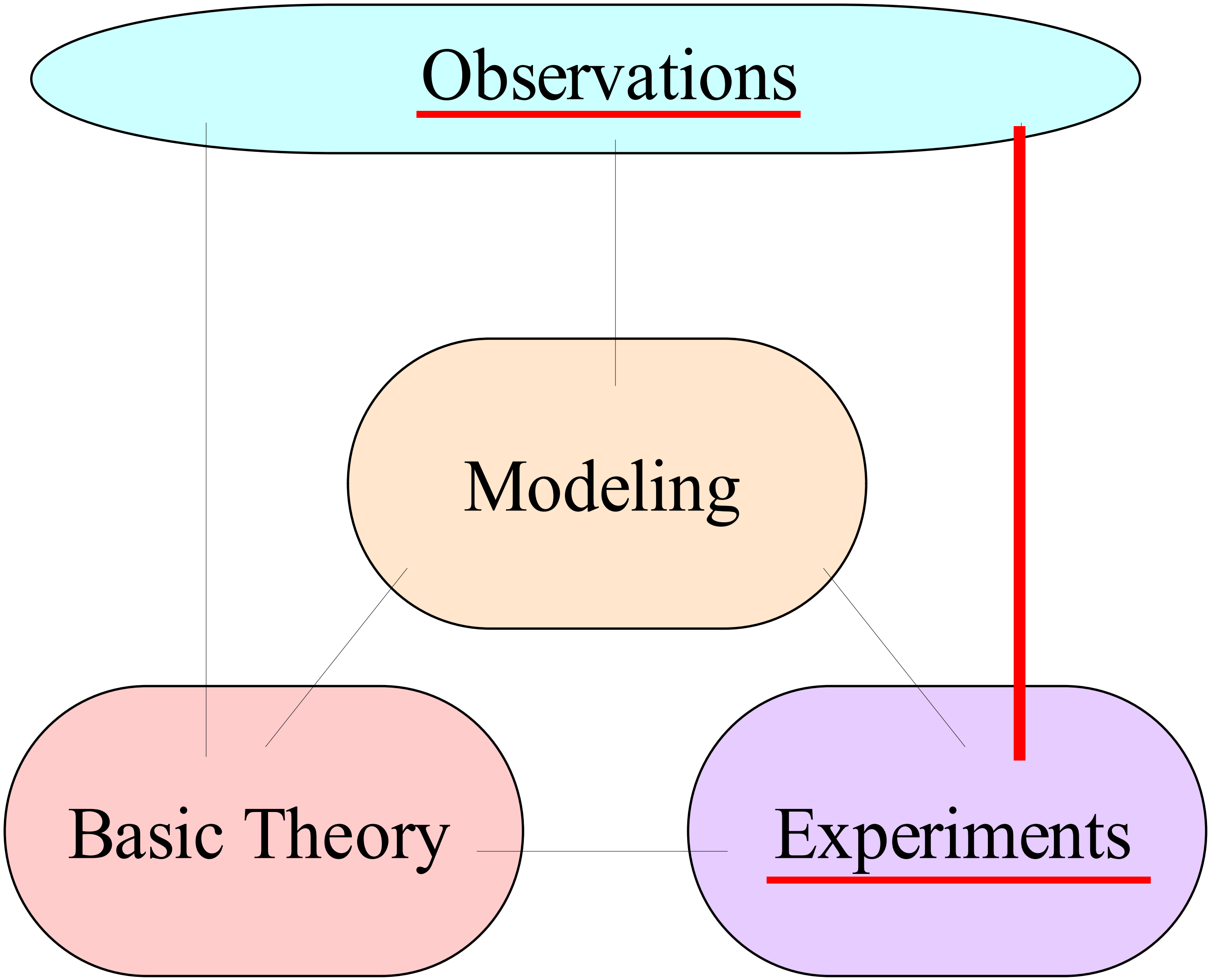
Forschergruppe Laboratory Astrophysics



Interstellar Molecules

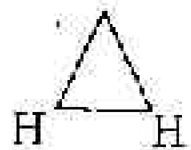
H_2
CH
CH^+
CN
CO
CS
OH
SiO
NS
SO
SiS
SiC

NO
CC
HCl
SO^+
PN
NaCl
AlCl
KCl
AlF
CP
NH
AlCl

H_2O
H_2S
HCN
HNC
HCO^+
HCO
CCH
HN_2^+
HNO

OCS
SO_2
SiC_2
HCS^+
CCS
CCC
CCO
H_3O^+
CCCS
HCCN

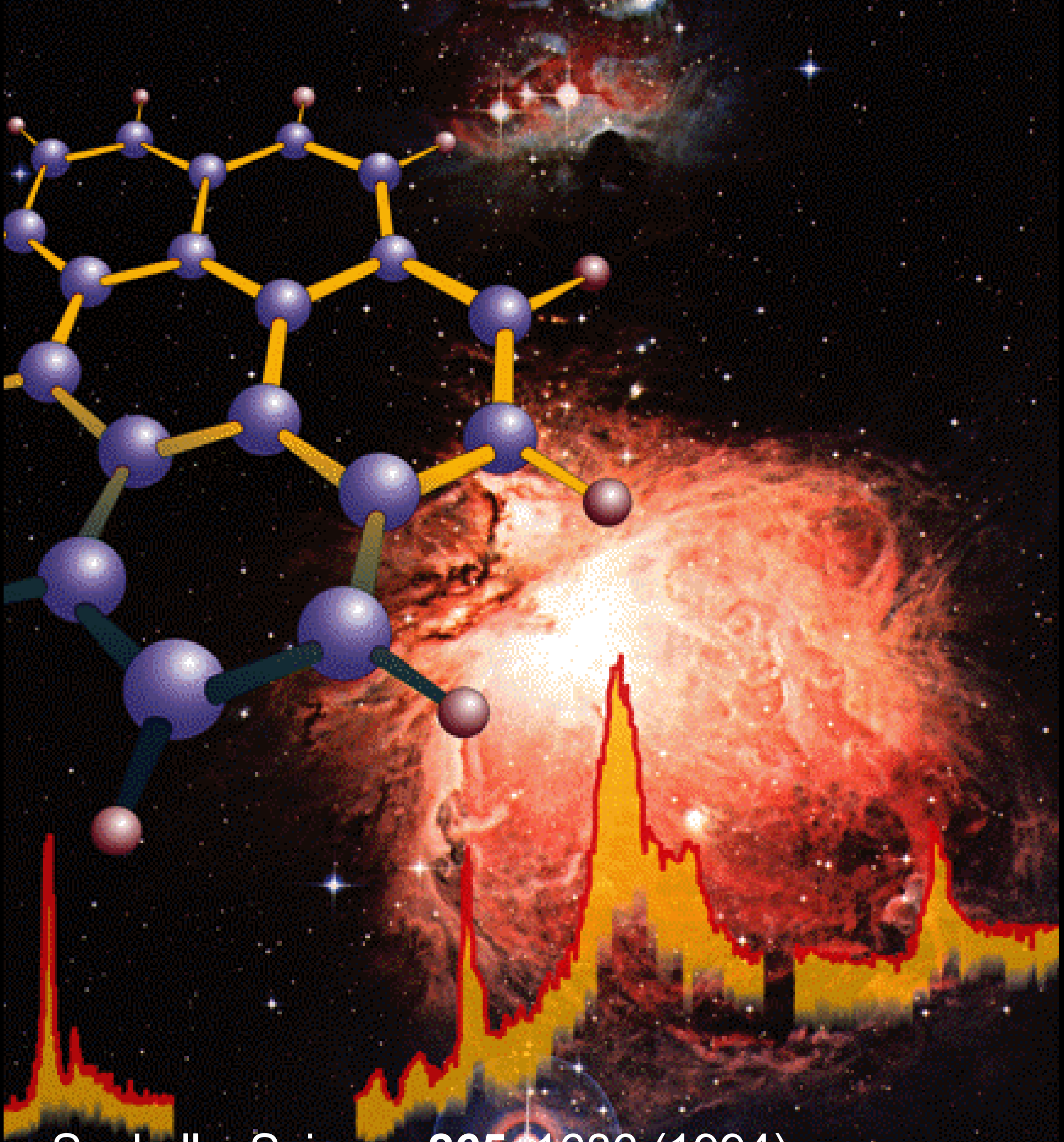
NH_3
H_2CO
H_2CS
HNCO
HNCS
CCCN
CCCH
CCCO
$HOCO^+$
$HCNH^+$
C_2H_2
c-CCCH

H_2CNH
H_2NCN
HCOOH
HCCCN
C_4H
CH_4
SiH_4
CH_2CO


CH_2CN
HCCNC
HNCCC

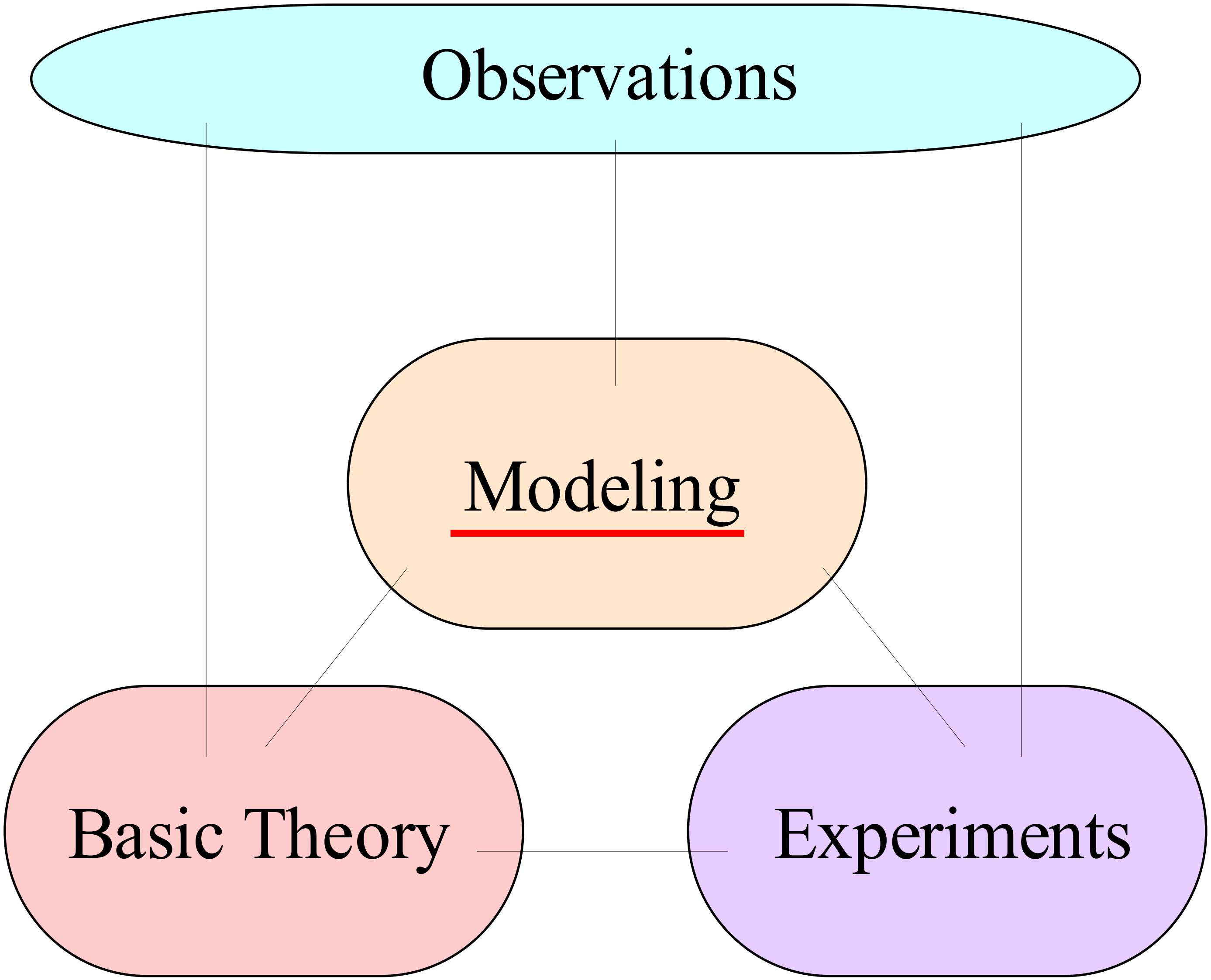
CH_3OH
CH_3SH
CH_3CN
C_2H_4
$HCONH_2$
C_5H
CH_3NC
HC_2CHO
H_2CCC
C_5
C_4Si

