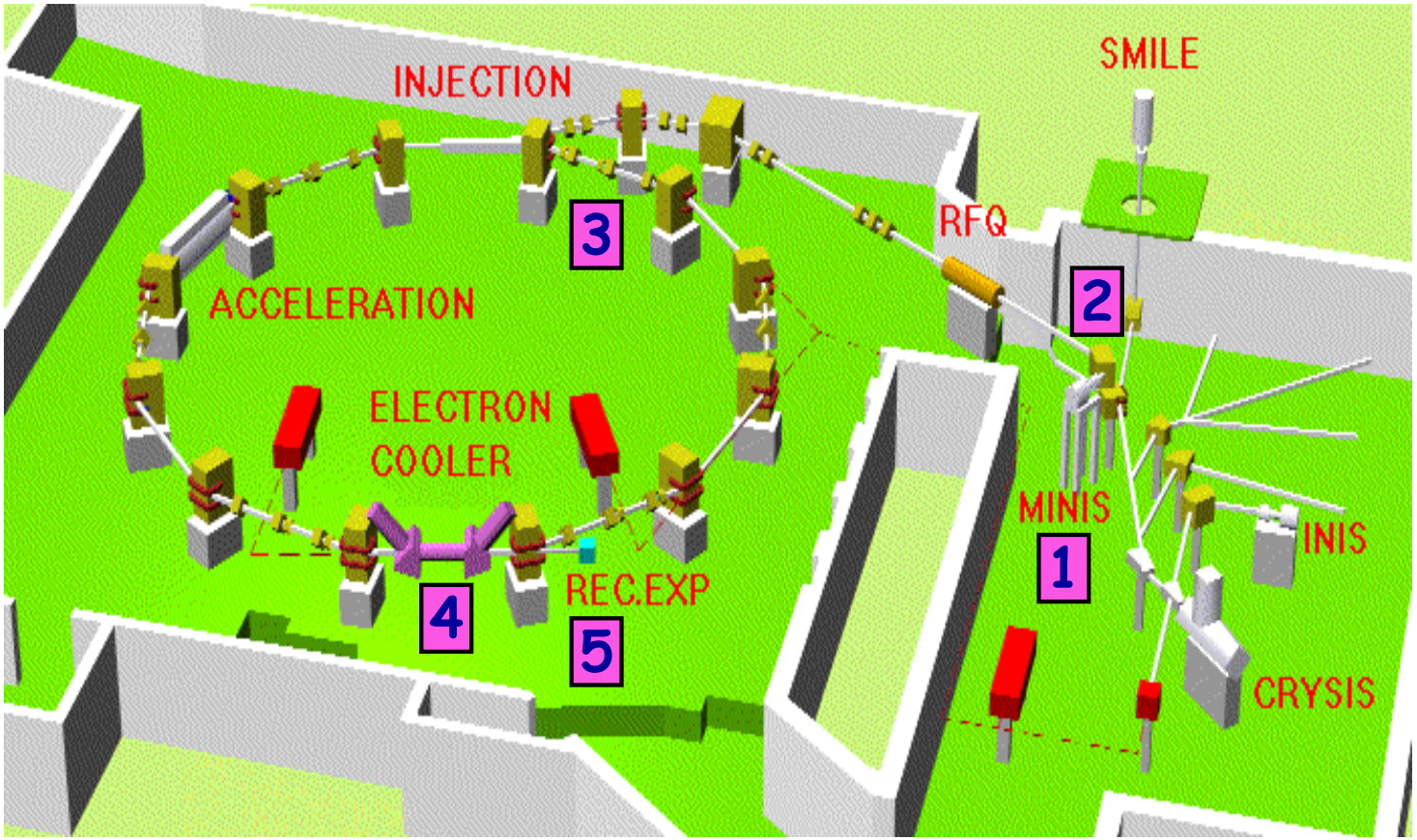
- Difficult to obtain reliable potential surfaces due to involvement of highly excited states
- Potential surfaces quite complex in larger molecules even in lower states.

