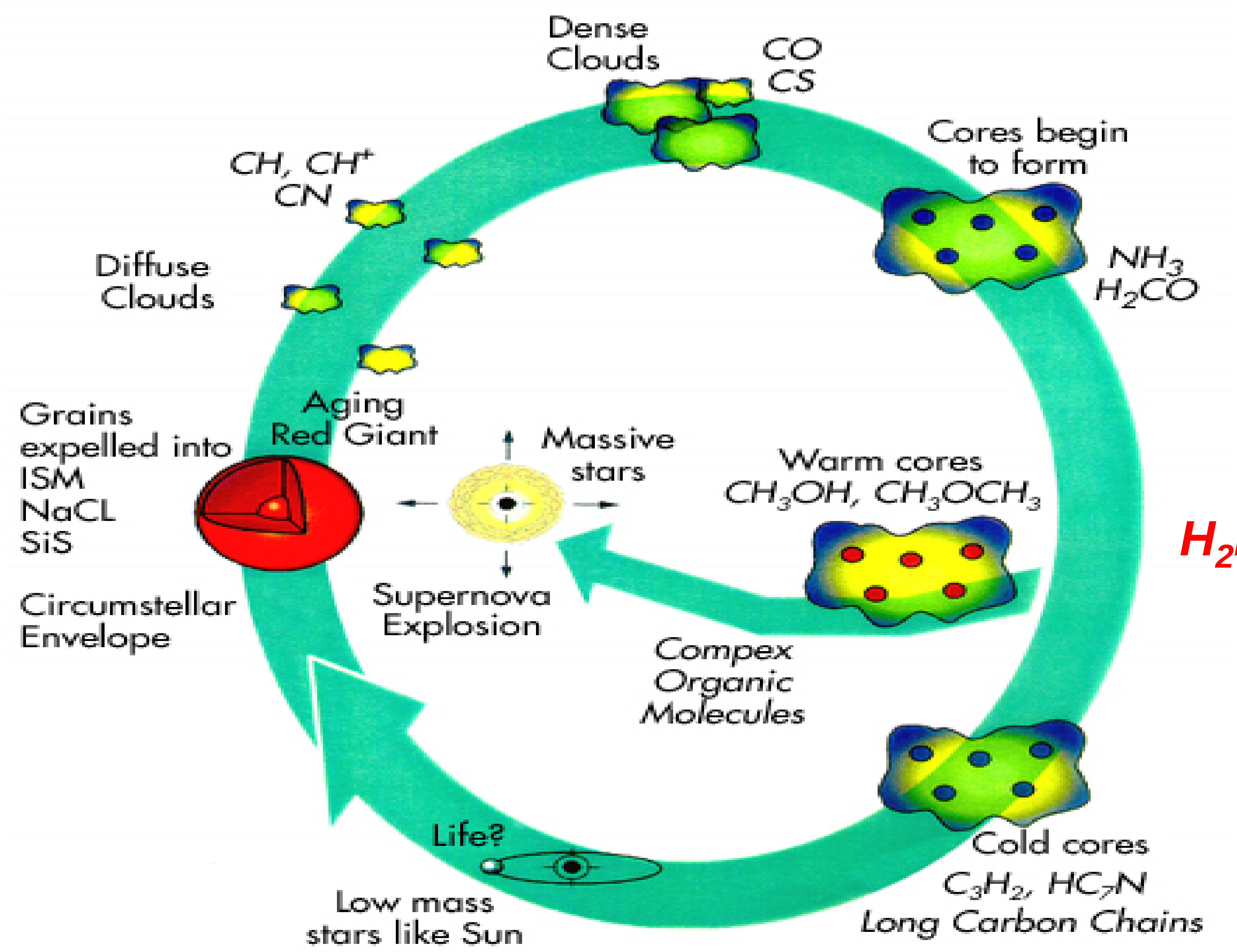
Cold Chemistry in Space and Laboratory

Stephan Schlemmer
Universität zu Köln

- H_2 Formation, OPR and Chemical Clocks
- H_3^+ / H_2D^+ Isotopic Fractionation, H_3^+/H_2D^+, OPR
- $H_2D^+ + H_2$ THz Spectroscopy in Lab and Space