CH_3NH_2
CH_3CCH
CH_3CHO
C_2H_3CN
HC_5N
C_6H
H_2CCCC

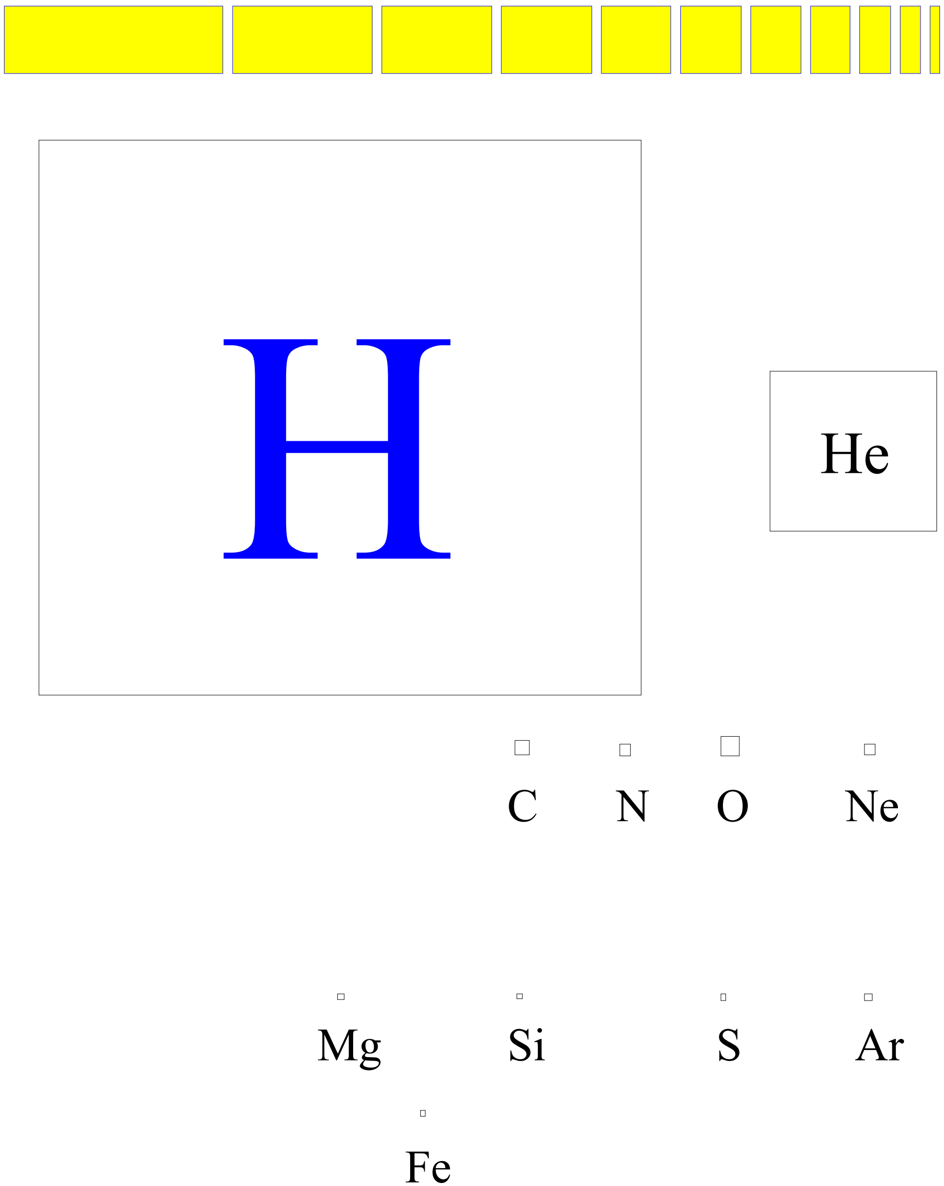


Schlemmer, Cook , Saykally, Science **265**, 1686 (1994)
Cook, Schlemmer, Saykally, Nature **380**, 227 (1996)
Cook, Schlemmer, et al. J.Phys.Chem. A**102**, 1465 (1998)

Forschergruppe Laboratory Astrophysics



The Astronomer's Periodic Table



Cosmic Abundance
of some elements

Element	Abundance
hydrogen (H)	1.000.000
helium	80.147
oxygen	739
carbon	445
neon	138
nitrogen	91
magnesium	40
Silcon	37
Sulfur	19

INTERSTELLAR MEDIUM

H:1 He: 0.1

O: C: N = 8:3:1 (0.001)

gas phase
99 %

cold molecular clouds

T = 10 K

$\rho = 10^2 - 10^6\ cm^{-3}$

119 molecules

solid state
1 %

grains (< 0.1um)

T = 10 K

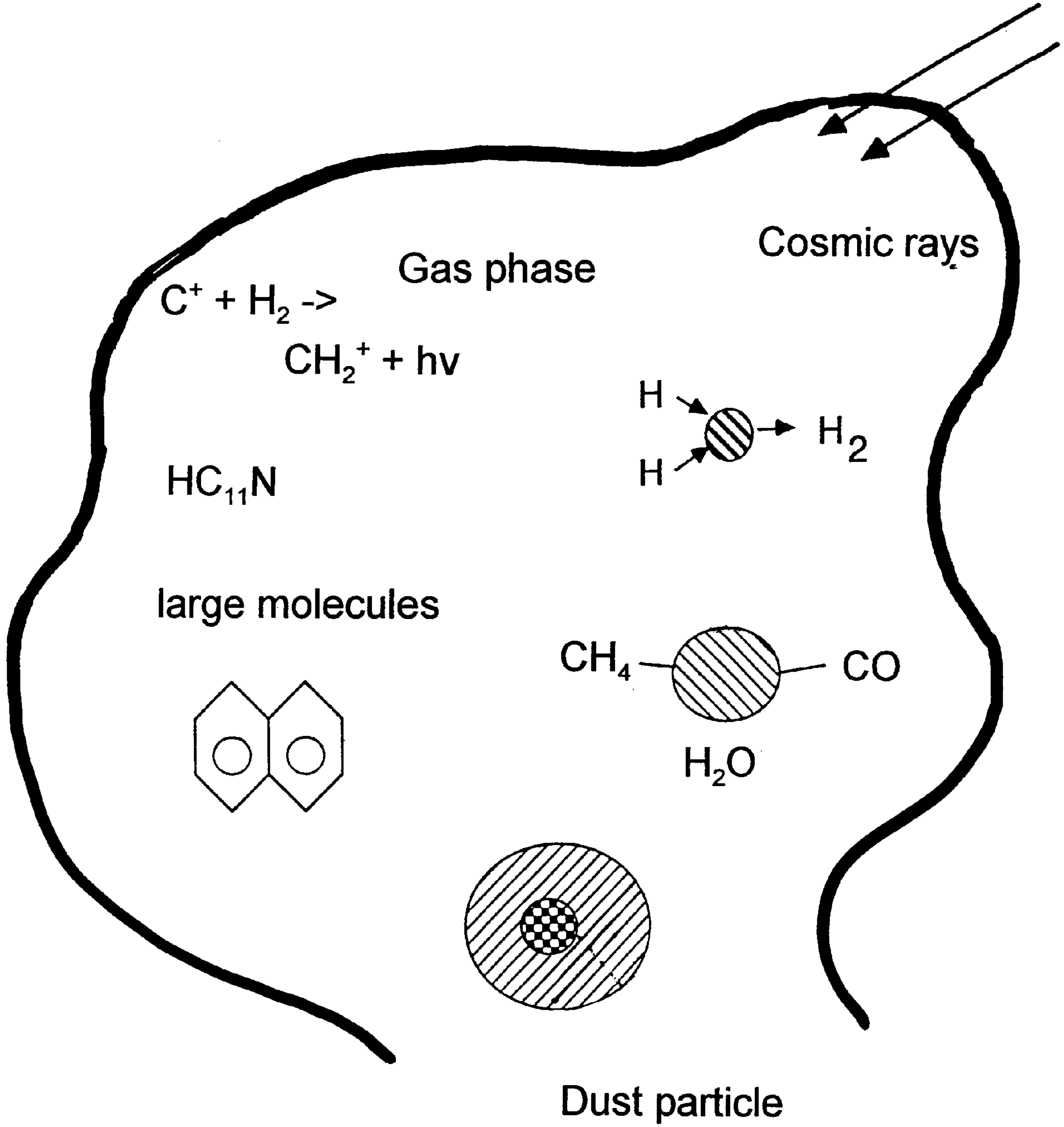
$\rho = 10^{-9} cm^{-3}$

8 molecules

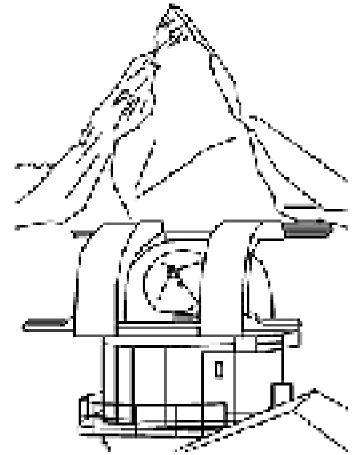
Physics and Chemistry of the Interstellar Medium

$T = 10$ K

$n = 10^4$ cm^{-3}



Les Houches *September 26, 2005*



Laboratory Studies of Astrophysical Reactions

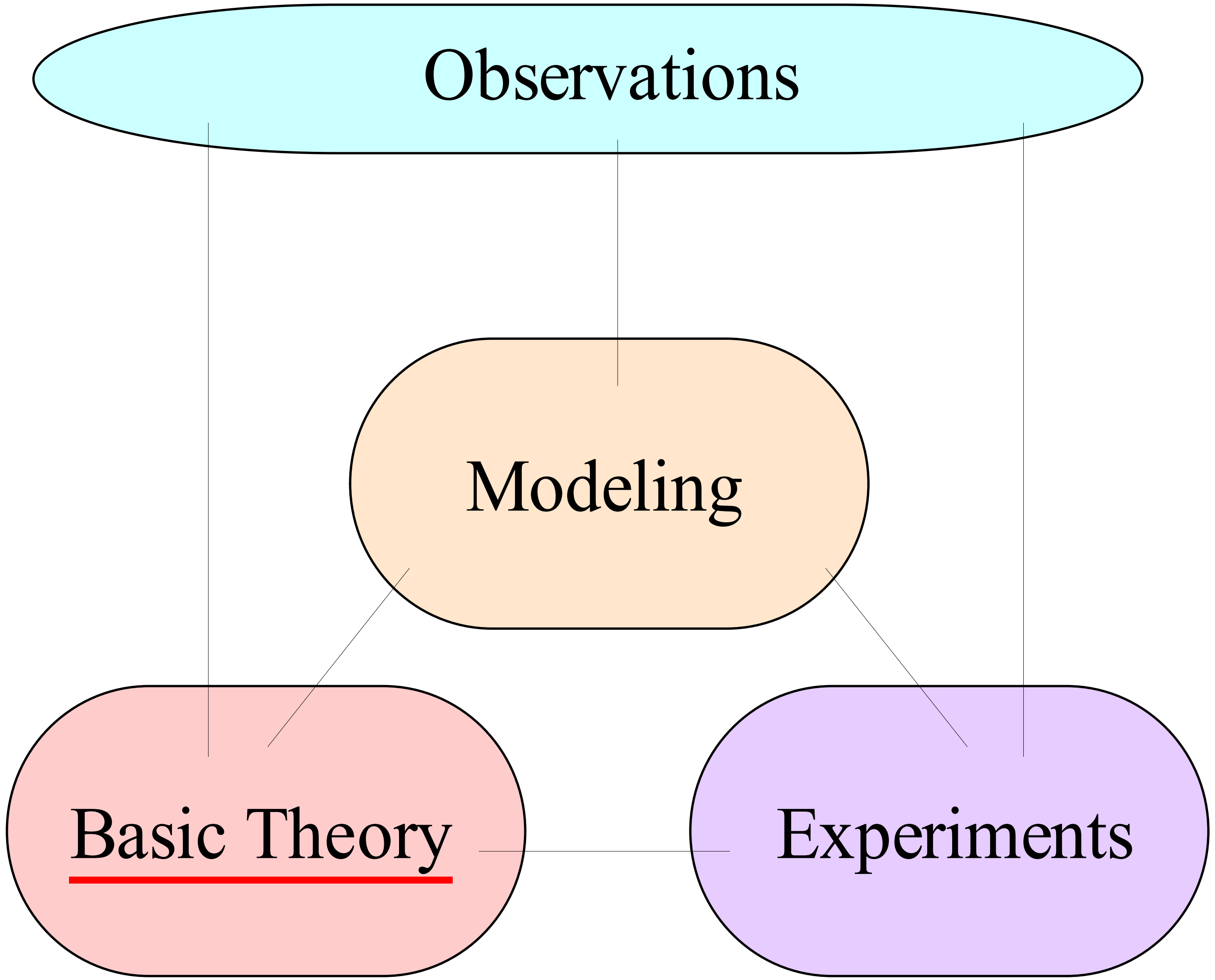
Stephan Schlemmer

WHAT? Kinetics of ion-molecule reactions
radiative association (one example)

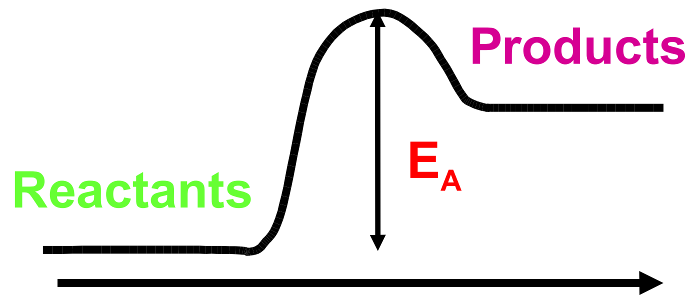
WHY? Identification of Species
(Column Densities)
Formation and Destruction

HOW? Experimental Techniques (Laboratory work)

Forschergruppe Laboratory Astrophysics



Importance of Ion-Molecule Reactions



Arrhenius:

$$k(T) = \langle \sigma v \rangle = \mathbf{A} \exp(-E_A/kT)$$

Neutral-Neutral Reactions

$$\mathbf{A} \approx 10^{-11}\ \mathrm{cm^3/s}$$

$$E_A \approx 2000\ \mathrm{K}$$

$$T_{MC} = 10\ \mathrm{K}$$

Ion-Molecule Reactions

$$10^{-7}\ \mathrm{cm^3/s} > \mathbf{A} > 10^{-9}\ \mathrm{cm^3/s}$$

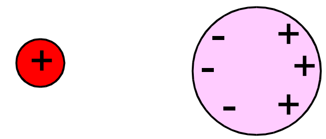
$$E_A \approx 0\ \mathrm{K}$$

Cosmic Ray Ionization → **Ion-Molecule Reactions** → Recombination

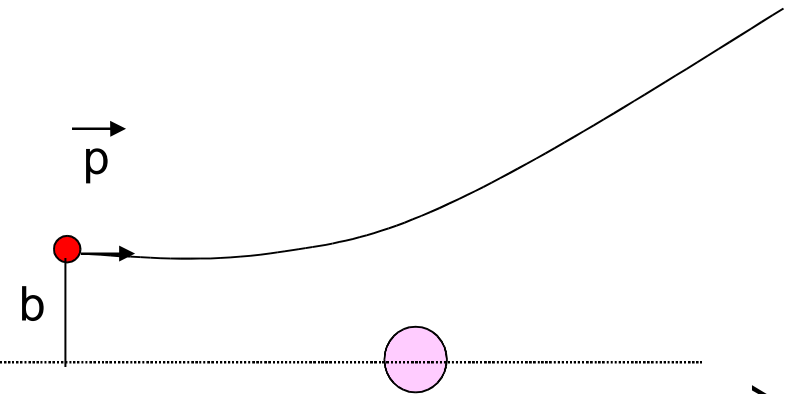
E. Herbst, The Physics and Chemistry of Interstellar MCs (1993)