⟶ very few high-level *ab initio* studies on DR reactions available

Bates's theory 1986: Dissociative recombinatons favour the pathway(s) which involve(s) least orbital rearrangement, e. g.:

$$CH_3OH_2^+ + e^- \longrightarrow CH_3OH + H$$

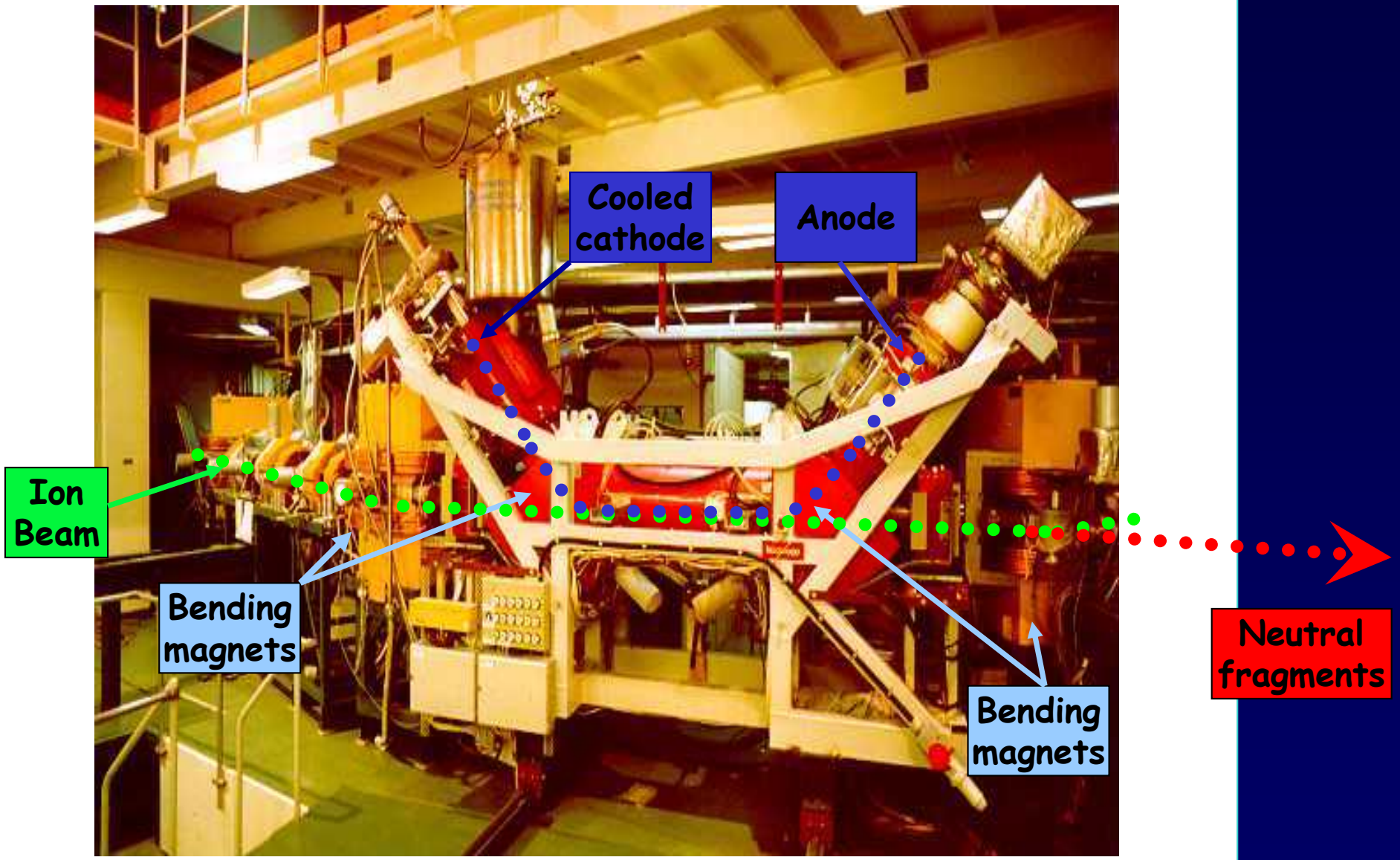
The CRYRING storage ring



Schematic view of CRYRING

Steps during the experiment

1. Formation of the ions in the source
2. Mass selection by bending magnet
3. Injection via RFQ and acceleration
4. Merging with electron beam
5. Detection of the neutral products