Life cycle of Stars

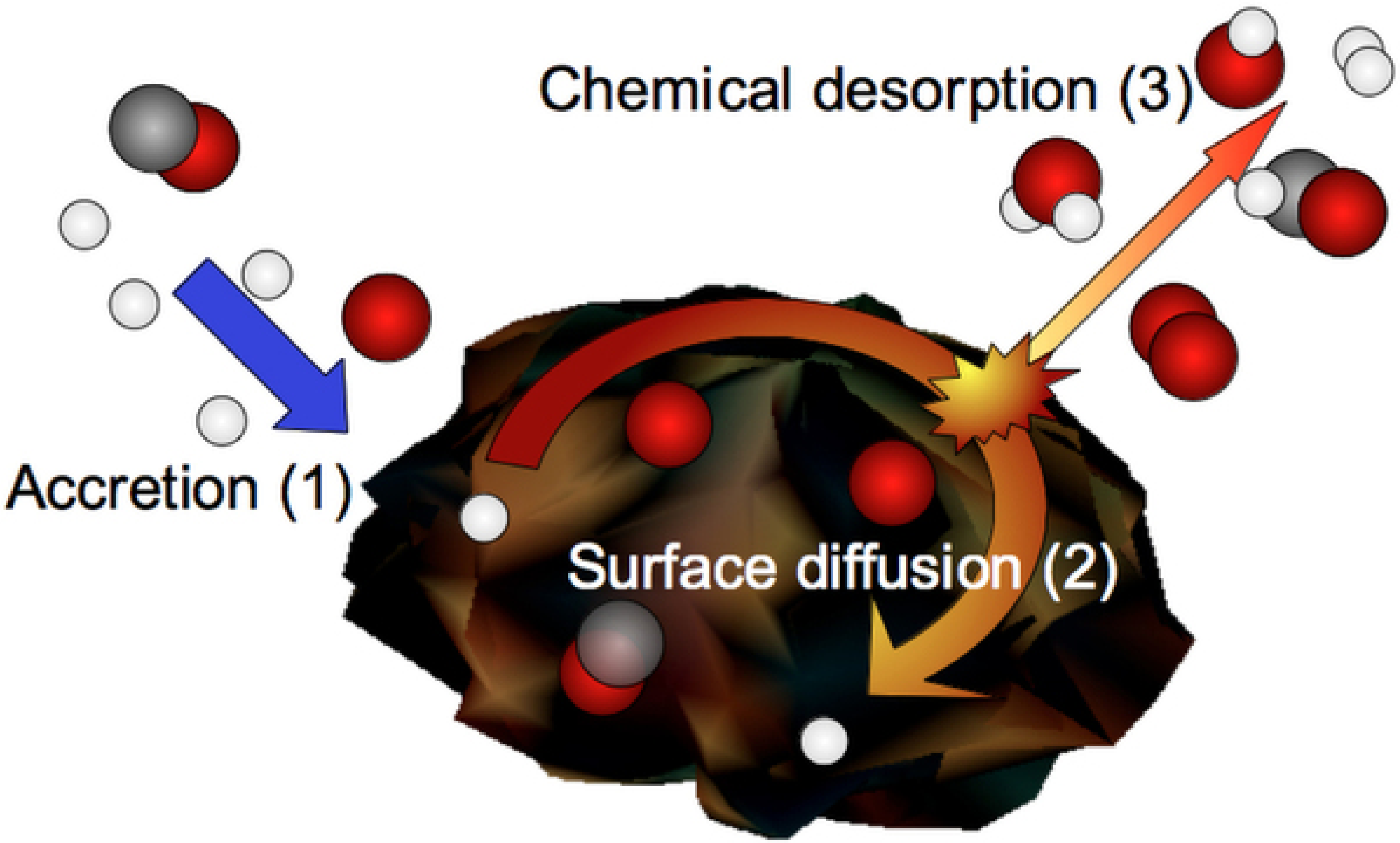


H_2D^+

http://herschel.jpl.nasa.gov

Hydrogen Formation on Grain Surfaces

$$H + H + g \rightarrow H_2 + g$$

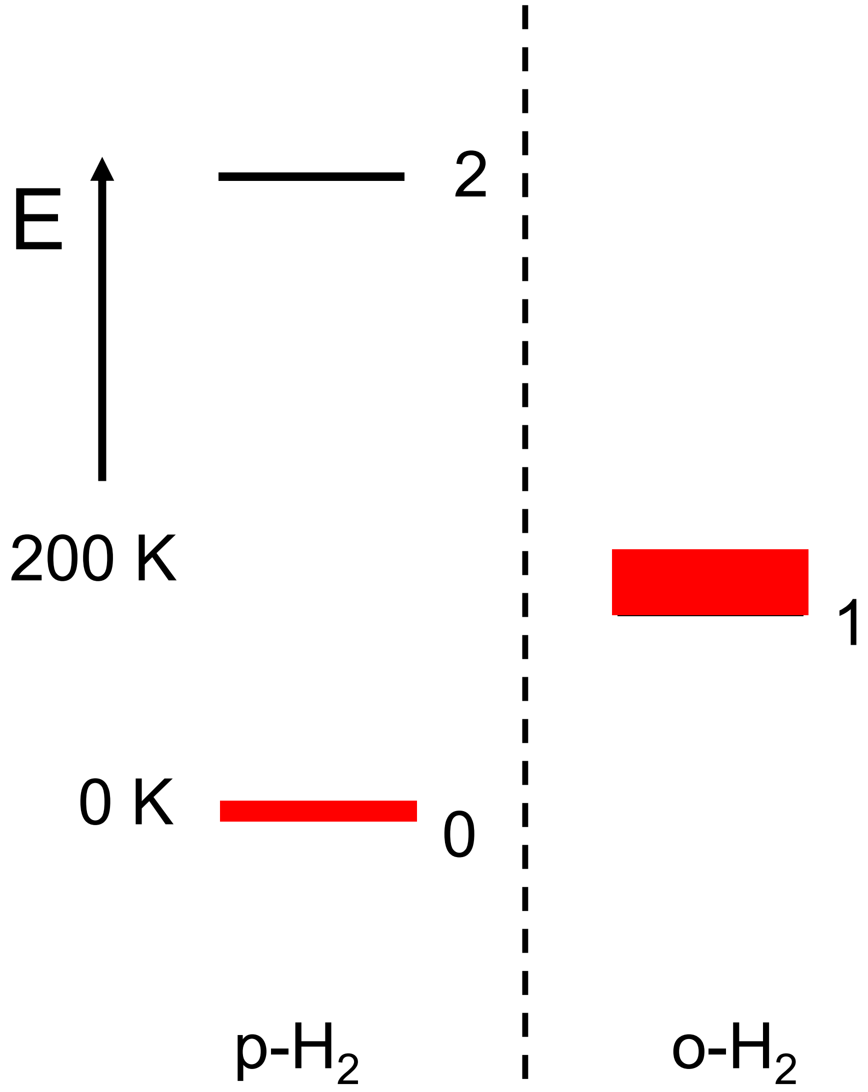


Symmetry considerations and Pauli Principle