Ion – induced dipole interaction

long range forces



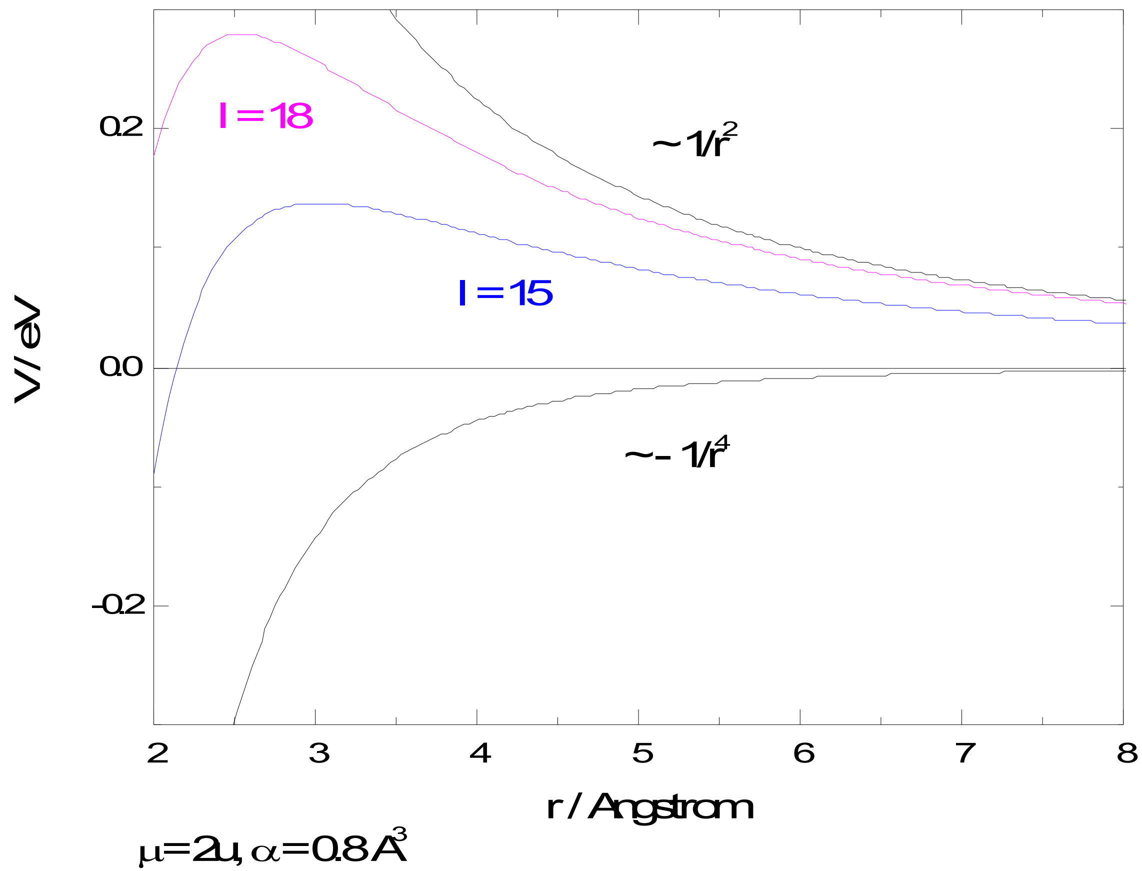
$V = -\, q\, \alpha \,/\, r^4$



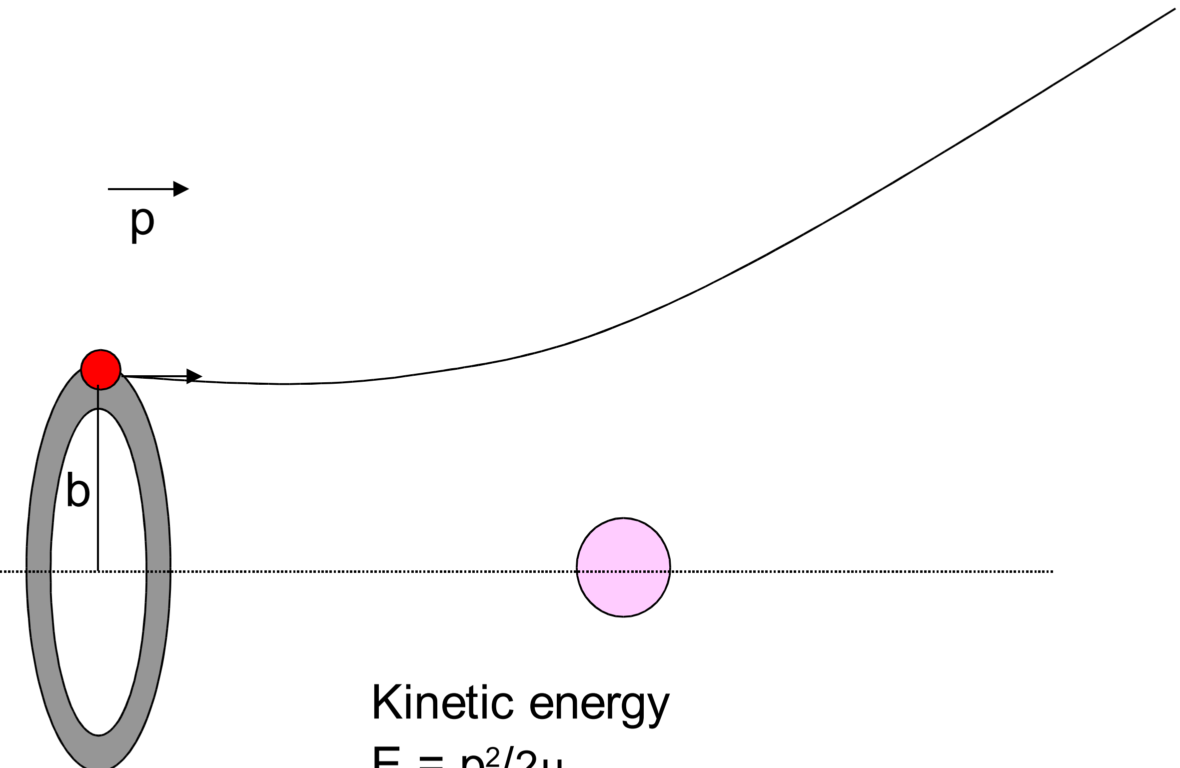
Kinetic energy
$E = p^2/2\mu$

Angular momentum
$L = b\, p = l\, h$

Centrifugal barrier
$V = +\, L^2/(2\mu r^2)$



Ion – induced dipole interaction
Rate of Reaction



Kinetic energy
$E = p^2/2\mu$

Angular momentum
$L = b\ p = l\ h$

Cross section $\sigma(E)$:

$$\sigma(E) = 2\pi * b\, db = \pi\, b_{max}^2$$

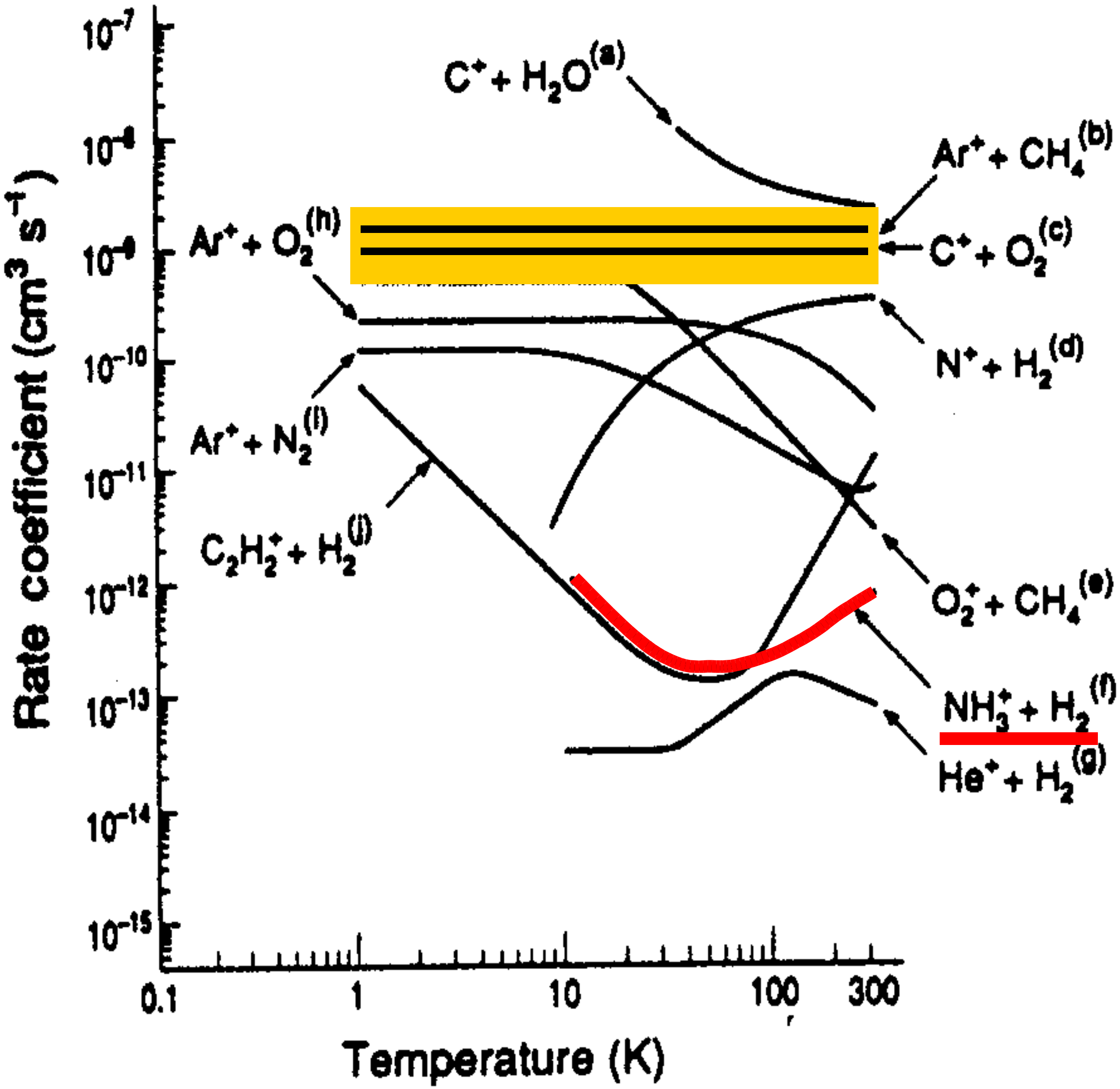
Rate coefficient:

$$k = <\sigma\, v>_T$$

ion-induced dipole:

$$k_L = const.$$

Temperature Dependence of Ion-Molecule Reactions

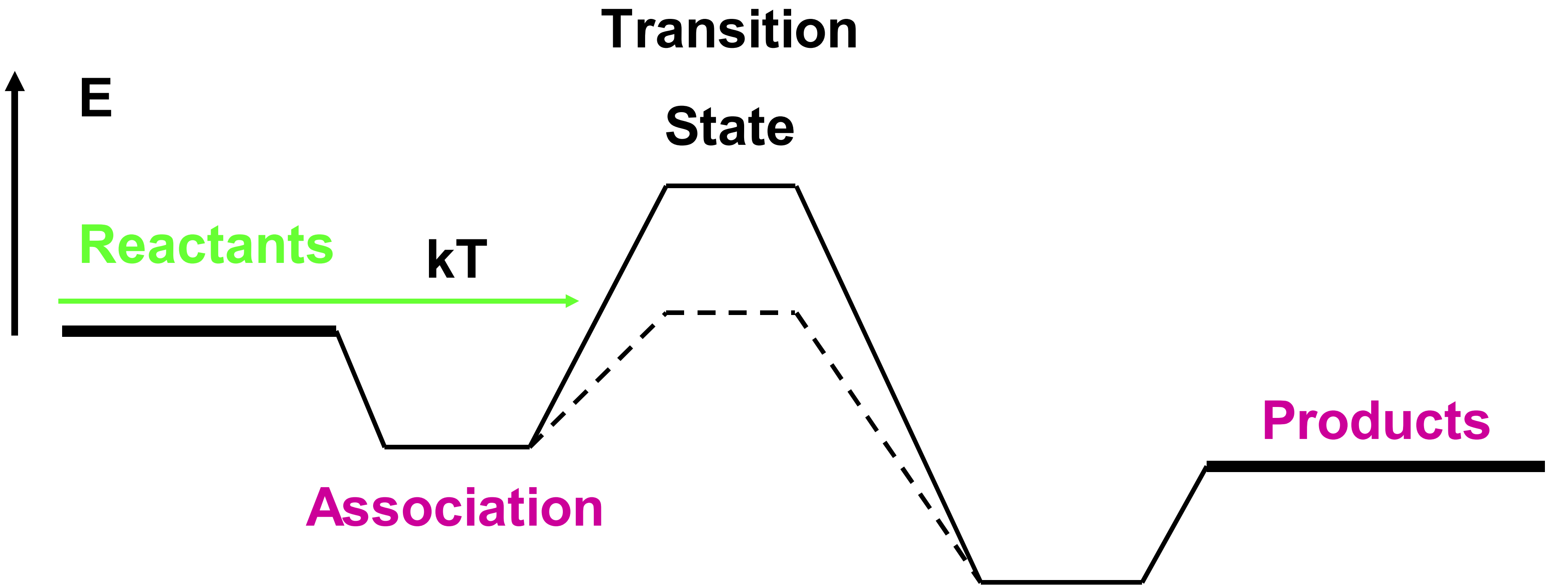


Langevin Rate Coefficient:

$$k_L = 2\pi\, q \sqrt{\frac{\alpha}{\mu}}$$

M.A. Smith (1994)