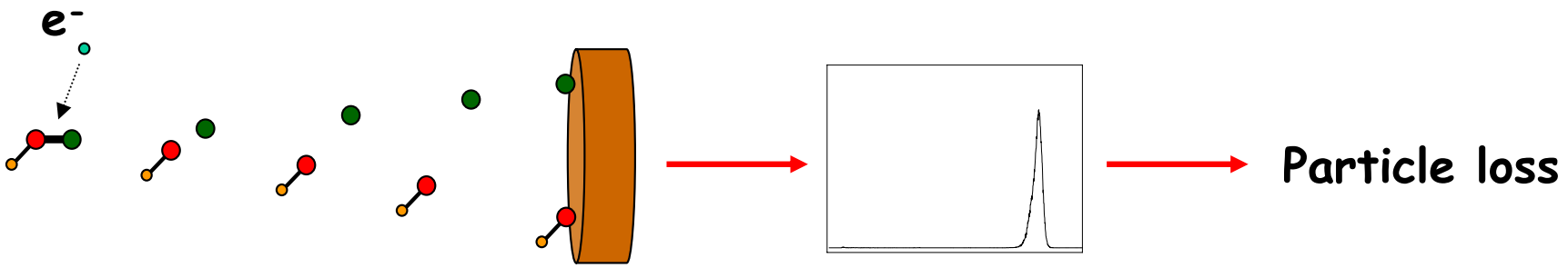
Electron cooler

Advantages of storage rings

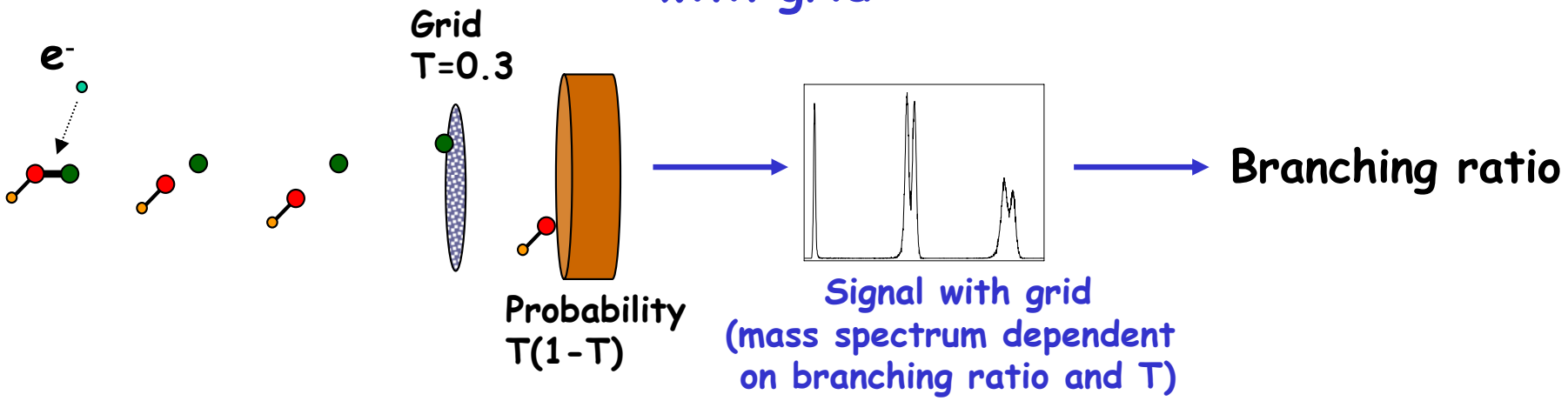
- Mass selection of probe ions.
- Measurements at interstellar collision energies possible.
- Detection of all products and product channels.
- Stepless variation of relative kinetic energy.