$$\Psi_{tot} = \Psi_{el} \cdot \Psi_{vib} \cdot \Psi_{rot} \cdot \Psi_{nuc}$$

para	even J = 0	↑↓ - ↑↓	a
ortho	odd J = 1	↑↑ ↑↓ + ↑↓ ↓↓	s

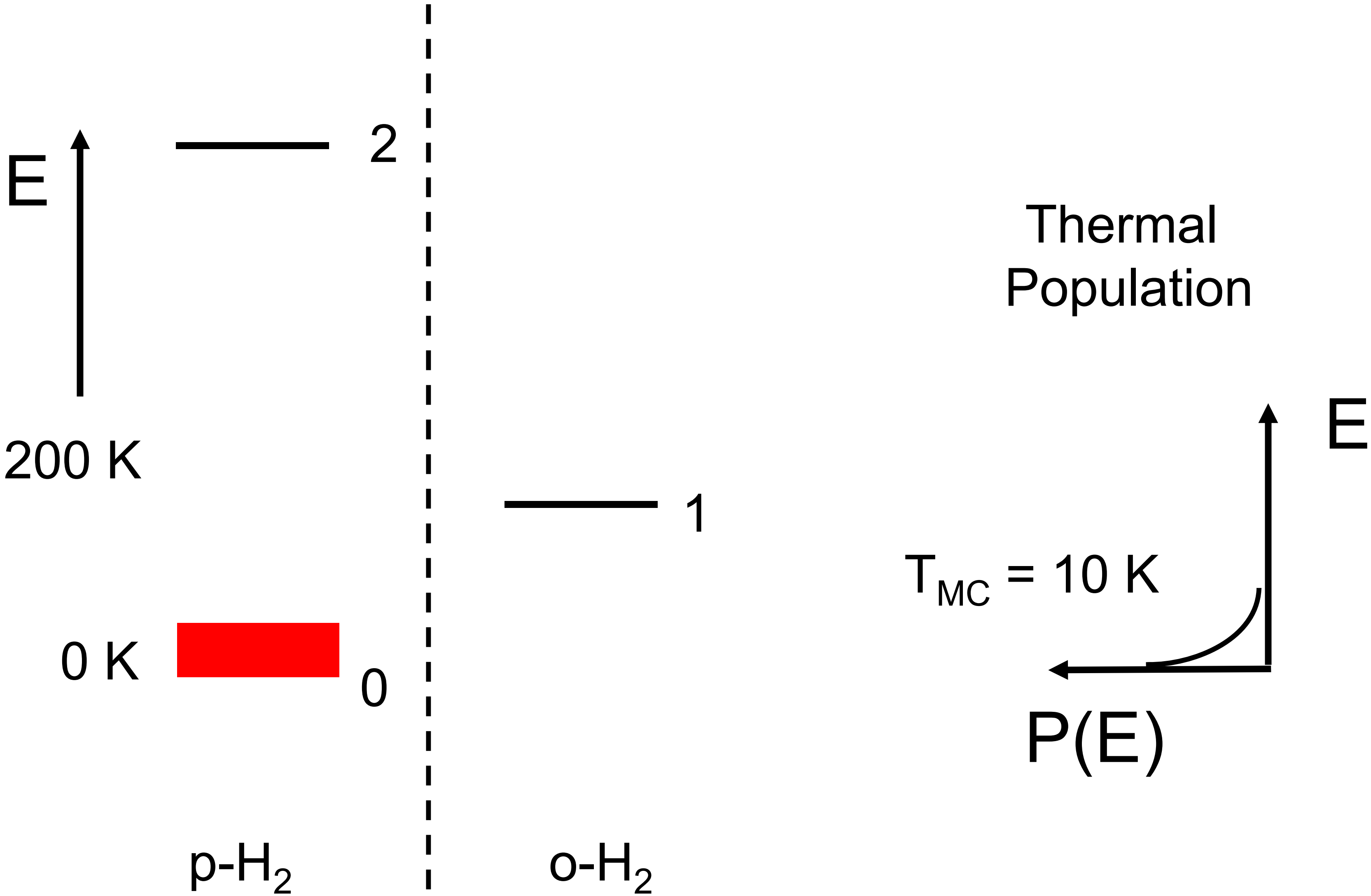
Lowest Rotational States of H_2



Statistical
&
Thermal
Population

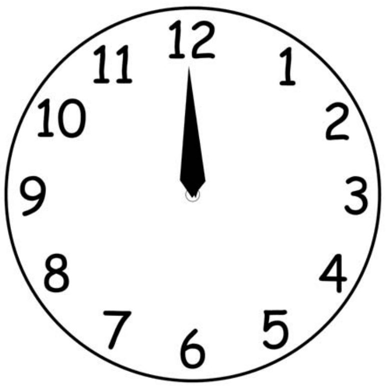
ortho / para ratio
3 : 1

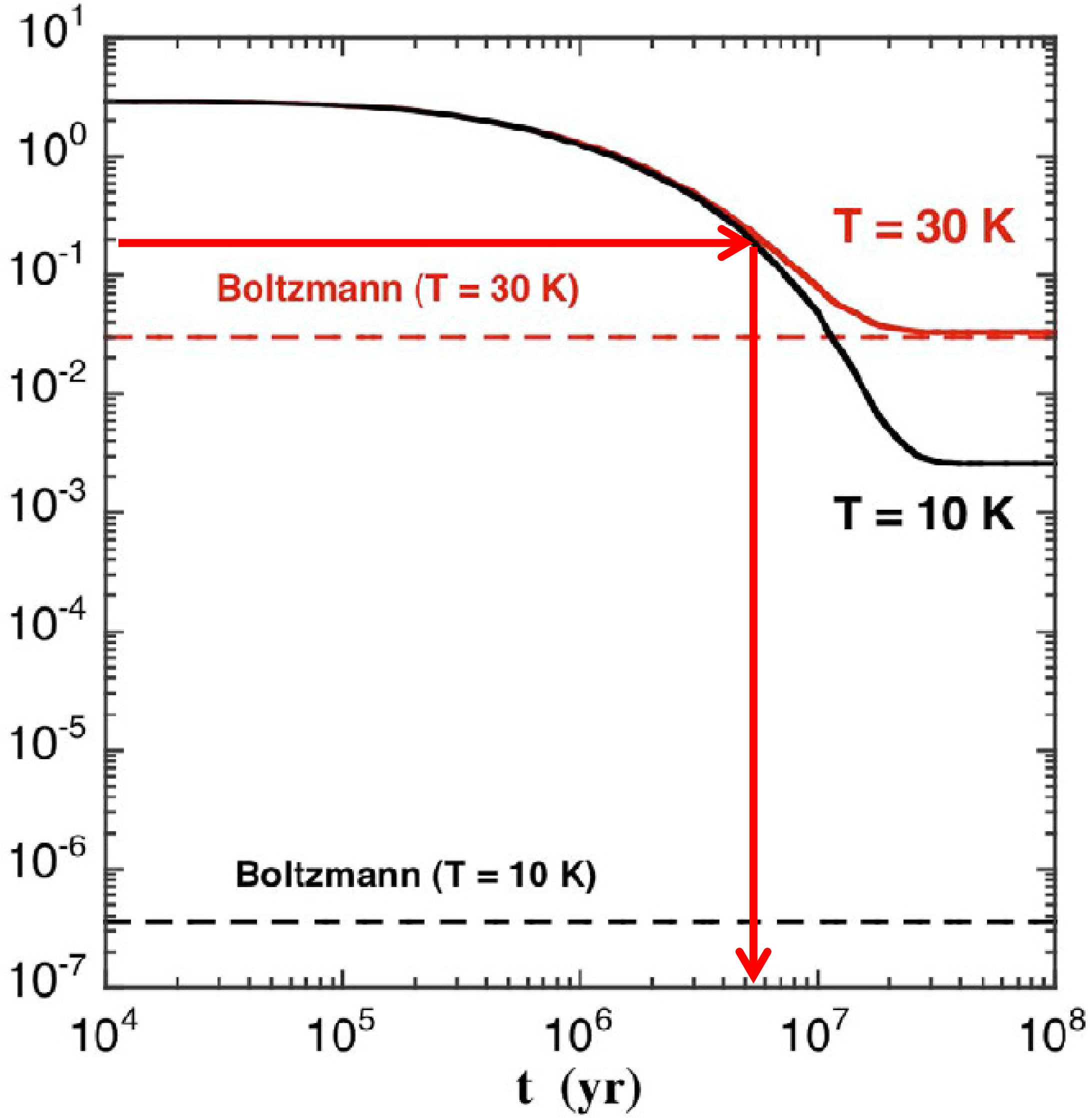