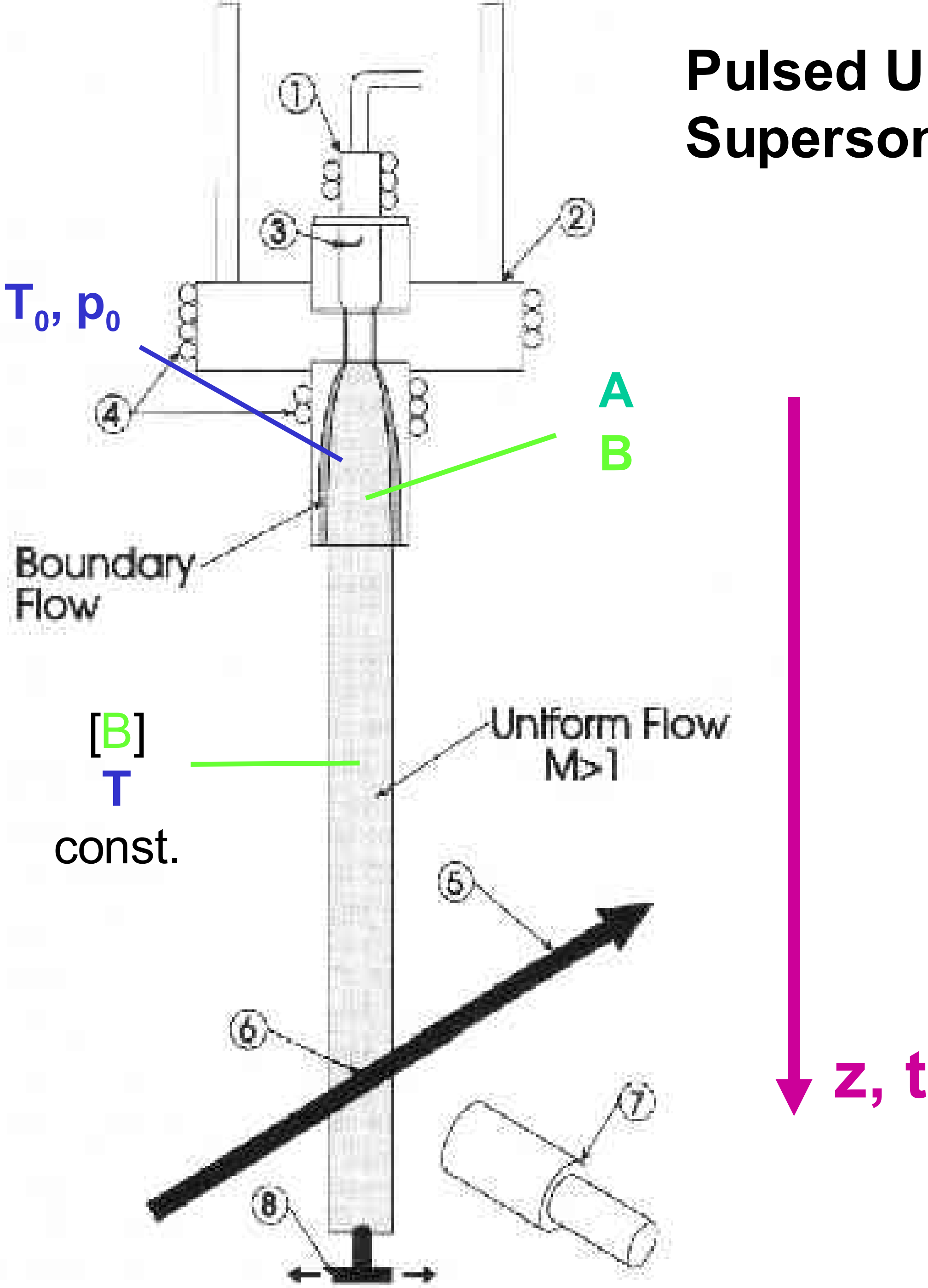
Details of Potential Energy Surface



Low Temperature Collisions in Flow Systems and Traps

(state-of-the-art experiments)

Pulsed Uniform Supersonic Expansion



k(T)

$$A + B \rightarrow \text{Products}$$

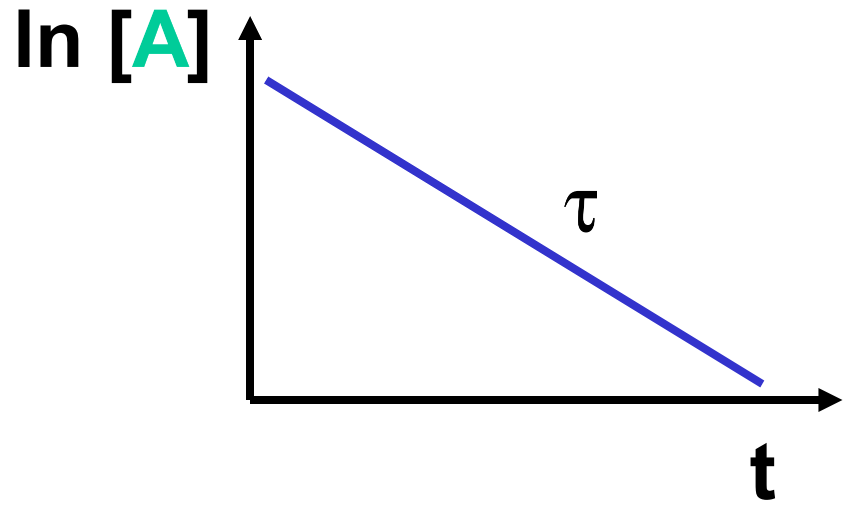
$$k = (\tau\,[B])^{-1}$$

CRESU: Cinétique de Réaction en Ecoulement Supersonique Uniforme

B. Rowe (Rennes), I. Sims (Birmingham), M. Smith (Tucson)

Pulsed Uniform Supersonic Expansion

A + B $\rightarrow$ Product



$d[A]/dt = -k\,[A]\,[B]$

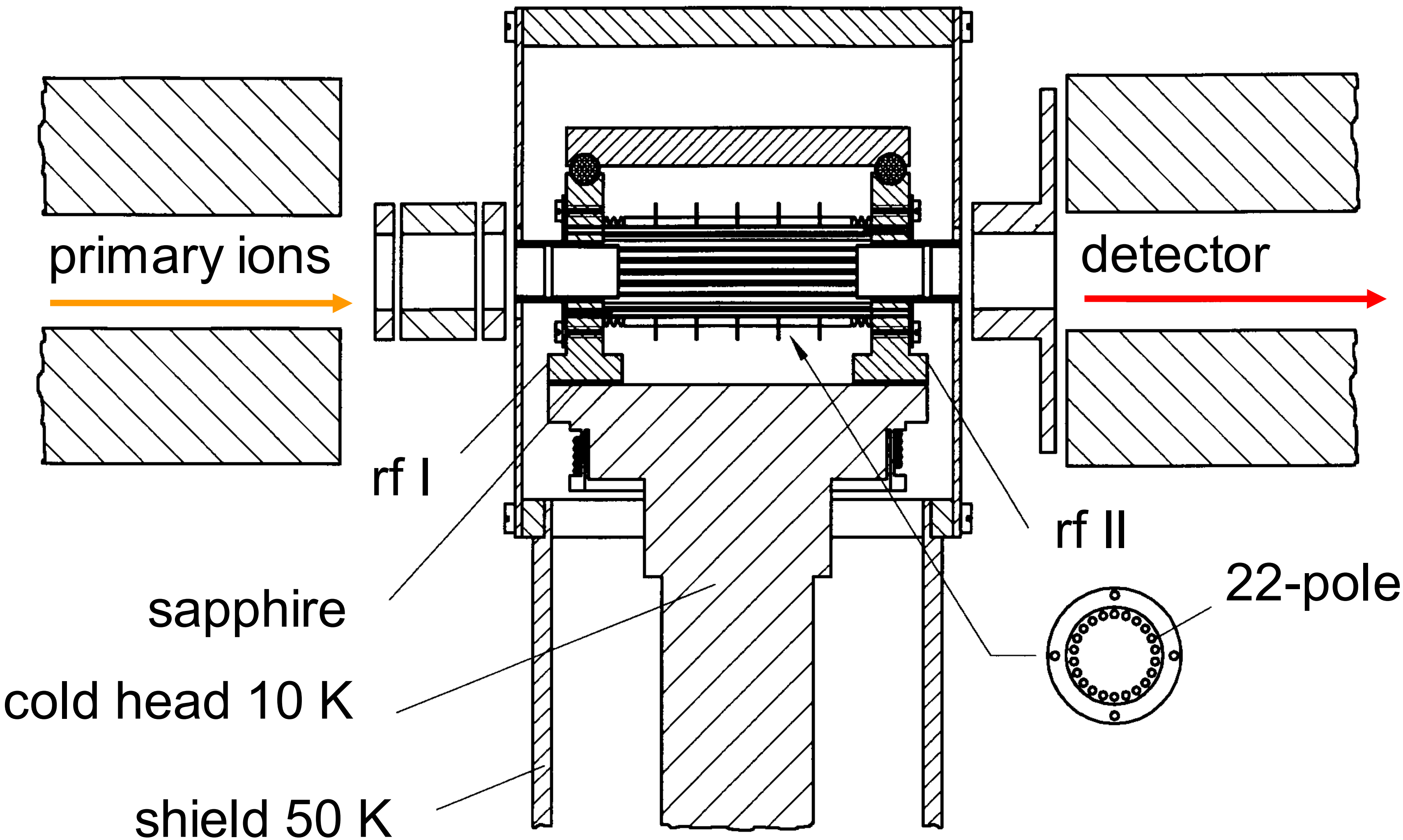
$k = (\tau\,[B])^{-1}$

$\tau \leq \Delta z/v \sim 0.1/500$ s ~ 200 μs

$[B] \leq 10^{15}$ cm^{-3}

$k \geq 5\times10^{-12}$ cm^3/s

22-Pol Low Temperature Ion Trap



Trap Experiment

$A + B \rightarrow \text{Products}$

$d[A]/dt = -k[A][B]$

$k = (\tau [B])^{-1}$

$1 \text{ ms} \leq \tau \leq 100 \text{ s}$

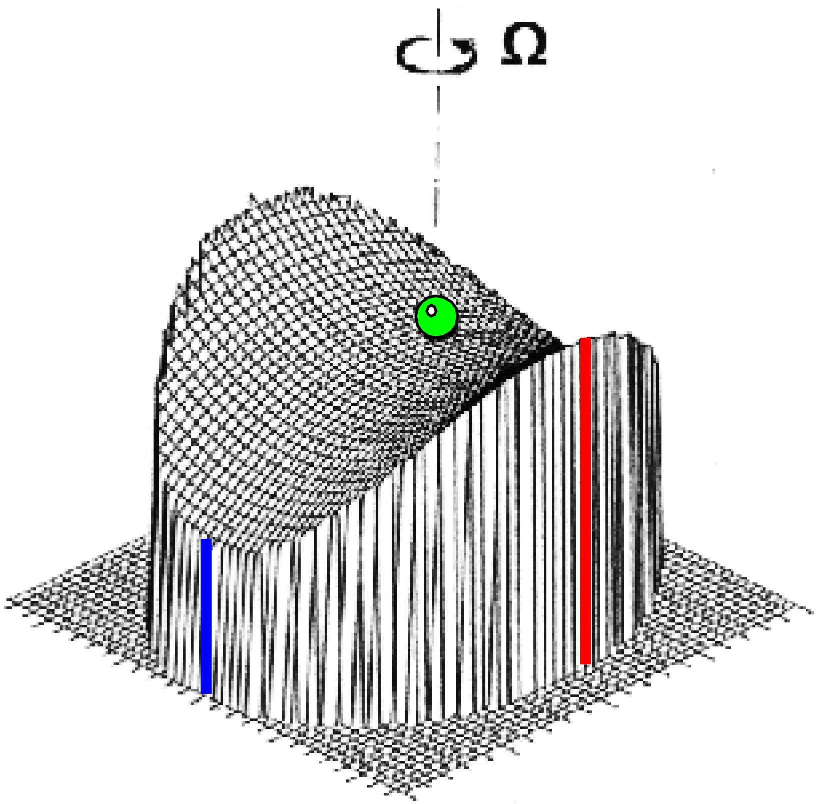
$10^{8} \text{ cm}^{-3} \leq [B] \leq 10^{15} \text{ cm}^{-3}$

$k \geq 10^{-17} \text{ cm}^3/\text{s}$

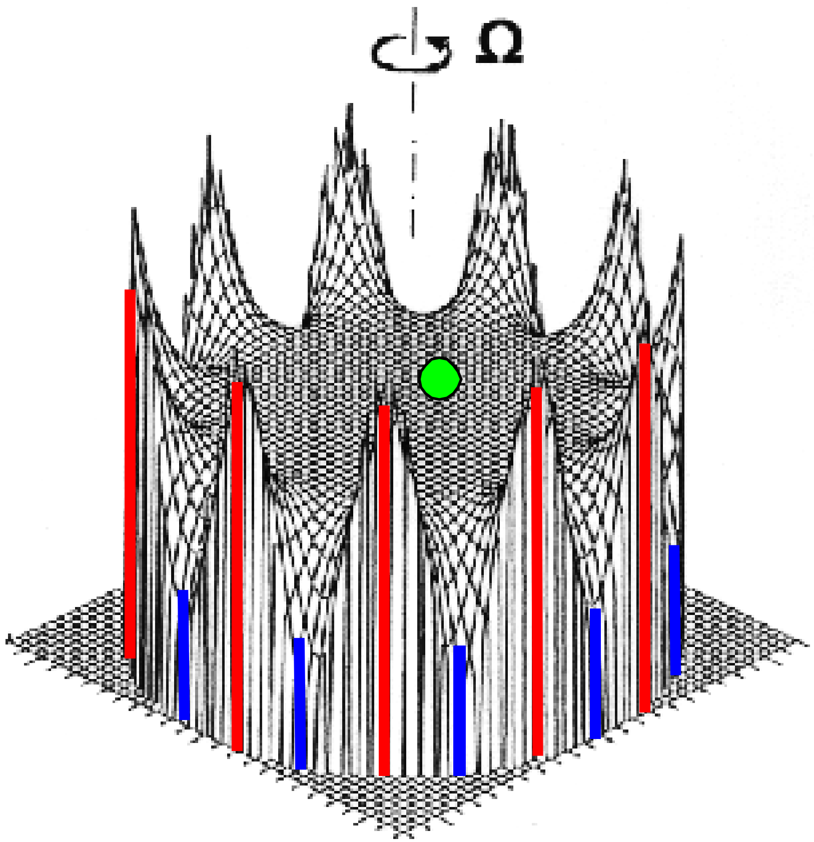
Method:

Electrodynamical Trapping

RF Ion Trap
Mechanical Model

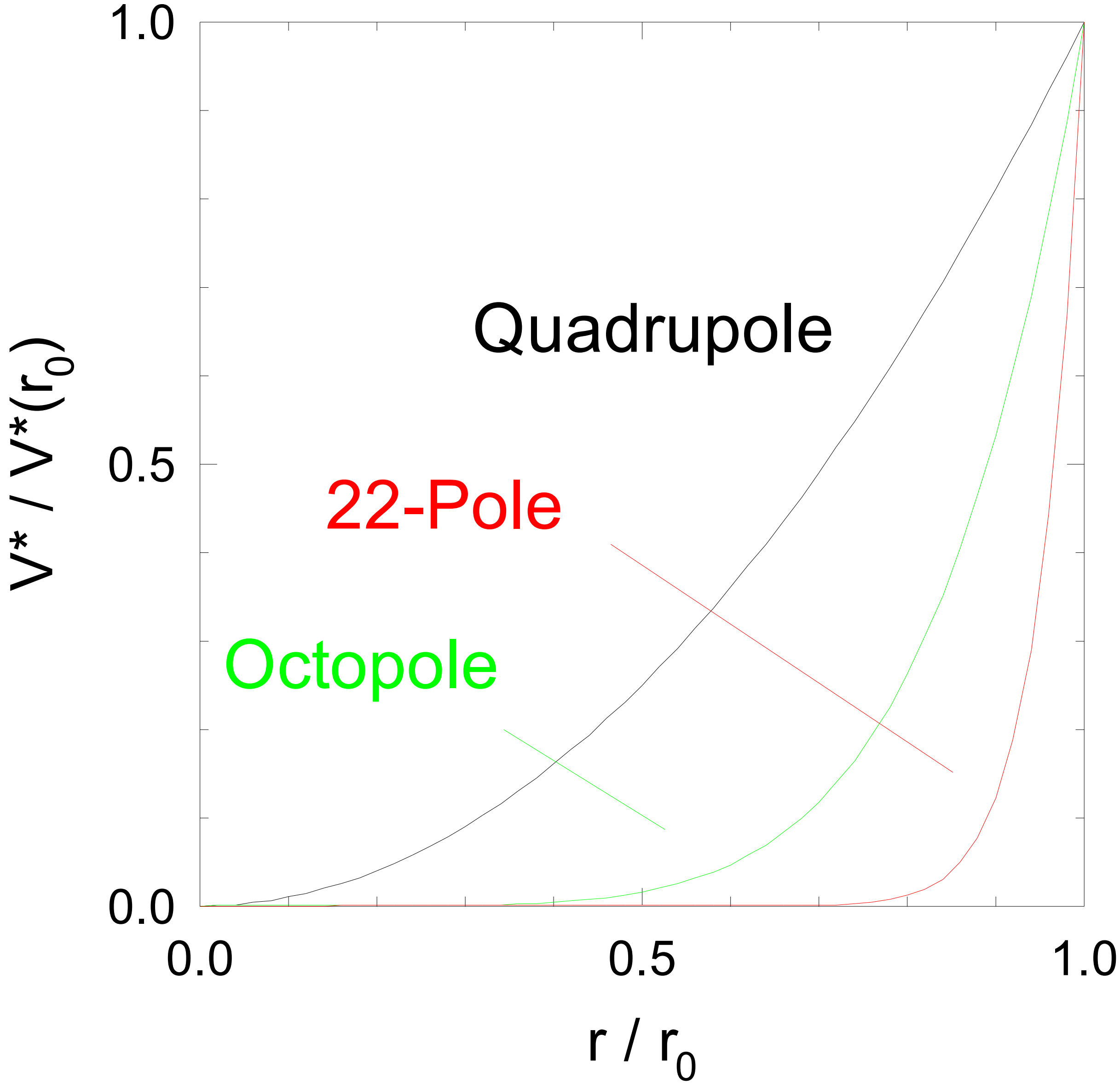


Quadrupole

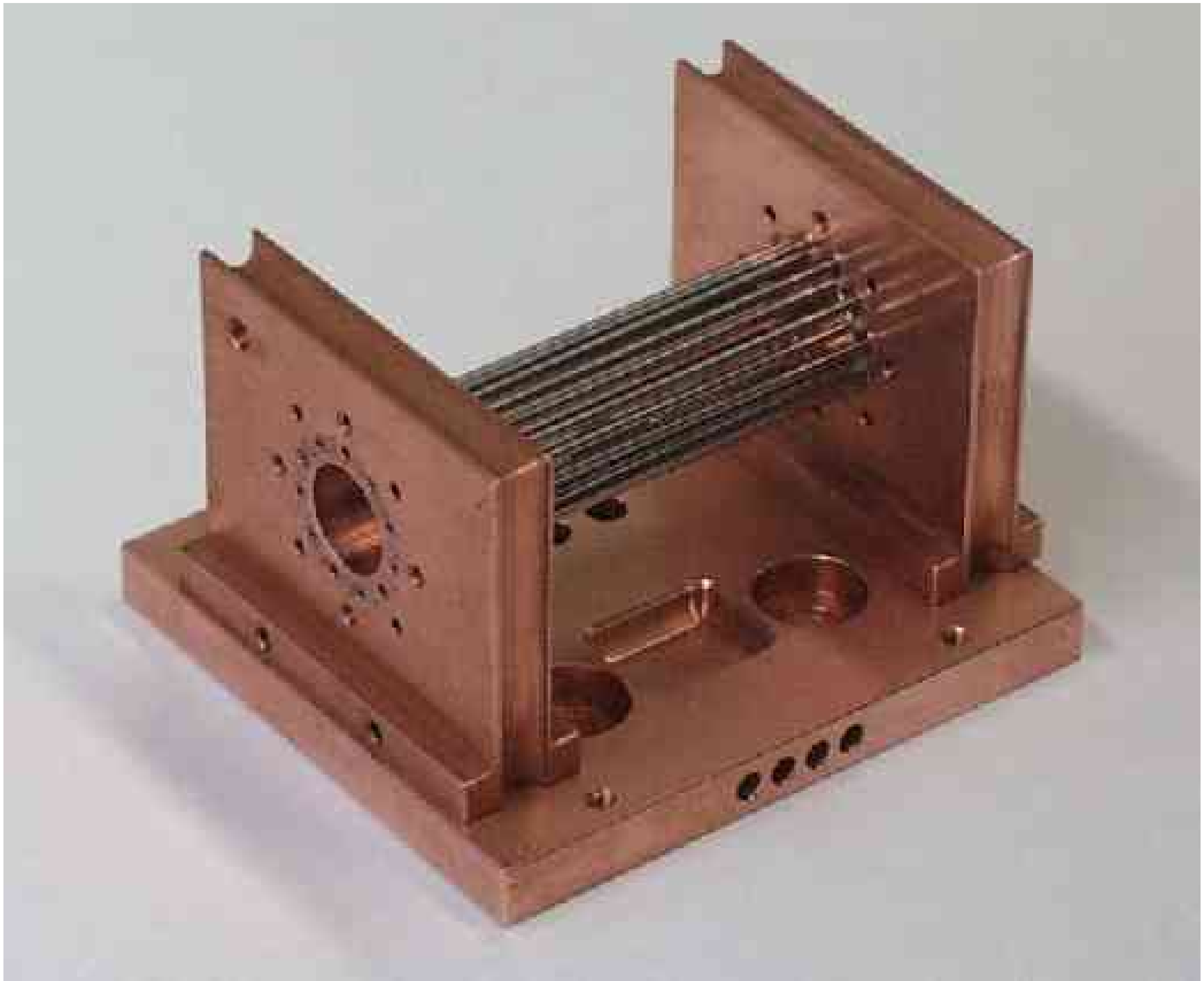


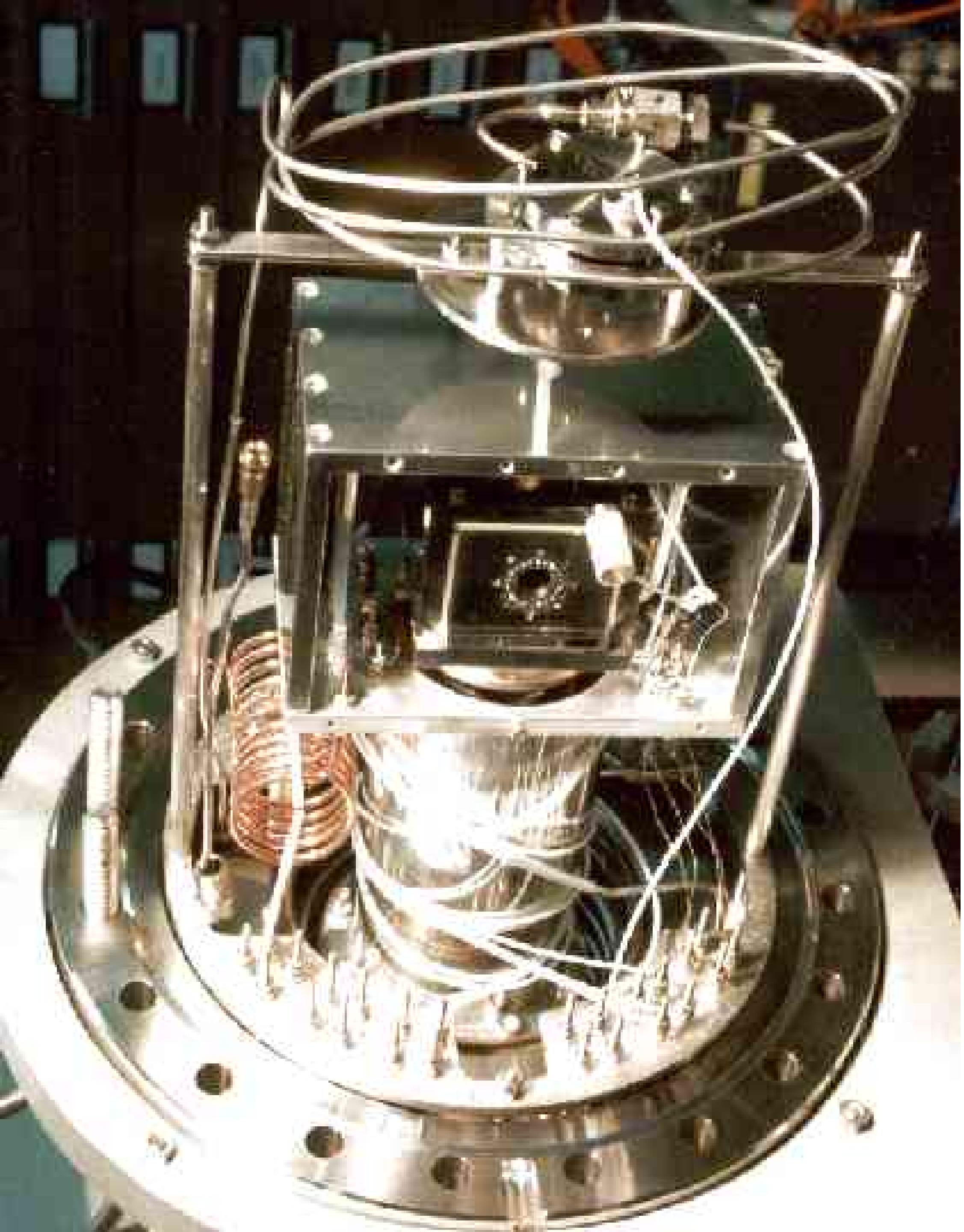
22-Pole

Effective Potential



Low Temperature 22 Pole Ion Trap

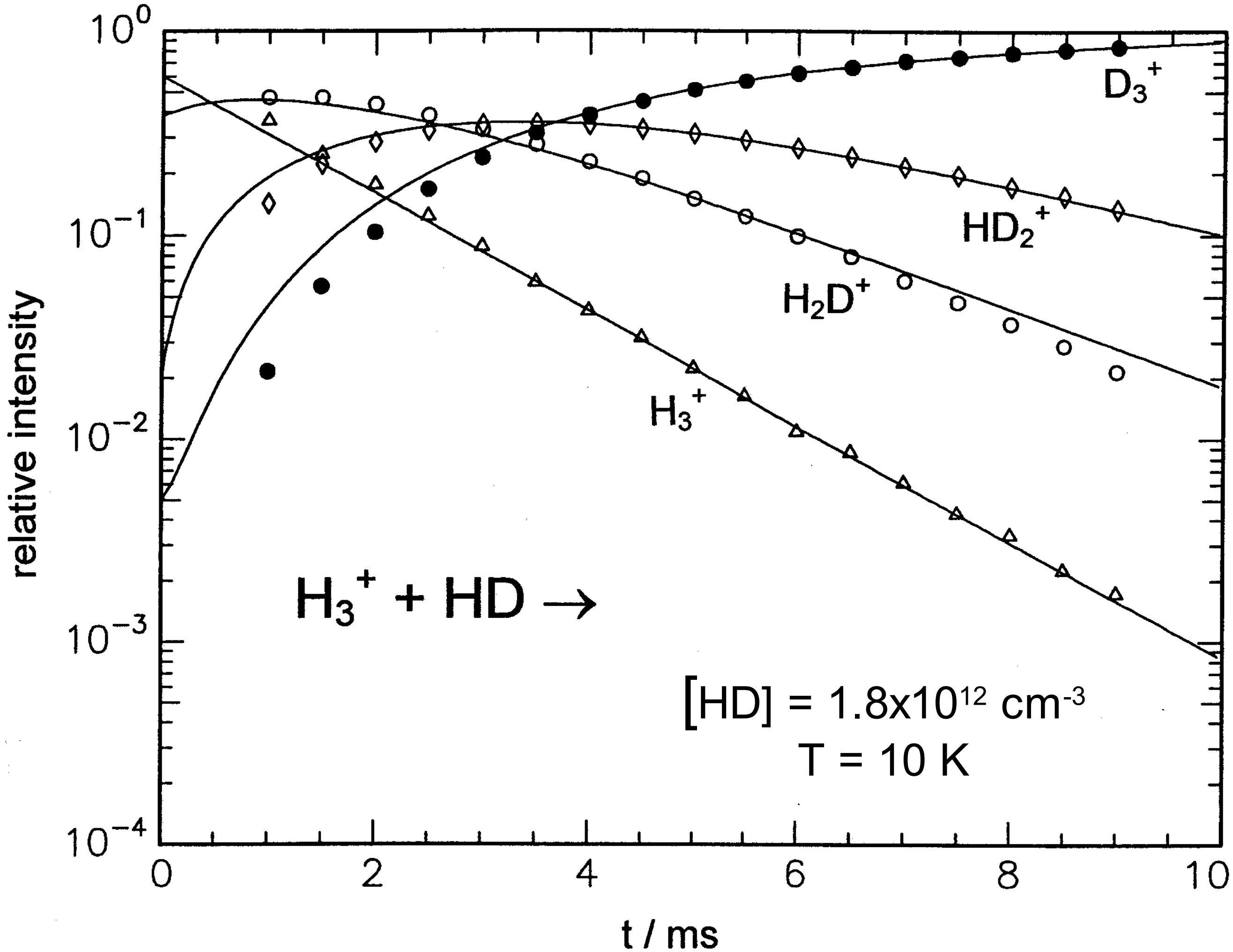




Low Temperature 22 Pole Trap