Grid technique

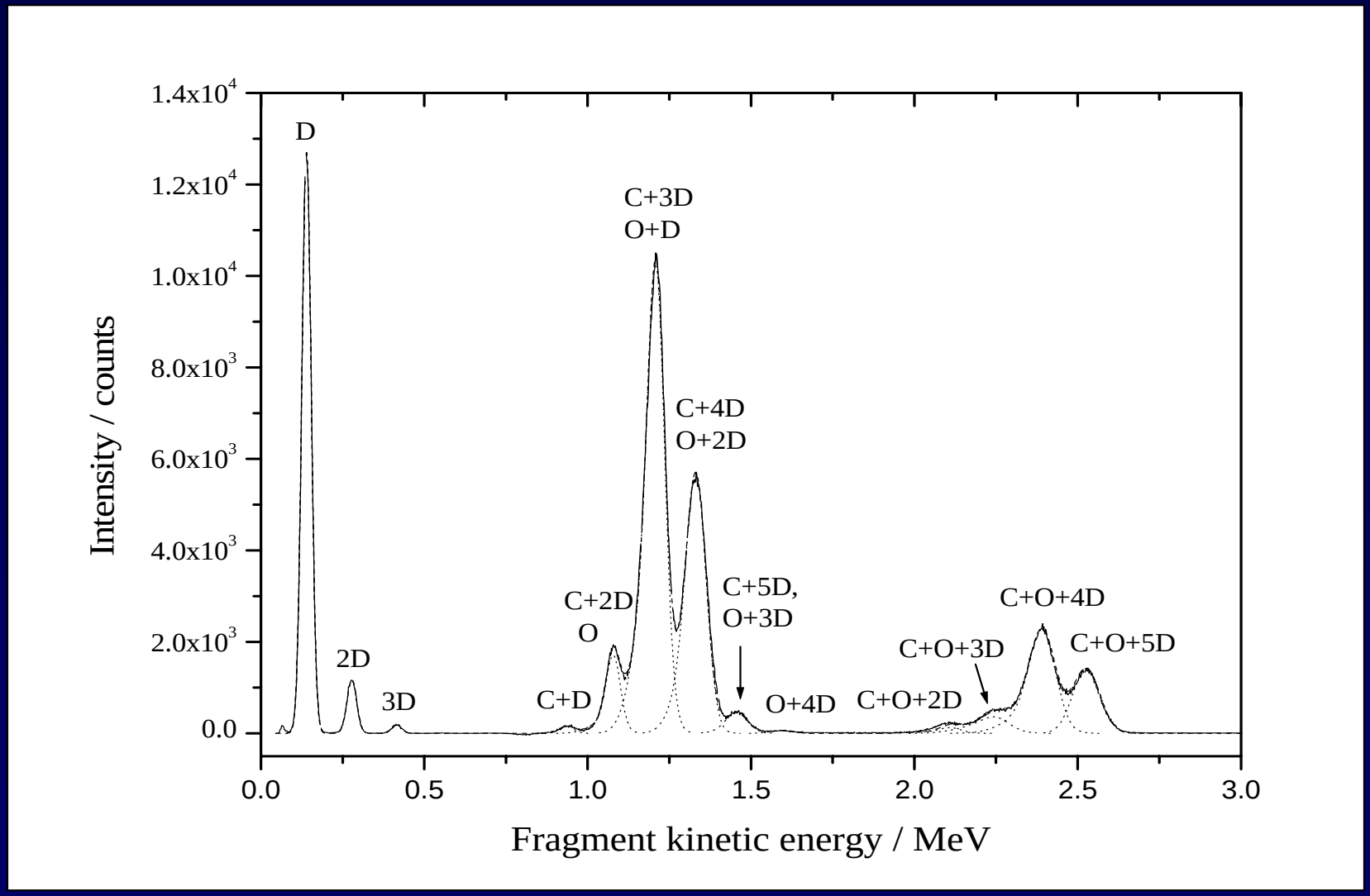
without grid



with grid



Fragment energy spectrum of $CD_3OD_2^+$



Deuterium isotopomere used for better mass resolution

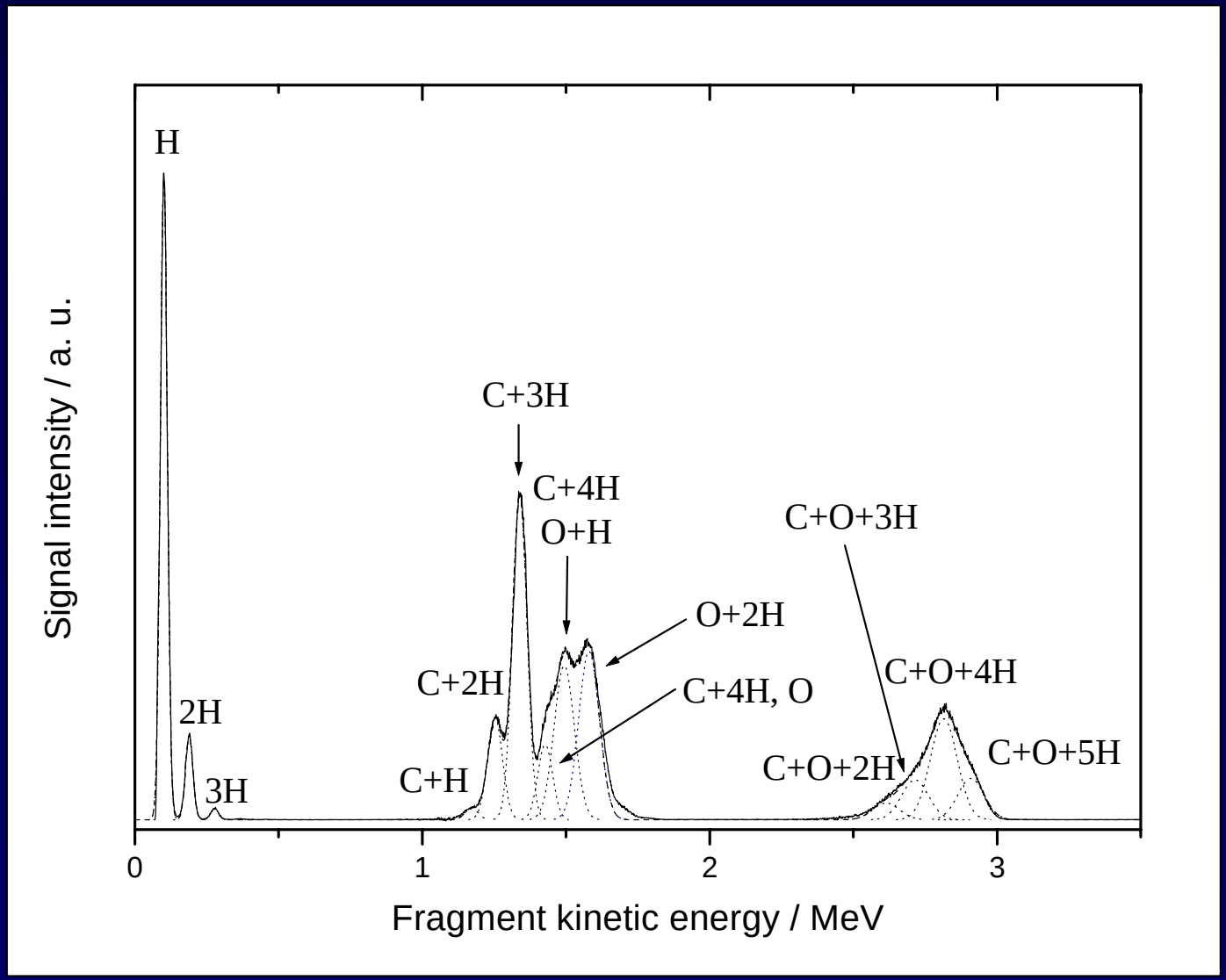
Exoergic reaction channels of the DR of $CD_3OD_2^+$