Lowest Rotational States of H_2



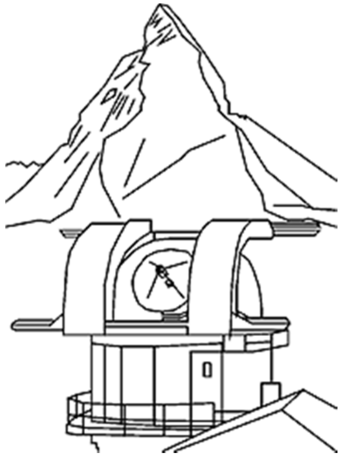
Chemical Clock

o/p H_2





Flower et al. A&A,**449**,621, 2006



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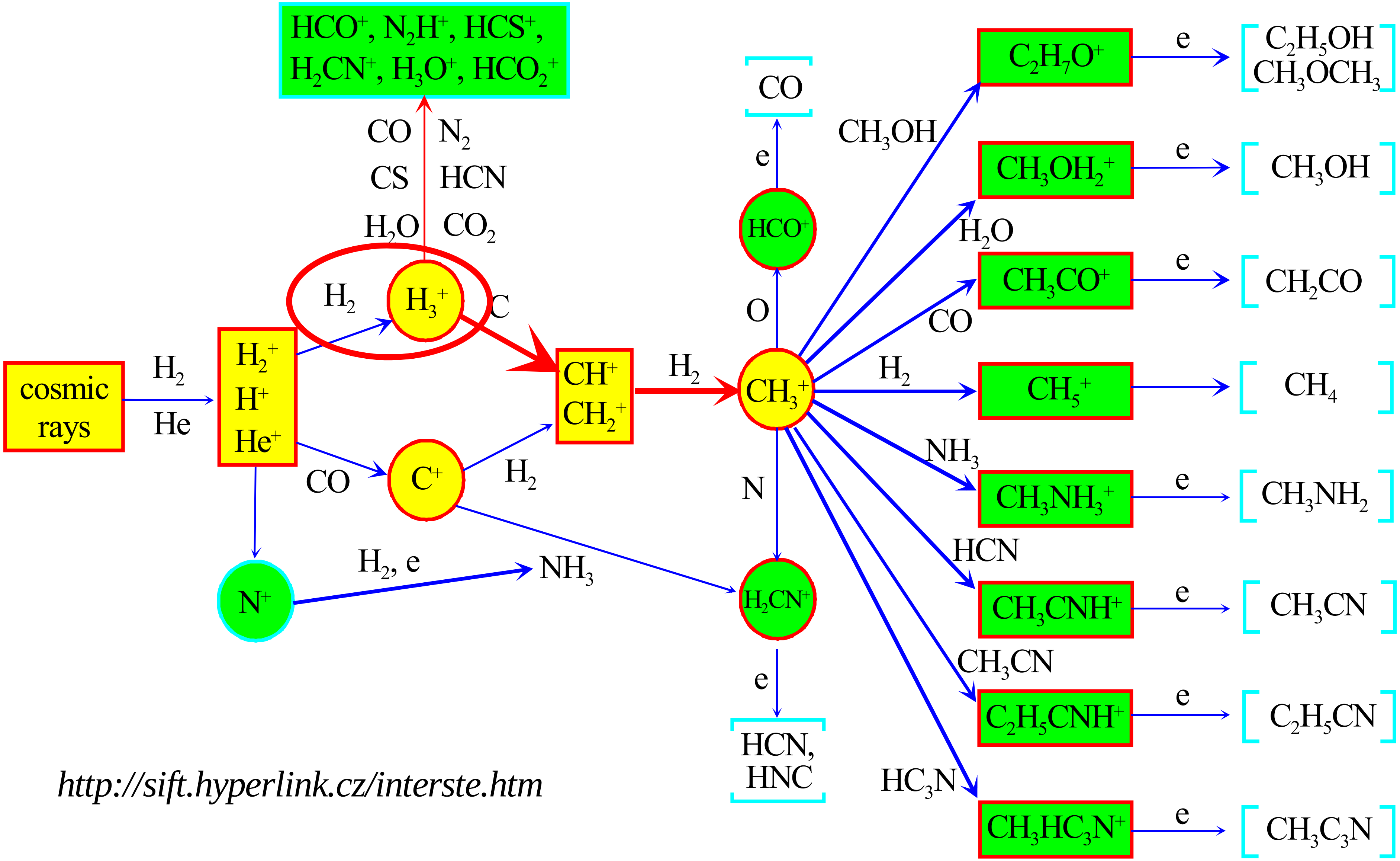
Initial Reactions in Dense Interstellar Clouds