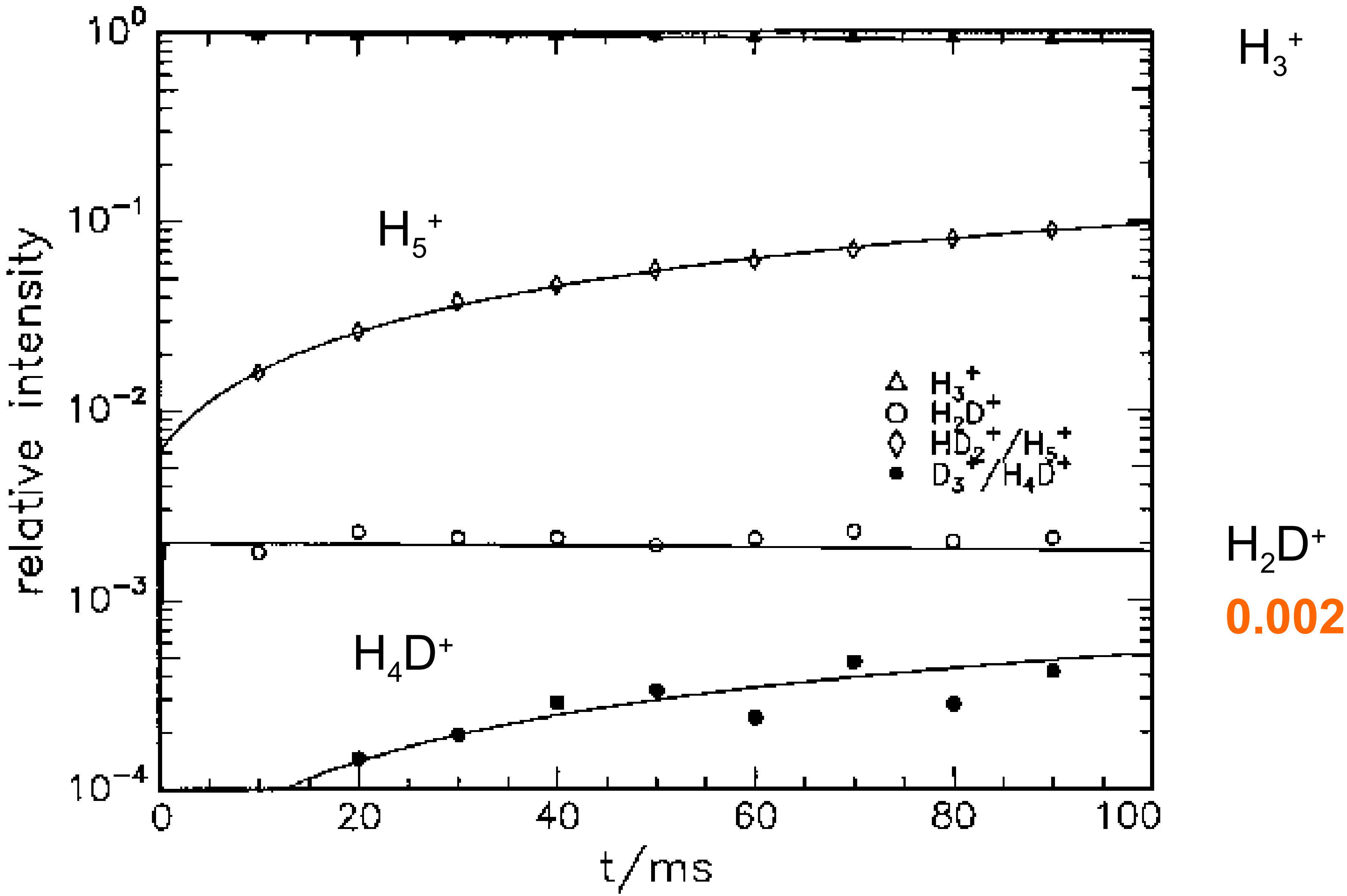
Deuteration of H_3^+

$$H_3^+ \xrightarrow[k_1]{HD} H_2D^+ \xrightarrow[k_2]{HD} D_2H^+ \xrightarrow[k_3]{HD} D_3^+$$



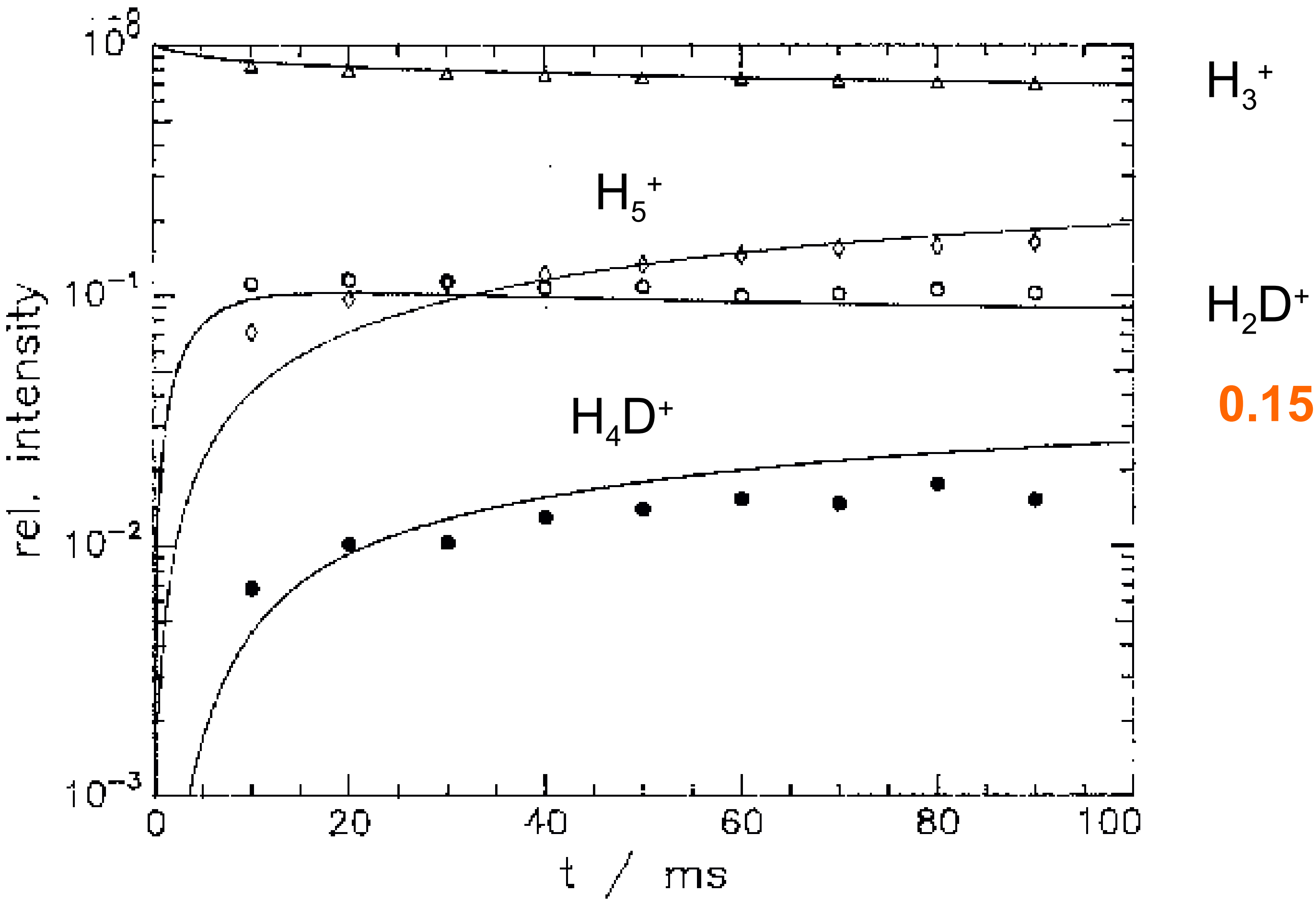
$H_3^+ + HD \Leftrightarrow H_2D^+ + H_2$

$[n\text{-}H_2] = 1.4\times10^{14}\ cm^{-3}$, $[HD]/[H_2] = 3*10^{-4}$, $T = 10\ K$