$CD_3OD_2^+ + e^-$	→	$CD_3OD + D$
	→	$CD_3 + OD + D$
	→	$CD_2 + D_2O + D$
	→	$CD + D_2O + D_2$
	→	$CD_3O + 2D$
	→	$CD_3O + D_2$
	→	$CD_2O + D_2 + D$
	→	$CD_2O + 3D$

$CD_3OD_2^+ + e^-$	→	$CD_4 + O + D$
	→	$CD_4 + OD$
	→	$CD_2 + OD + D_2$
	→	$CD_3 + D_2 + O$
	→	$CD_3 + D_2O$
	→	$CDO + 2D_2$
	→	$CDO + D_2 + 2D$
	→	$CO + 2D_2 + D$
	→	$CO + D_2 + 3D$

Some of the channels deliver products with the same mass
→ indistinguishable.

Fragment energy spectrum of $CH_3OH_2^+$



Branching ratios of the DR of $CD_3OD_2^+$ and $CH_3OH_2^+$

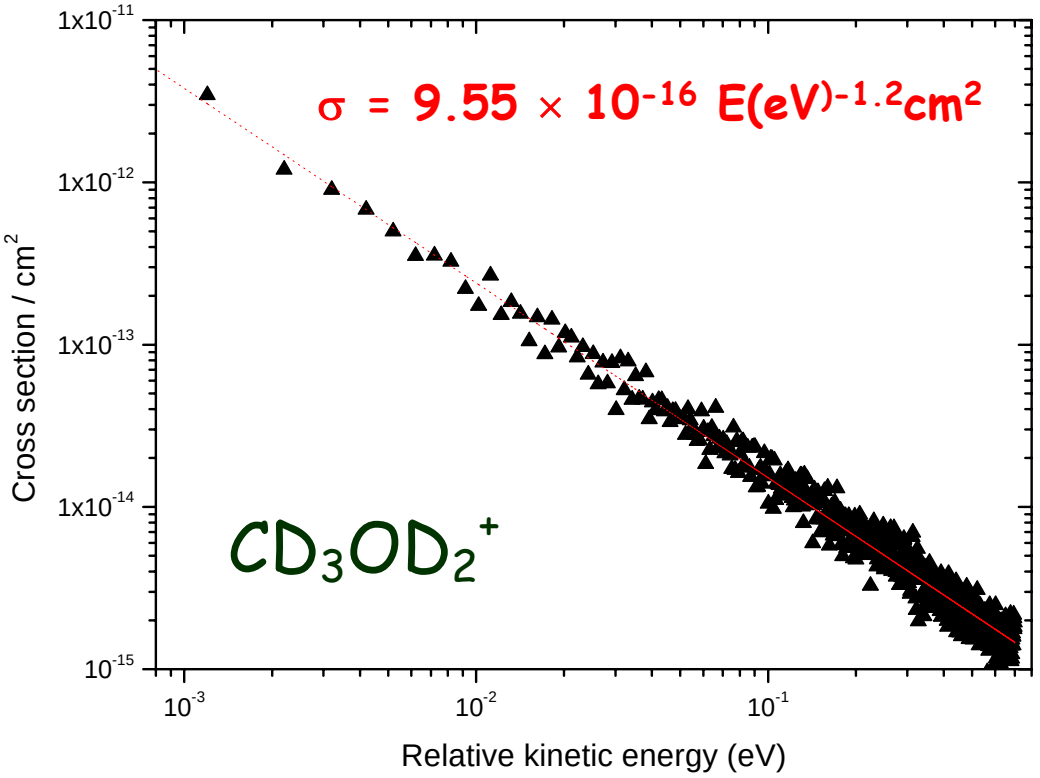
Reaction pathway	Branching ratio
$CD_3OD + D$	0.06
$CD_3 + D_2O$ ($CD_4 + OD$)	0.11
$CD_3O + D_2$	0.05
$CD_3 + OD + D$	0.59
$CD_2 + D_2O + D$ ($CD_4 + O + D$)	0.16
$CD + D_2O + D_2$	0.01
$CD_3O + 2D$	0.00
$CD_2O + D_2 + D$	0.02
$CD_2O + 3D$	0.00