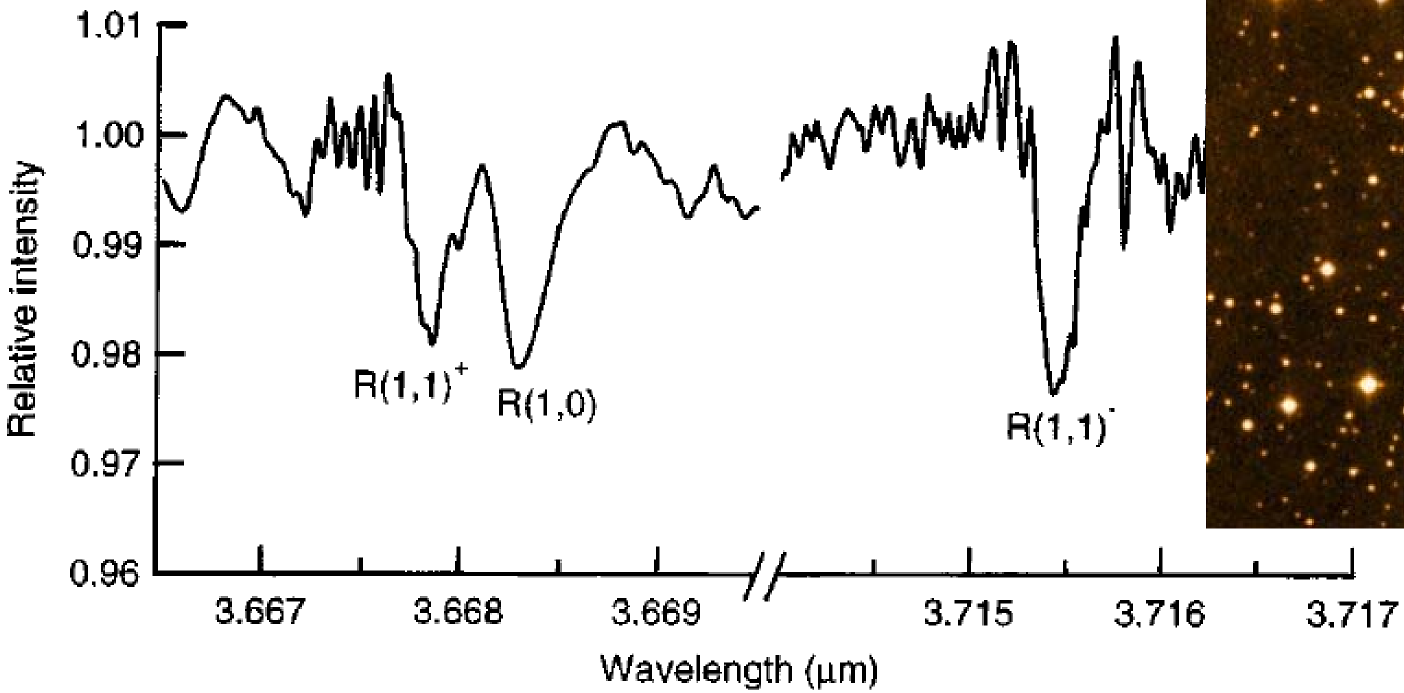
D. Smith and P. Spanel, Mass Spectrometry Reviews, 14 (1995) 255-278.

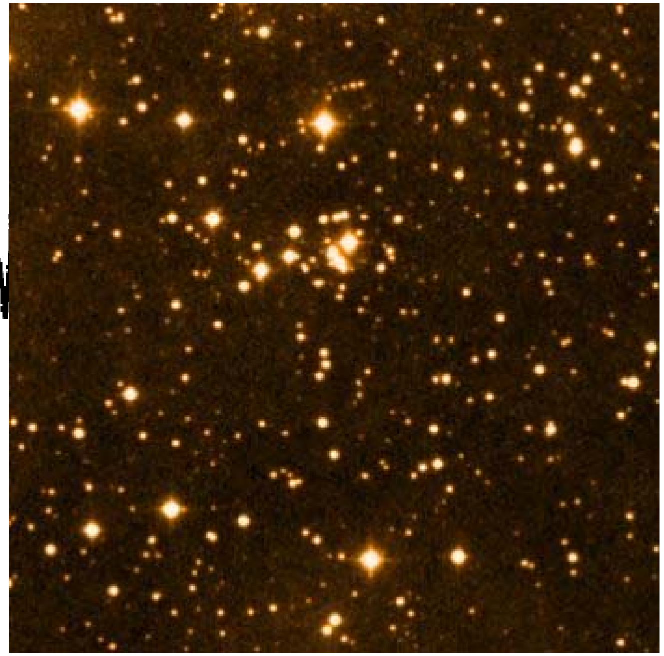
Detection of H_3^+ in the Diffuse Interstellar Medium Toward Cygnus OB2 No. 12

B. J. McCall,* T. R. Geballe, K. H. Hinkle, T. Oka

$$H_2 + c.r. \rightarrow H_2^+ + c.r. + e^-$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$