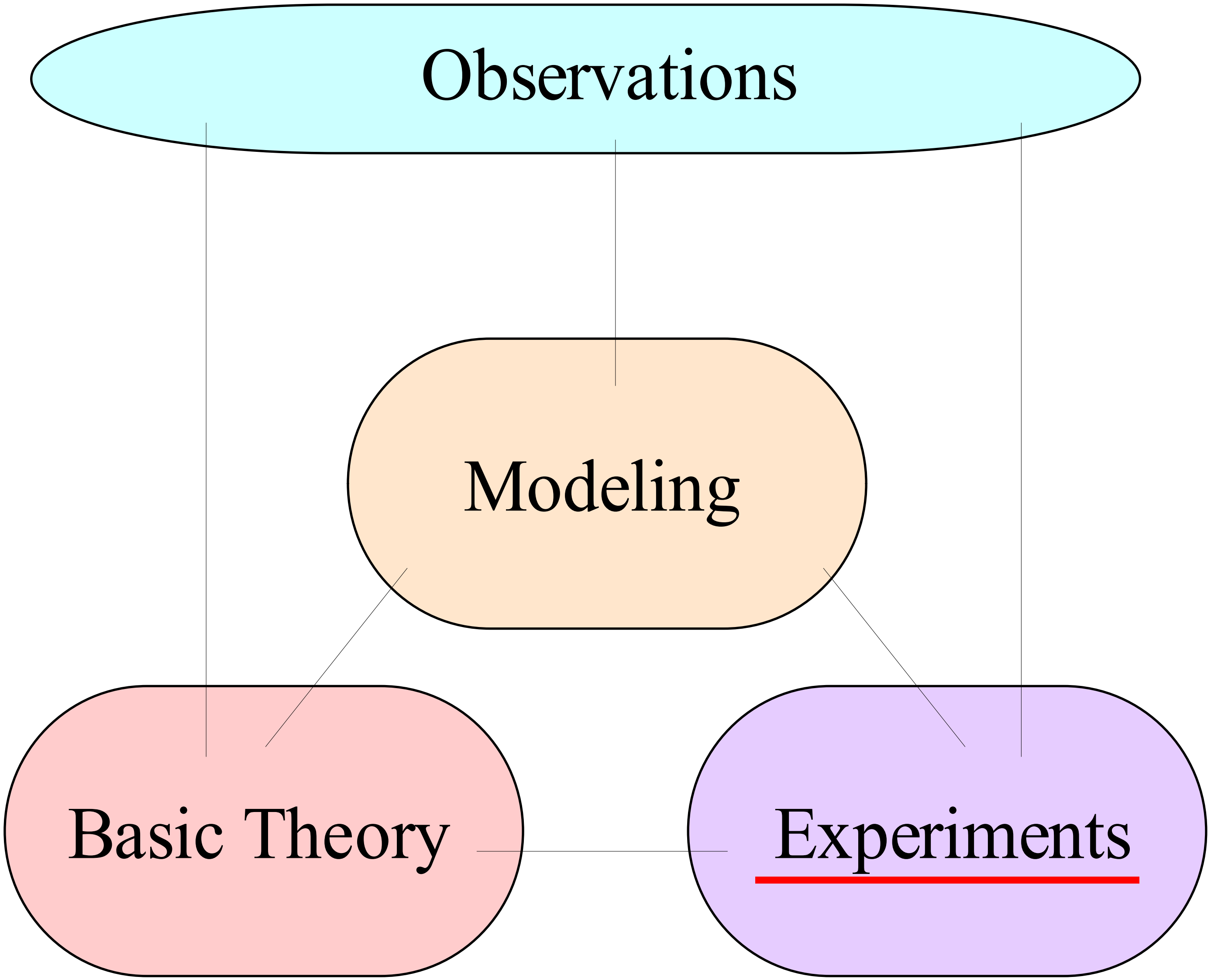


$H_3^+ + HD \Leftrightarrow H_2D^+ + H_2$

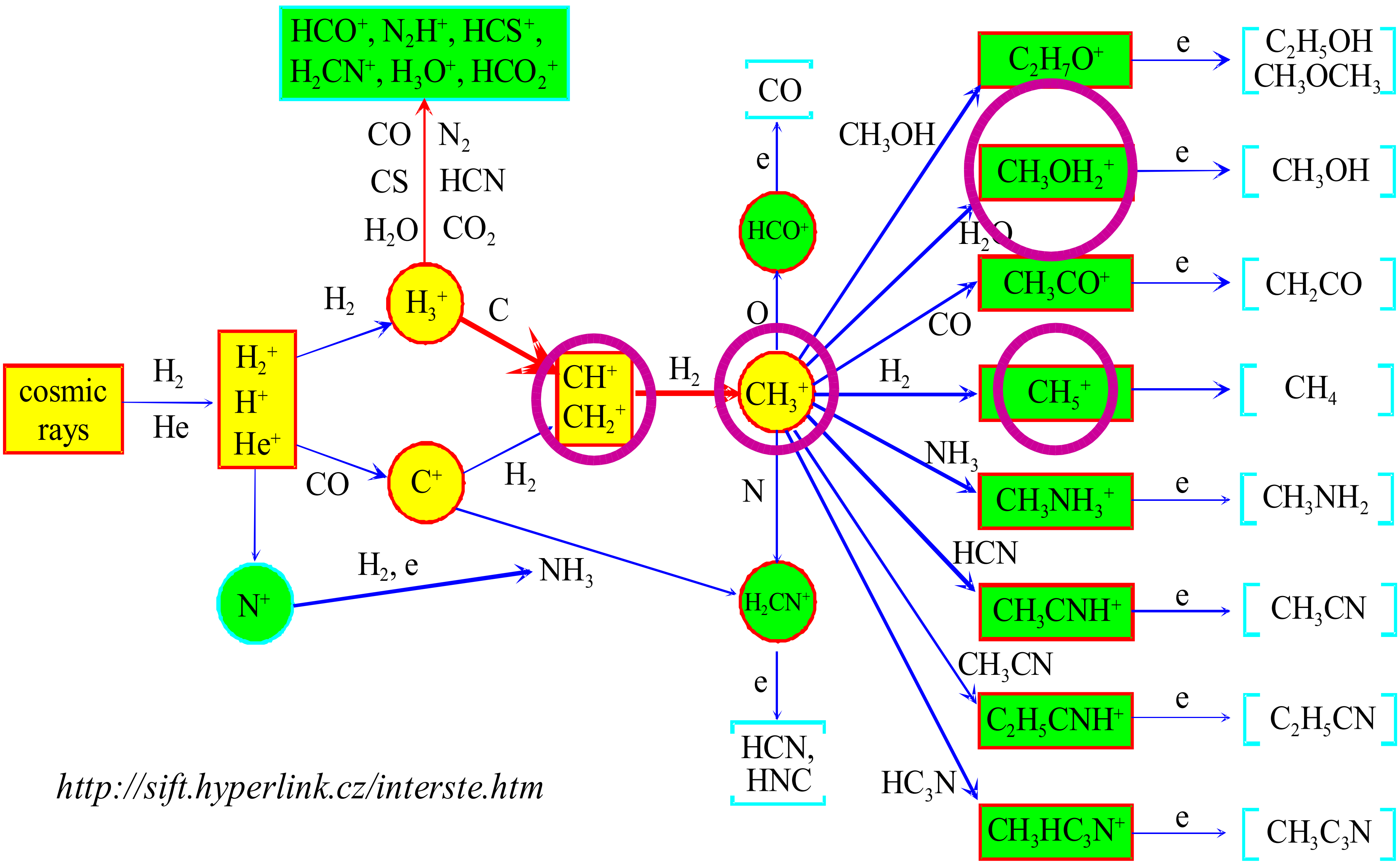
$[p\text{-}H_2] = 1x10^{14}\ cm^{-3}$, $[HD]/[H_2] = 3*10^{-4}$, $T = 10\ K$



Forschergruppe Laboratory Astrophysics



Initial reactions in dense interstellar clouds



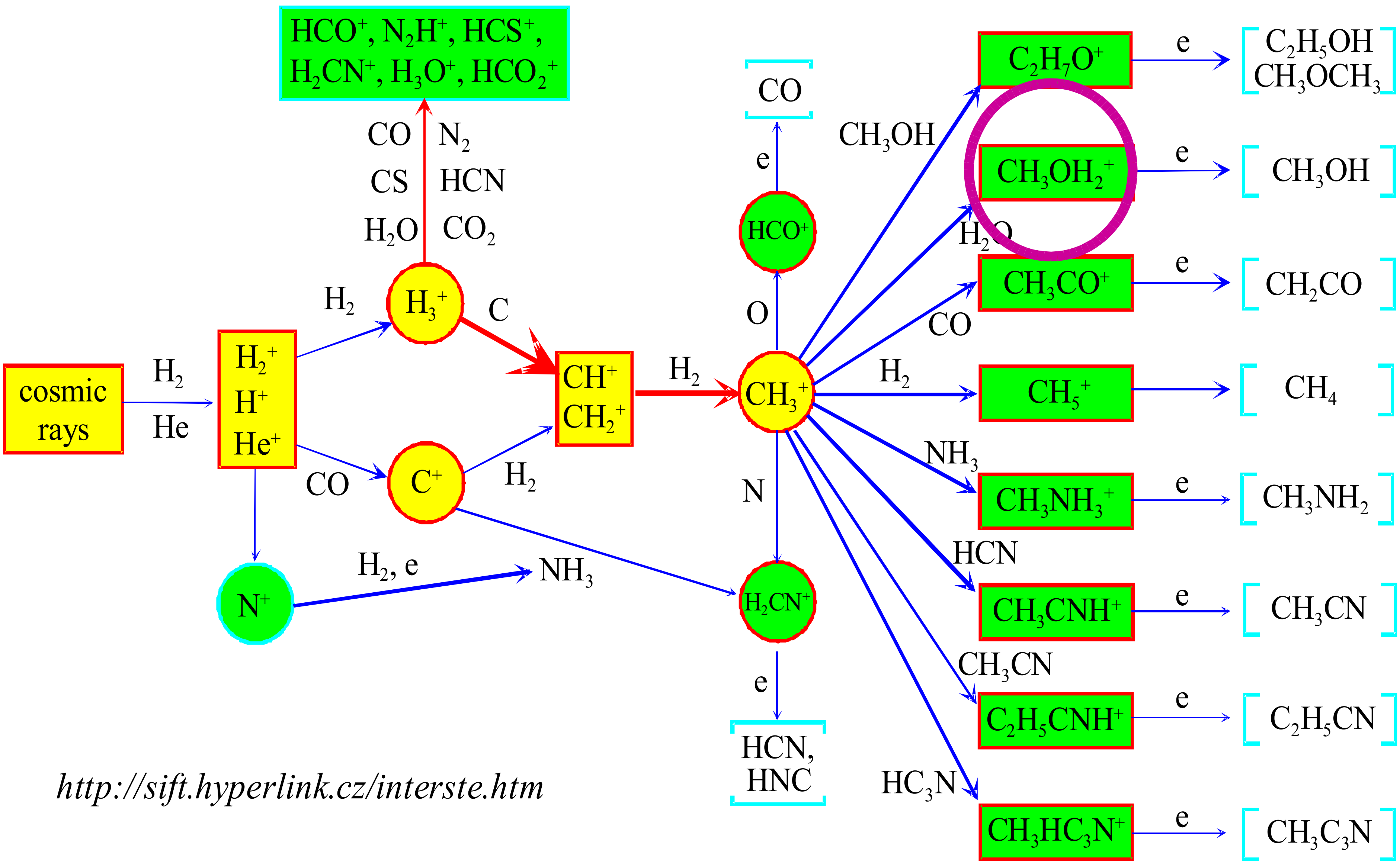
D. Smith and P. Spanel, Mass Spectrometry Reviews, 14 (1995) 255-278.

Example I:
Radiative Association

$$CH_3^+ + H_2O \rightarrow CH_5O^+ + h\nu$$

A. Luca, D. Voulot, and D. Gerlich, WDS'02 Proceedings of Contributed Papers, Part II, Safrankova (ed), Matfyzpress, 294-300 (2002)

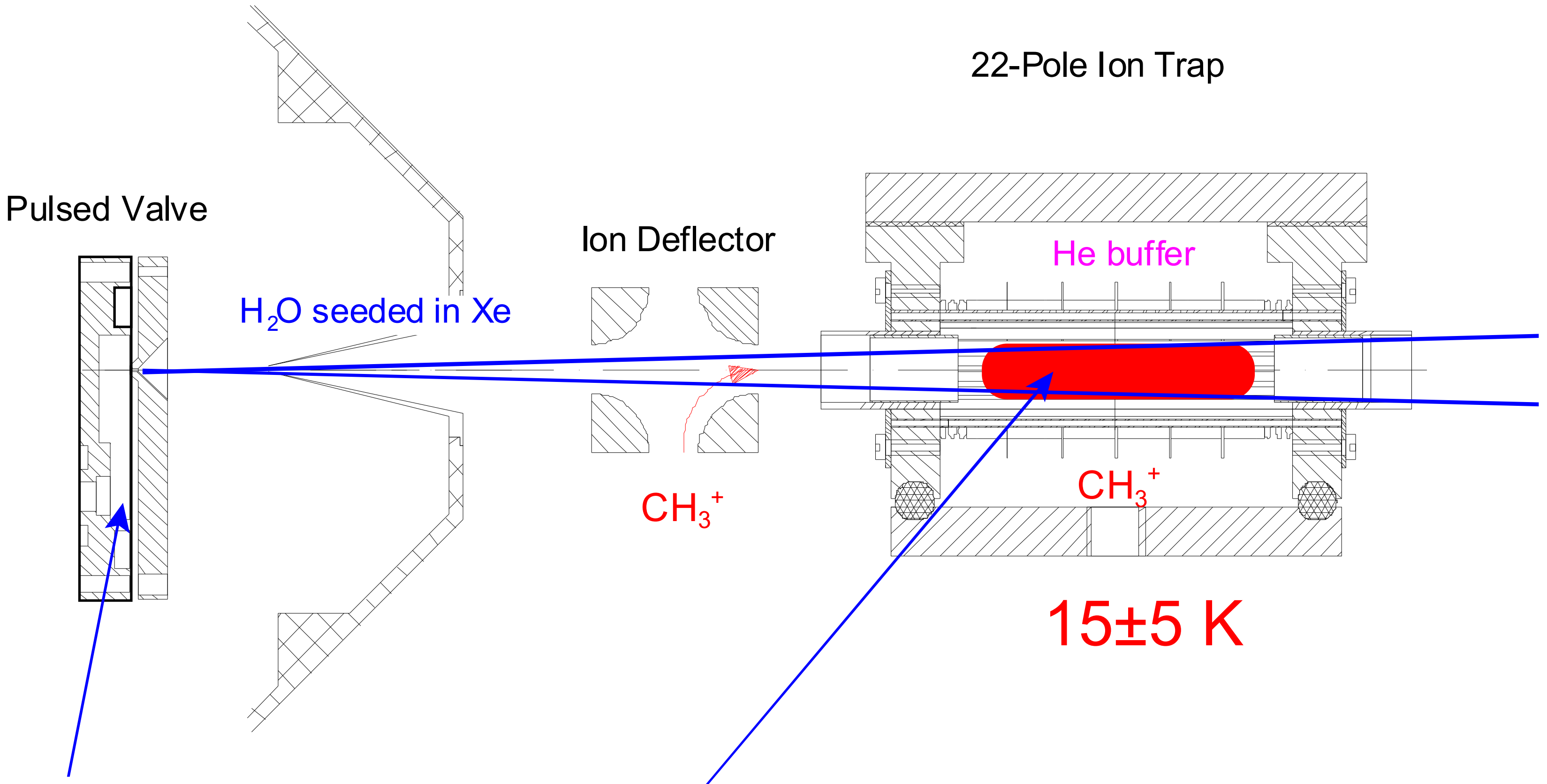
Initial reactions in dense interstellar clouds



http://sift.hyperlink.cz/interste.htm

D. Smith and P. Spanel, Mass Spectrometry Reviews, 14 (1995) 255-278.

Experimental Setup



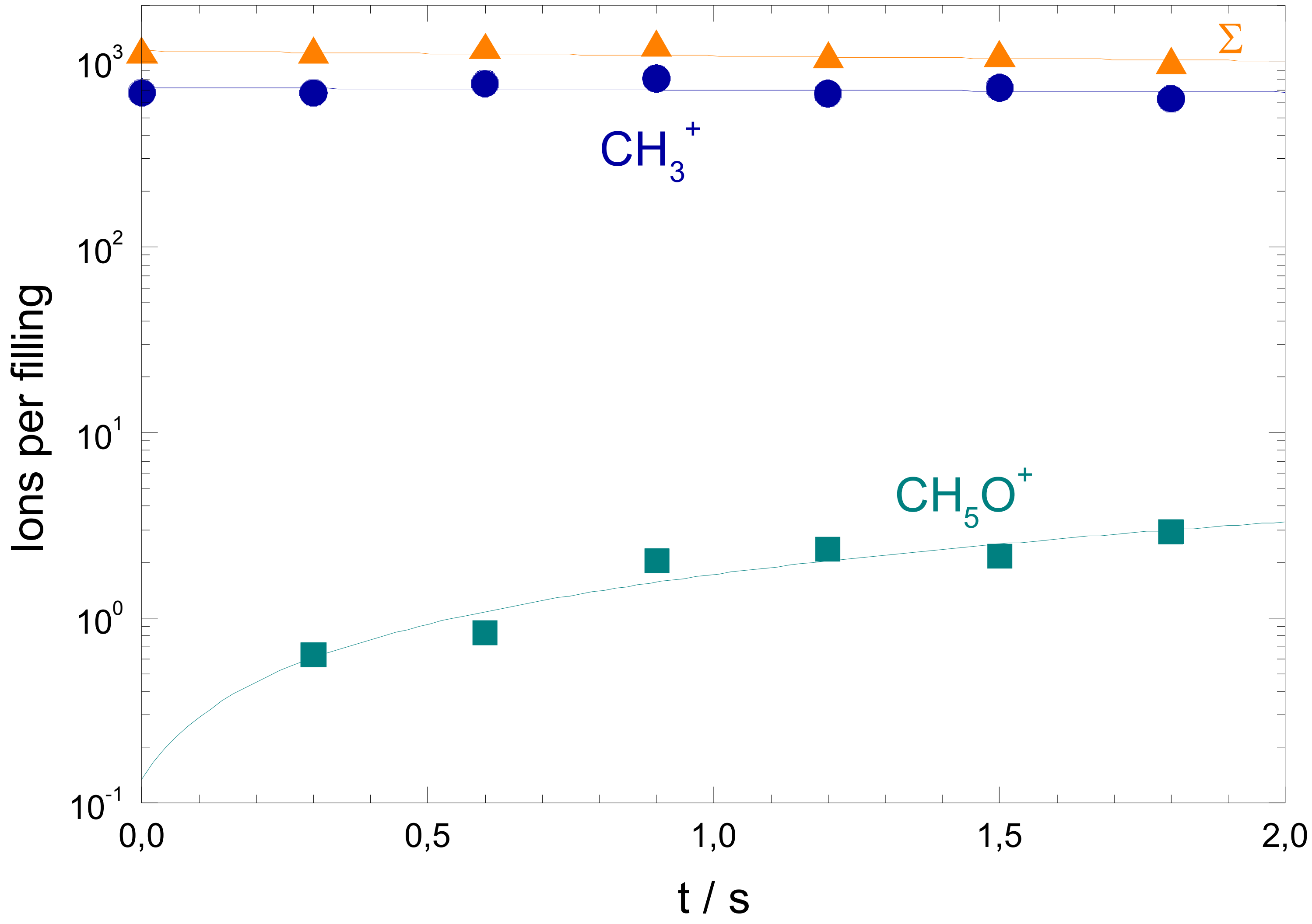
Stagnation pressure: 365 mbar
H_2O partial pressure: 26mbar at 295 K
H_2O 7%
Xe 93 %