Reaction pathway	Branching ratio
$CH_3OH + H$	0.03
$CH_3 + H_2O$	0.09
$CH_4 + OH$	0.00
$CH_3O + H_2$	0.07
$CH_3 + OH + H$	0.51
$CH_2 + H_2O + H$	0.21
$CH_4 + O + H$	0.00
$CH + H_2O + H_2$	0.00
$CH_3O + 2H$	0.00
$CH_2O + H_2 + H$	0.09
$CH_2O + 3H$	0.00

Distribution of 2-, 3- and 4-body processes

Processes	Sum of branching ratios ($CD_3OD_2^+$)	Sum of branching ratios ($CH_3OH_2^+$)
2-body	0.22	0.19
3-body	0.78	0.81
4-body	0.00	0.00

Cross sections of the DR processes



Cross-section vs. collision energy

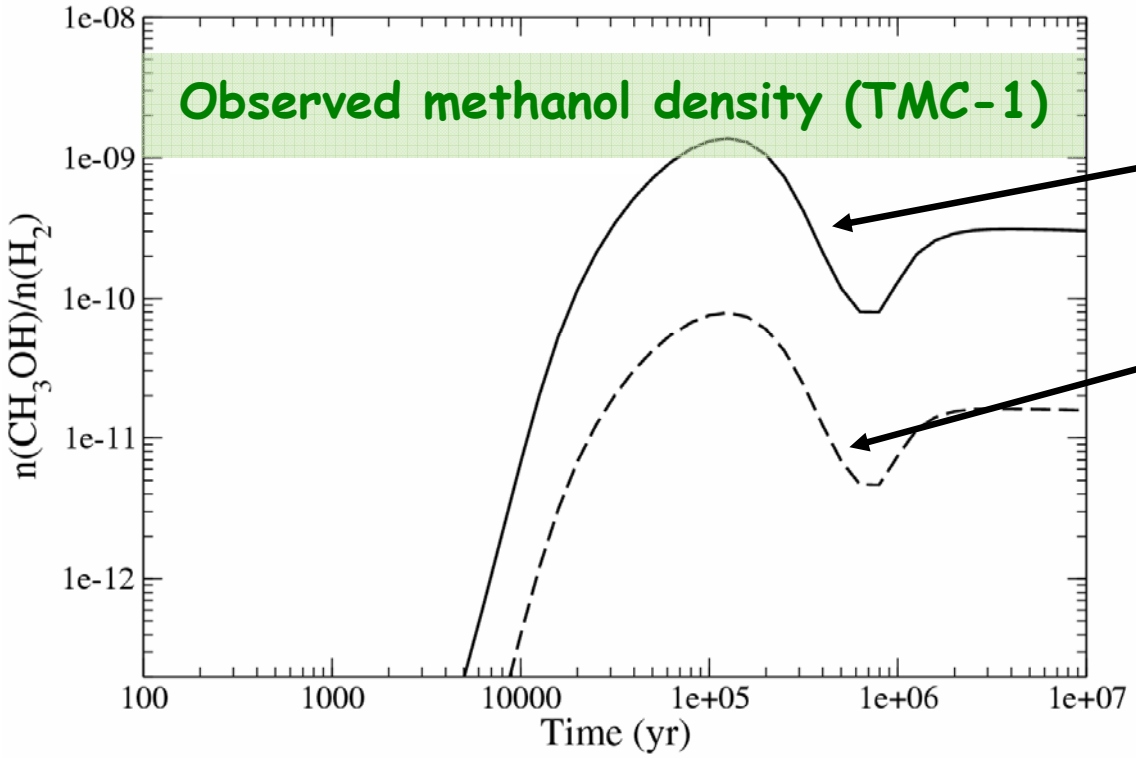
From the cross-section one is able to work out the thermal reaction rate ($CD_3OD_2^+$):