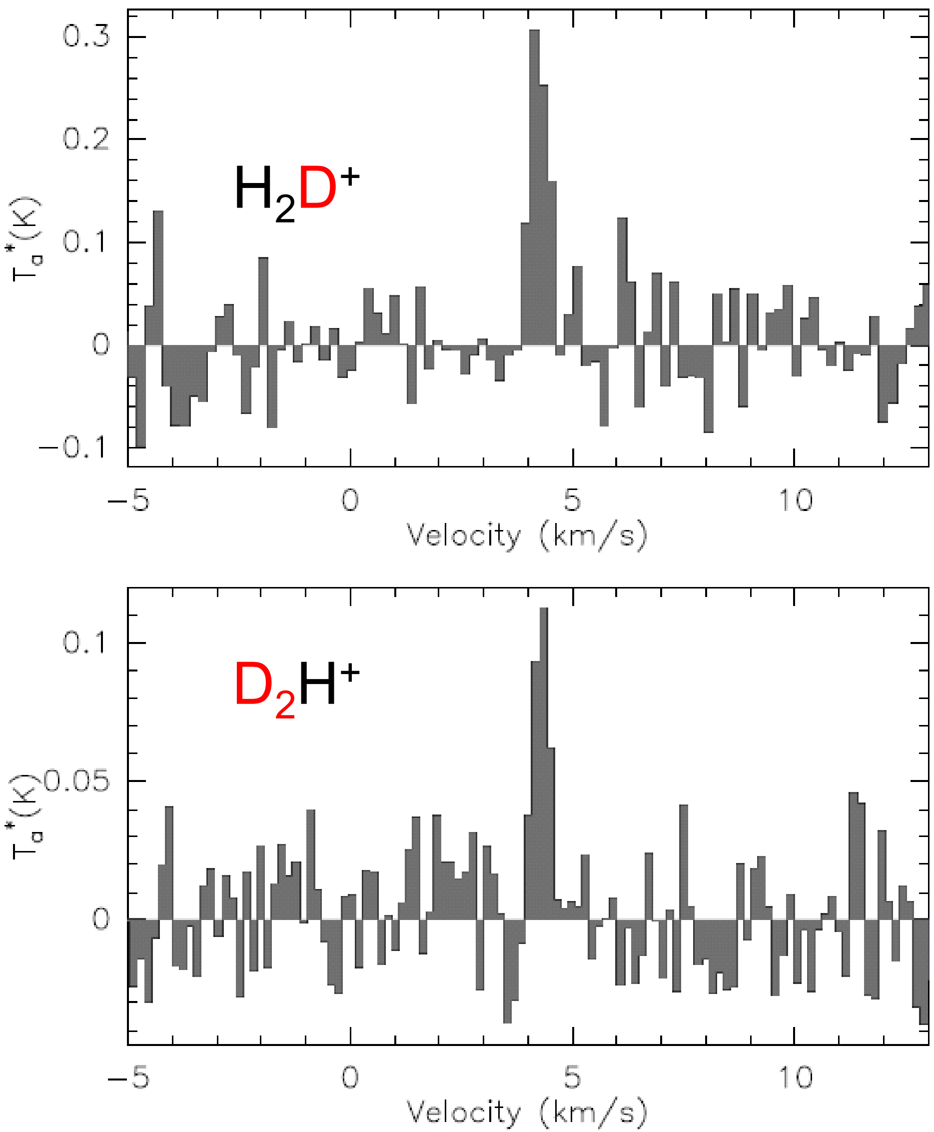
SCIENCE • VOL. 279 • 20 MARCH 1998

Isotopic Fractionation

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

E. Hugo, O. Asvany and S. Schlemmer, *J. Chem. Phys.* **130**, Art.-No. 164302 (2009)

Deuterated Molecules in Interstellar Medium



Cosmic [D]/[H] ~ $1.5 \cdot 10^{-5}$

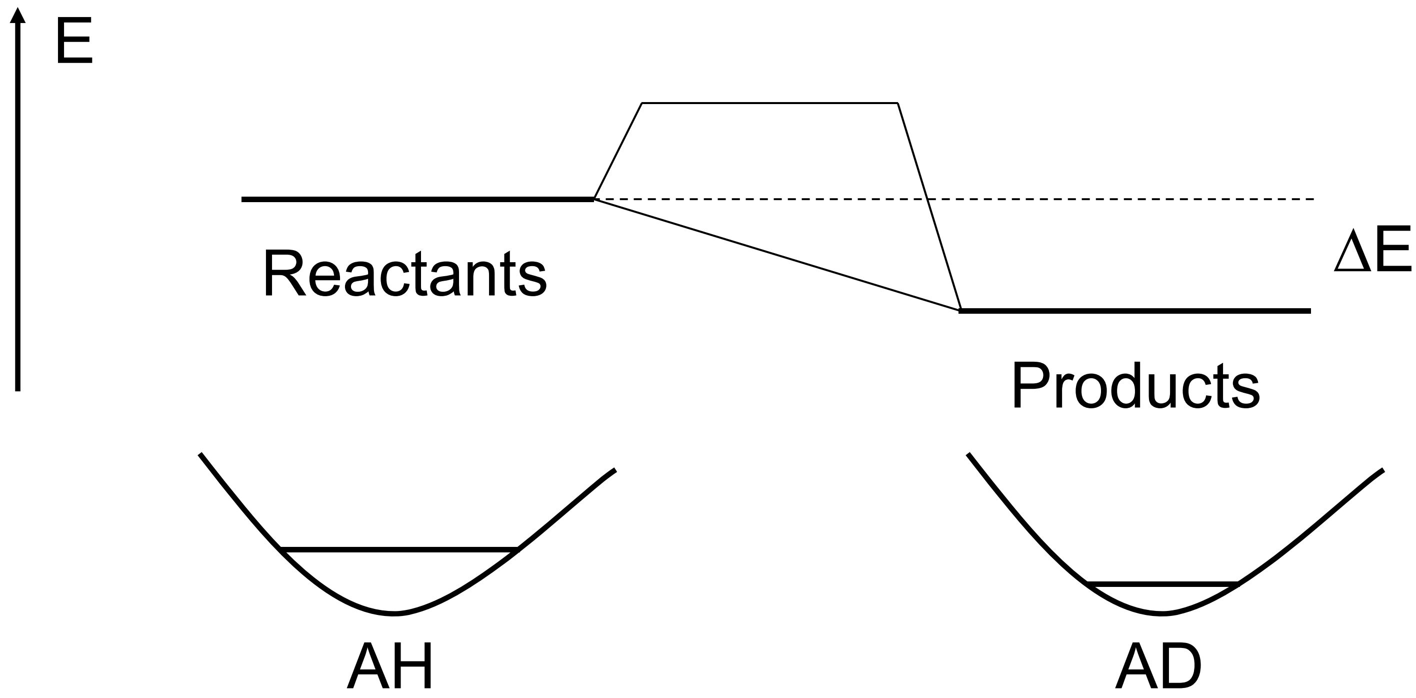
Deuteriumreservoir

[HD]/[H_2] ~ $3.0 \cdot 10^{-5}$

Isotope Enrichment
[AD]/[AH] ~ **0.1**

B. Parise, A. Belloche, F. Du, R. Güsten and K. Menten, A&A **526**, A31 (2011)
C. Vastel and T.G: Phillips, APJ, **606**, L127 (2004)