Instantaneouce densities:
$[H_2O] = 7 \cdot 10^8\ cm^{-3}$
$[Xe] = 1 \cdot 10^{10}\ cm^{-3}$

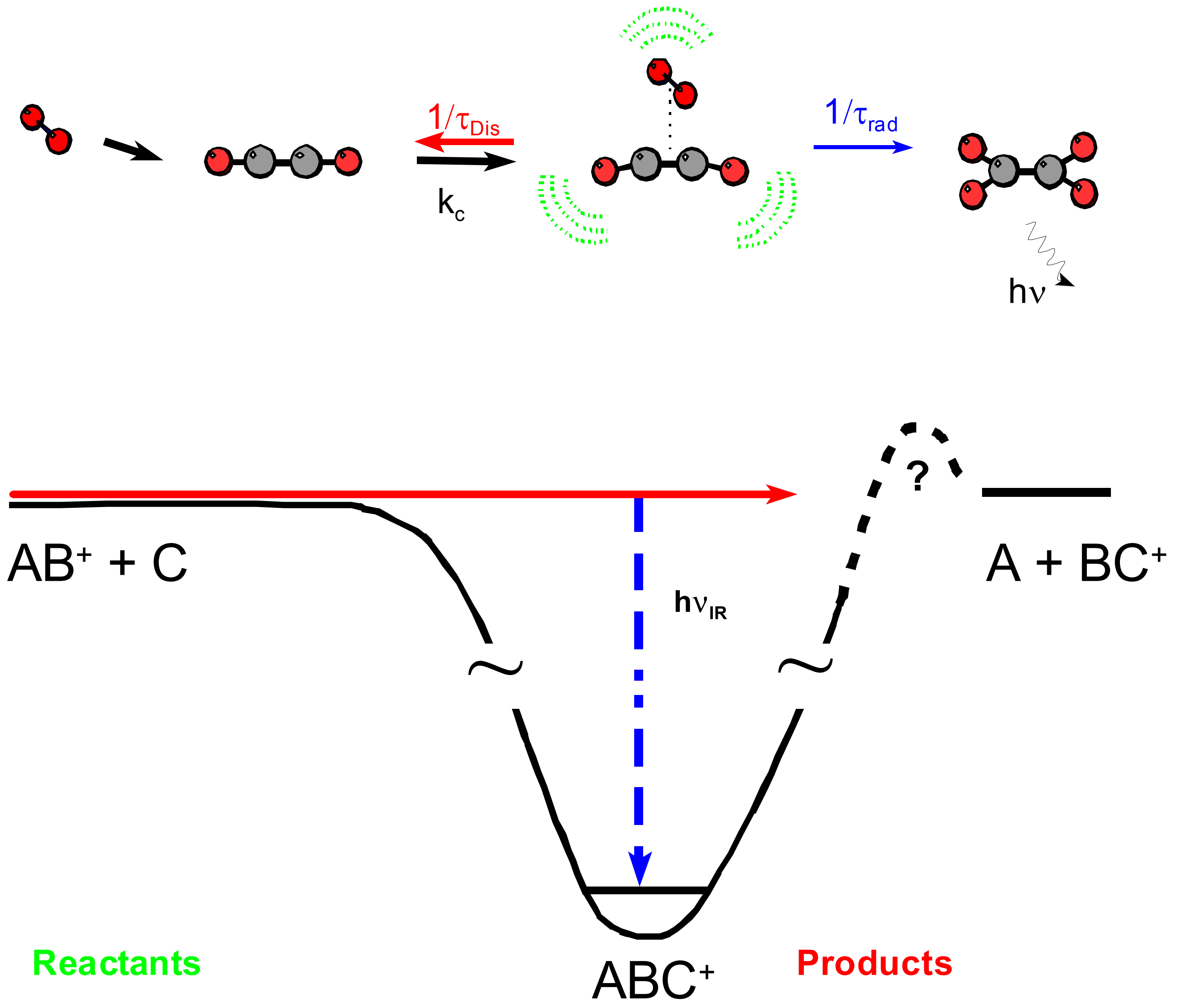
Effective temperature

$$T_{eff} = 50 \pm 30\ K$$

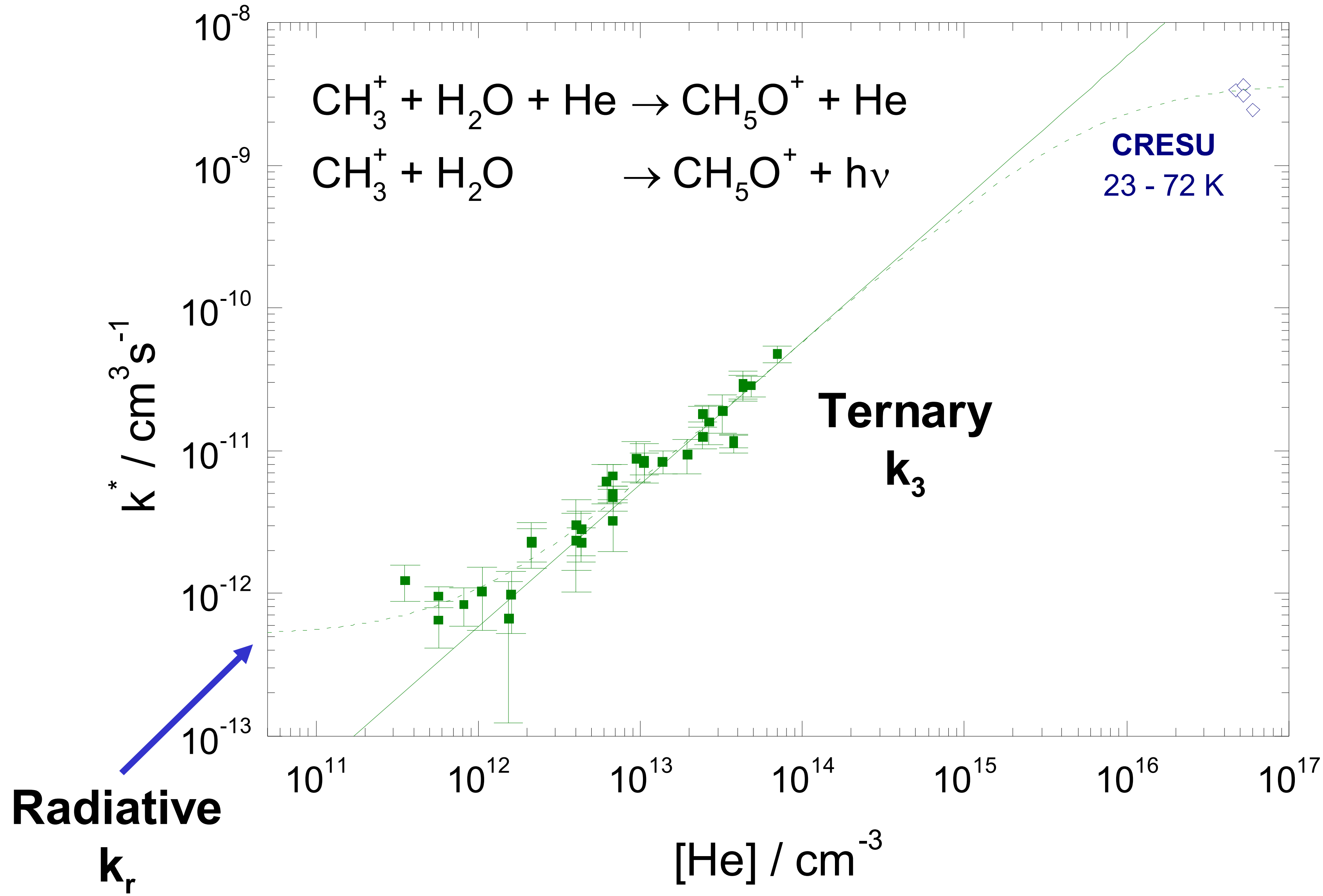
Results: Formation of protonated methanol



Radiative Association



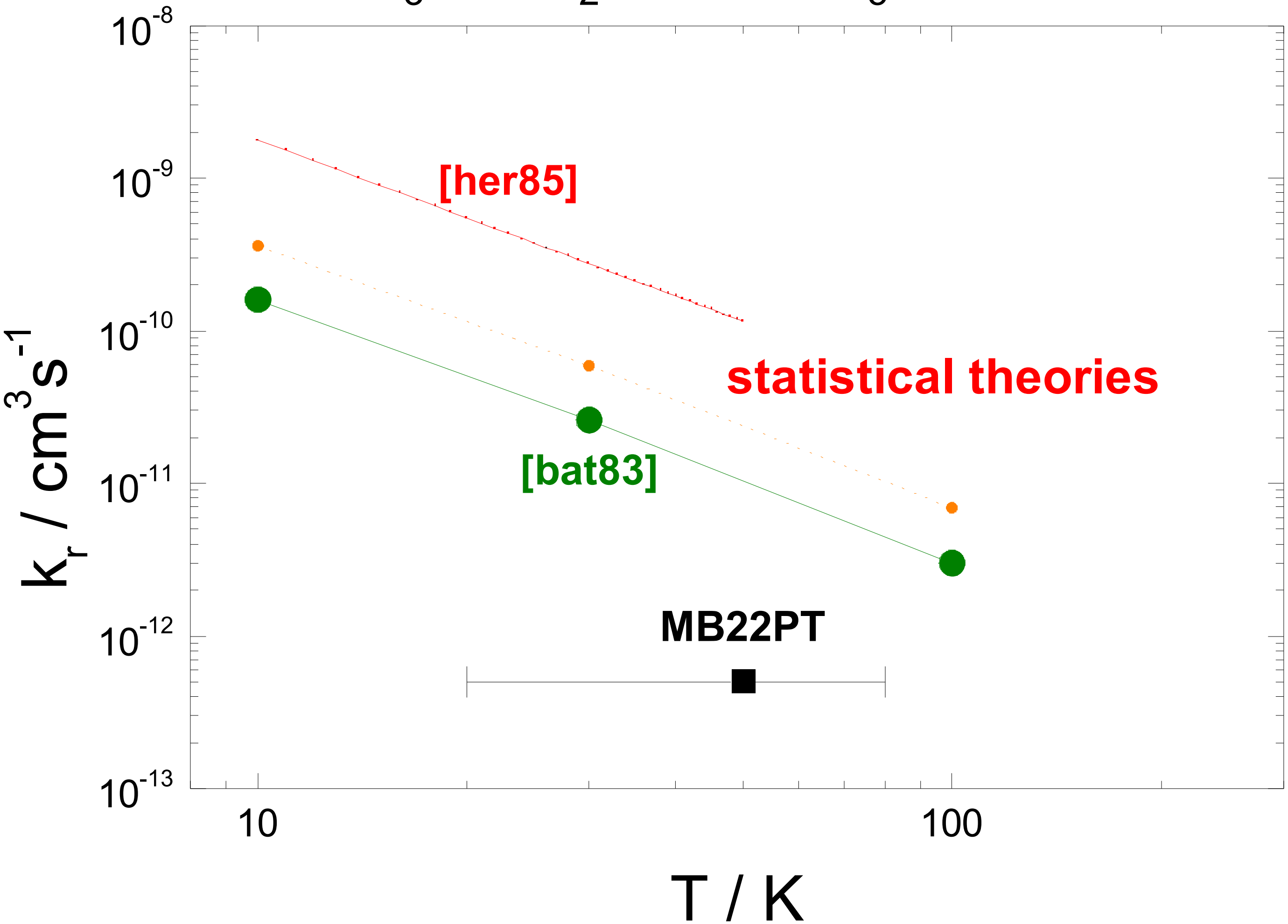
Density Dependence of Association Reaction

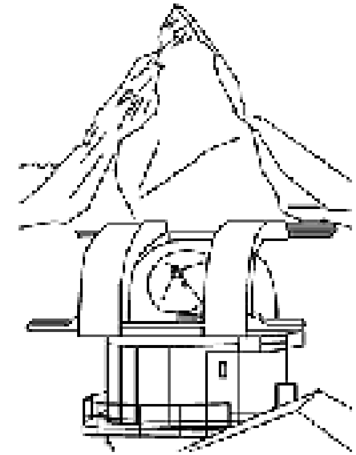


Radiative Association: k_r

Comparison to Statistical Theories

$$CH_3^+ + H_2O \rightarrow CH_5O^+ + h\nu$$





Laboratory Studies of Astrophysical Reactions

Stephan Schlemmer

WHAT?	More Examples of Important Reactions Negative Temperature Dependence Isomerisation Isotopic fractionation
WHY?	Identification of Species Formation and Destruction
HOW?	Experimental Techniques (Laboratory work)