$$k = 9.11 \times 10^{-7} (T/300)^{-0.63} \ cm^3 s^{-1}$$

For the undeuterated isotopomer ($CH_3OH_2^+$):

$$k = 8.91 \times 10^{-7} (T/300)^{-0.59} \ cm^3 s^{-1}$$

Model calculations



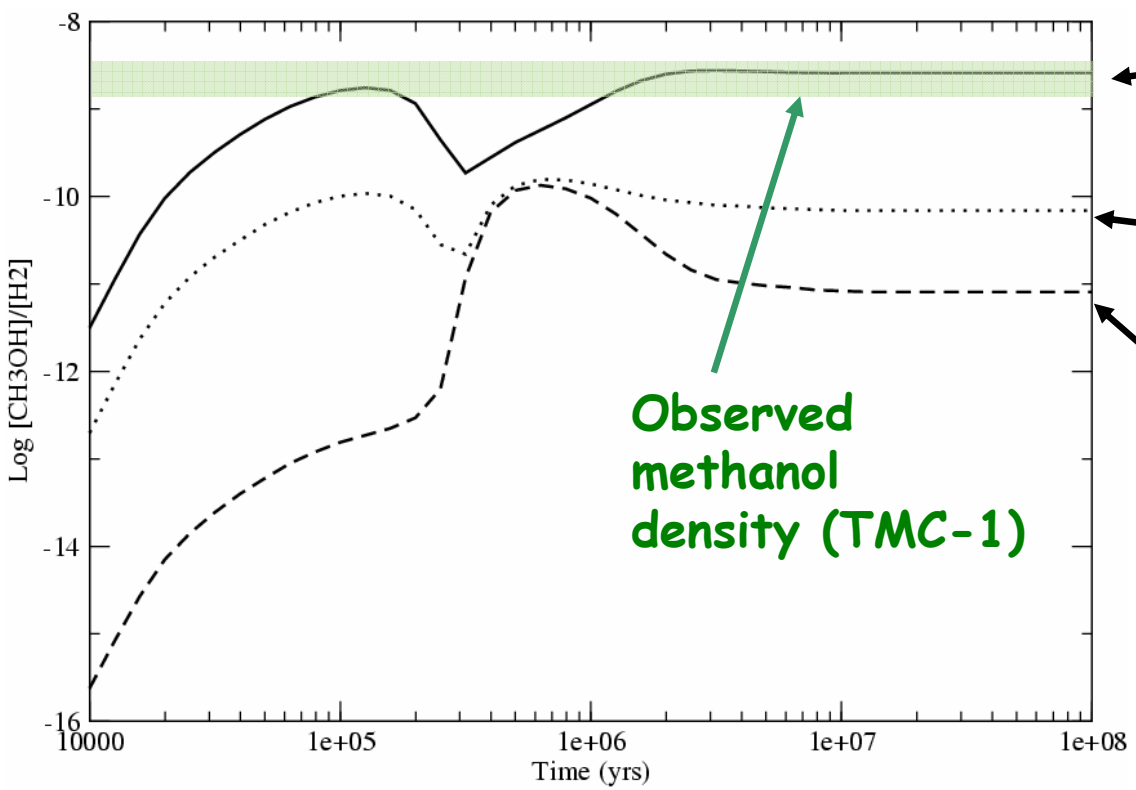
CH_3OH + H
branching ratio = 1

CH_3OH + H
branching ratio = 0.06

UMIST (Rate99) model predictions for methanol density in TMC-1

If one includes the new rates for the radiative association of CH_3^+ and H_2O, (Luca et al. 2002) the peak methanol relative abundance sinks to 7×10^{-13}.

New UMIST model



CH_3OH + H branching ratio = 1

CH_3OH + H branching ratio = 0.06

+ new rate for $CH_3^+ + H_2O$

UMIST (Rate04) model predictions for methanol density in TMC-1

Main gas phase route to CH_3OH is now $CH_3CHO + H_3^+ \rightarrow CH_3OH + CH_3^+$

$k = 1.4 \times 10^{-9} cm^3 s^{-1}$ at 300K

Conclusions

- Three-body break-ups dominate.
- Production of CH_3OH only 3 % (CD_3OD only 6 %).
- No big isotope effects
- Gas-phase mechanism for interstellar methanol very unlikely.

In line with the following facts:

- Formation of methanol on CO ice surfaces possible at 10 K. (Watanabe et al. 2004)
- Correlations between CO and methanol have been found to be strong in hot core regions (Bisschop et al. 2005)

- Models including grain surface desorption reproduce methanol densities
(Herbst 2006)

Can we close the books ?