Primary Deuteration Reactions



$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2 + 232\ K$$

$$CH_3^+ + HD \rightleftharpoons CH_2D^+ + H_2 + 375\ K$$

$$C_2H_2^+ + HD \rightleftharpoons C_2HD^+ + H_2 + 550\ K$$

Isotopic Fractionation

Ideal Case – Laboratory Situation

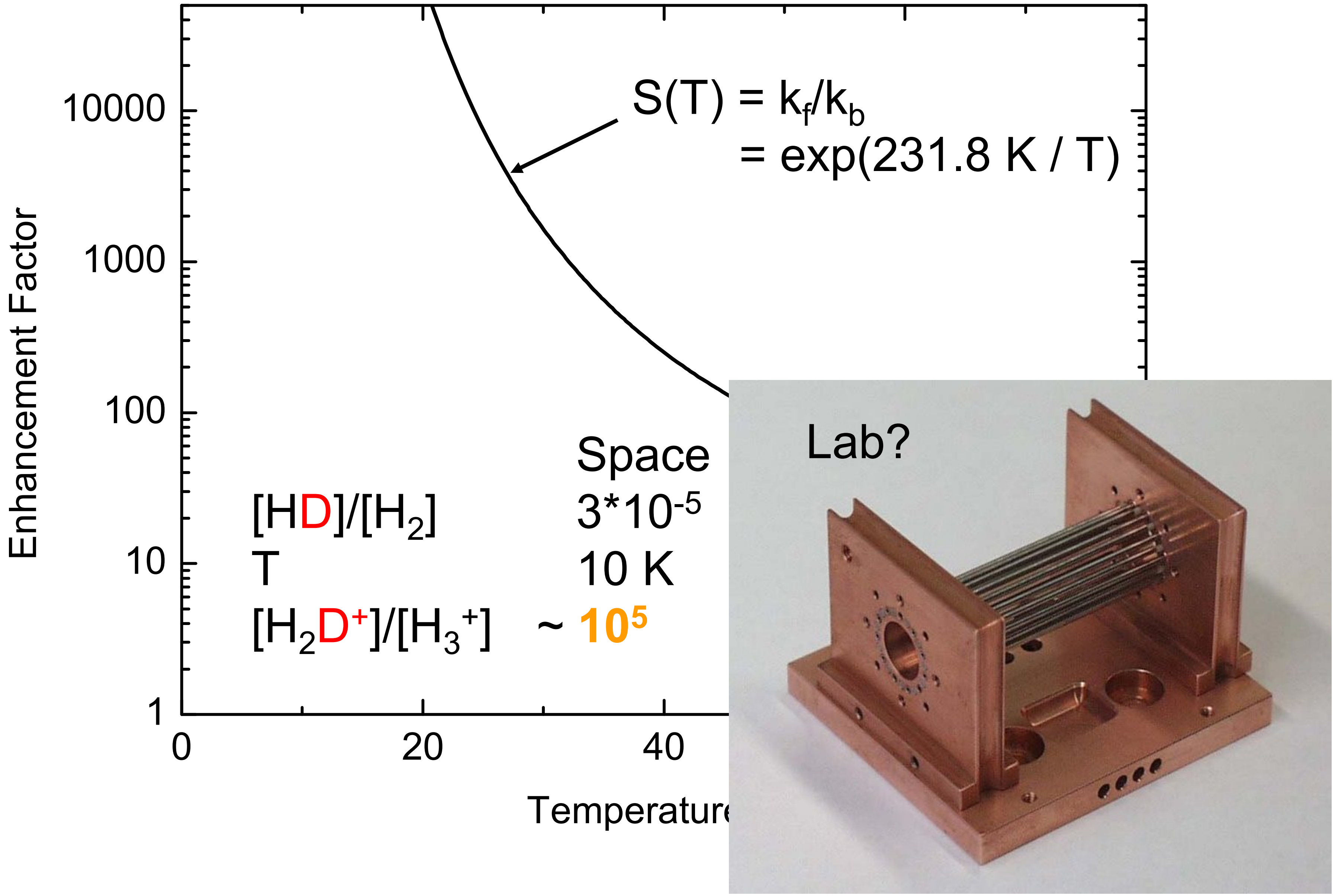
$$H_3^+ \underset{H_2}{\overset{HD}{\rightleftharpoons}} \mathbf{H_2D^+}$$