- Anticorrelation of CO and CH_3OH in dense clouds.
(Buckle, 2006)

- No experimental evidence for surface desorption of freshly formed methanol

DR of $(CD_3)_2OD^+$

- Similar mechanism to methanol postulated for dimethyl ether.

$$CH_3^+ + CH_3OH \rightarrow (CH_3)_2OH^+$$
$$CH_3OH^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O$$

$$(CH_3)_2OH^+ + e^- \rightarrow CH_3OH + H$$

- Similar problems ?

YES !

Production of $(CD_3)_2O$ only 6 %) !

AND:

Grain surface process for formation of dimethyl ether unlikely (Ehrenfreund and co-workers, 2006)

Graduate school Astrobiology at Stockholm University

Physics
2 Ph.D
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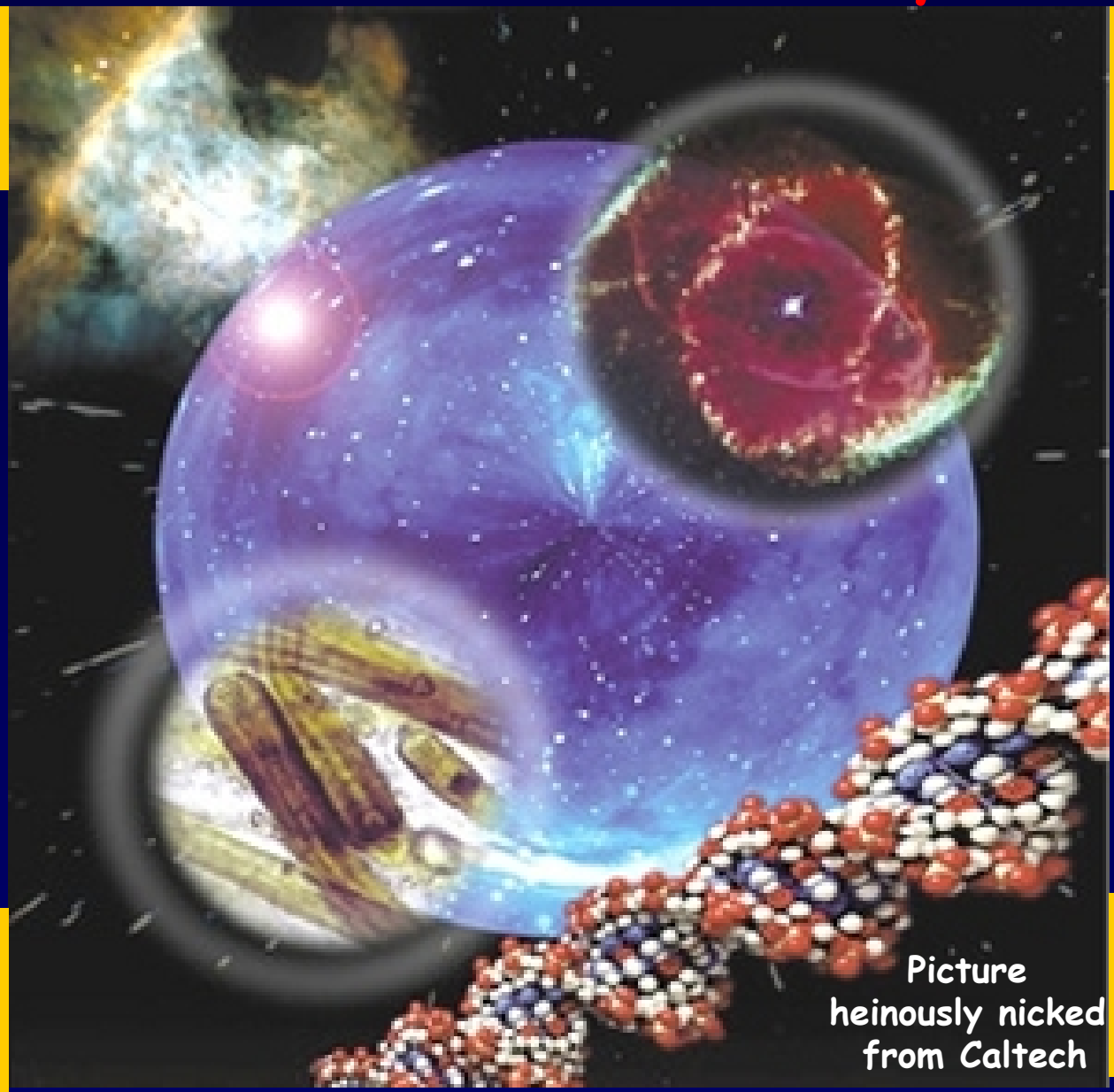

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