Equilibrium

$$[H_2D^+]/[H_3^+] = S(T)\ [HD]/[H_2]$$

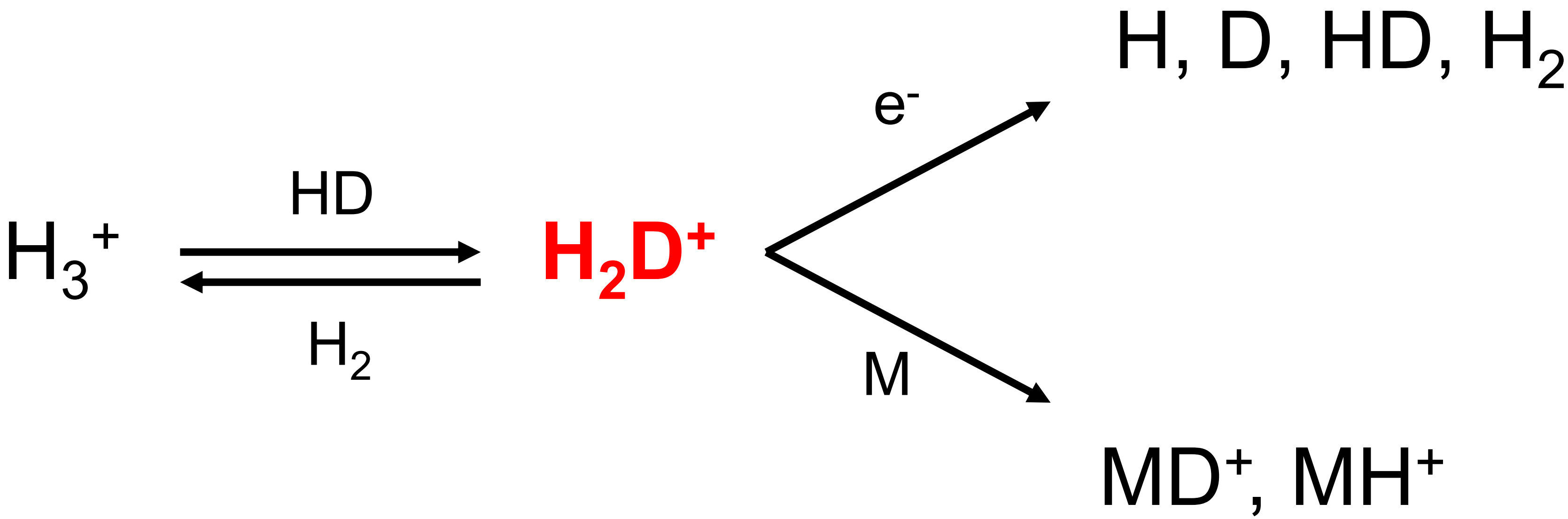
$$S(T) = k_f/k_b$$

Isotopic Fractionation



Isotopic Fractionation

Cloud Model

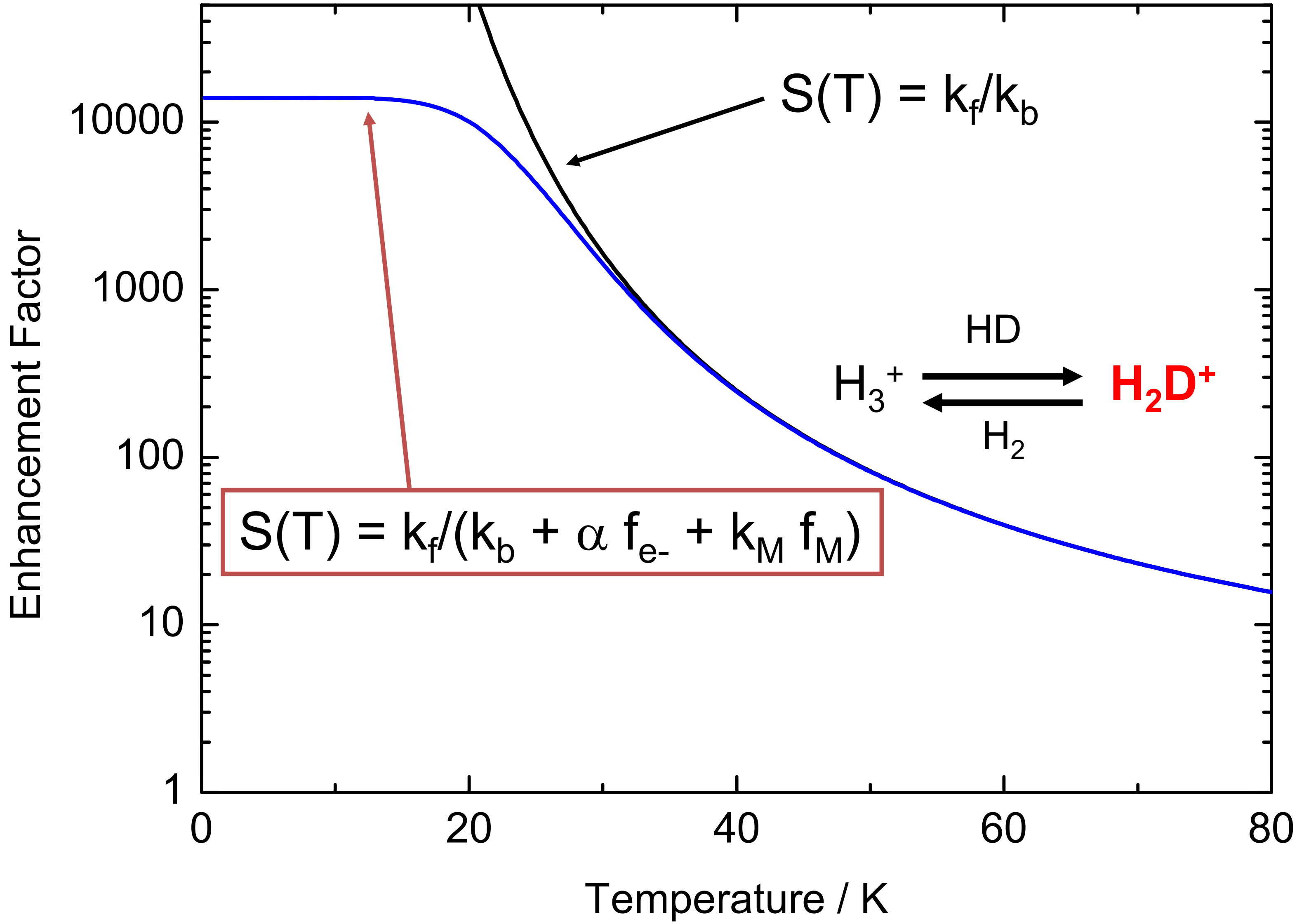


Equilibrium

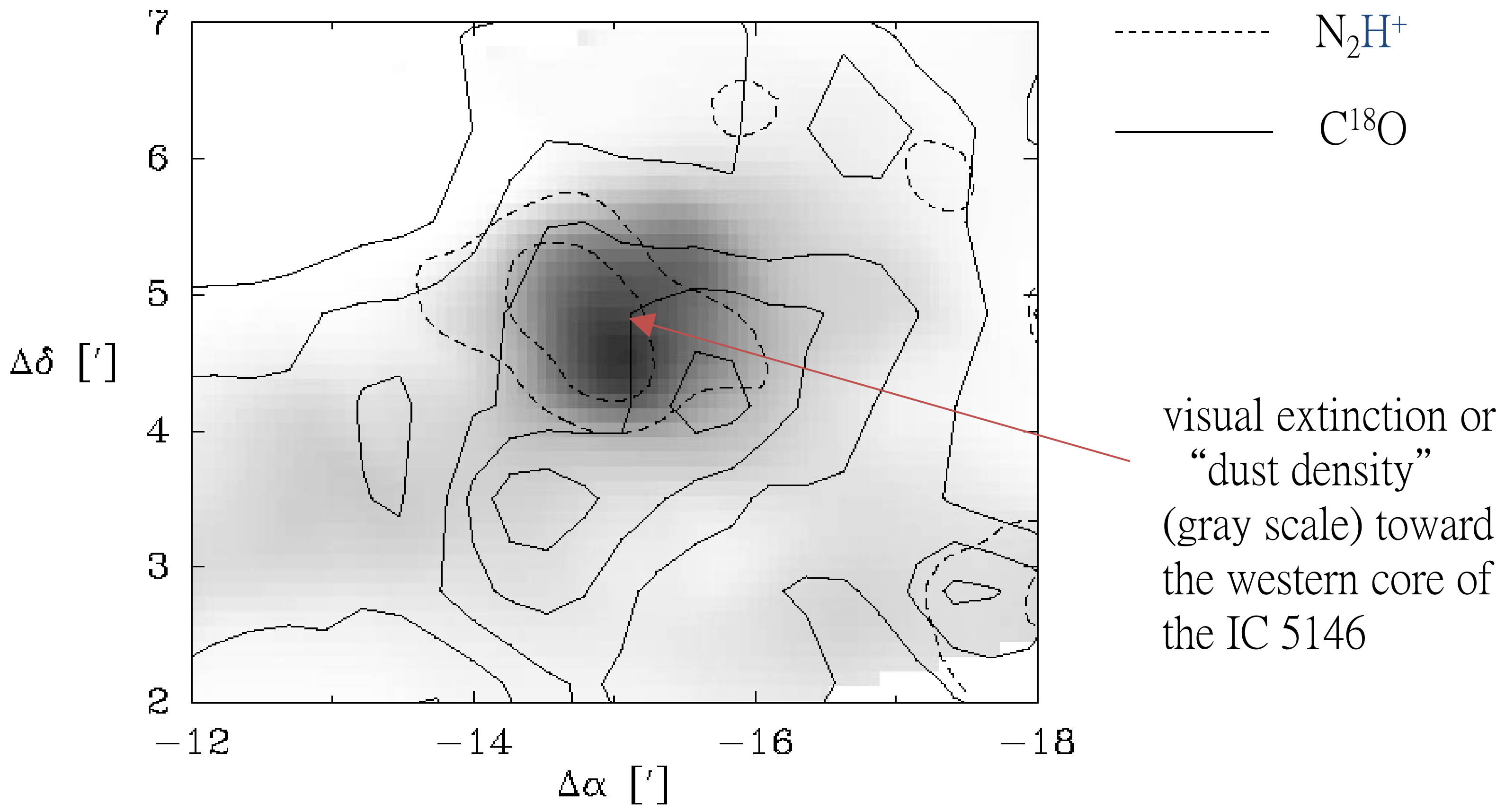
$$[H_2D^+]/[H_3^+] = S(T)\ [HD]/[H_2]$$

$$S(T) = k_f/(k_b + \alpha\ f_{e-} + k_M\ f_M)$$

Isotopic Fractionation

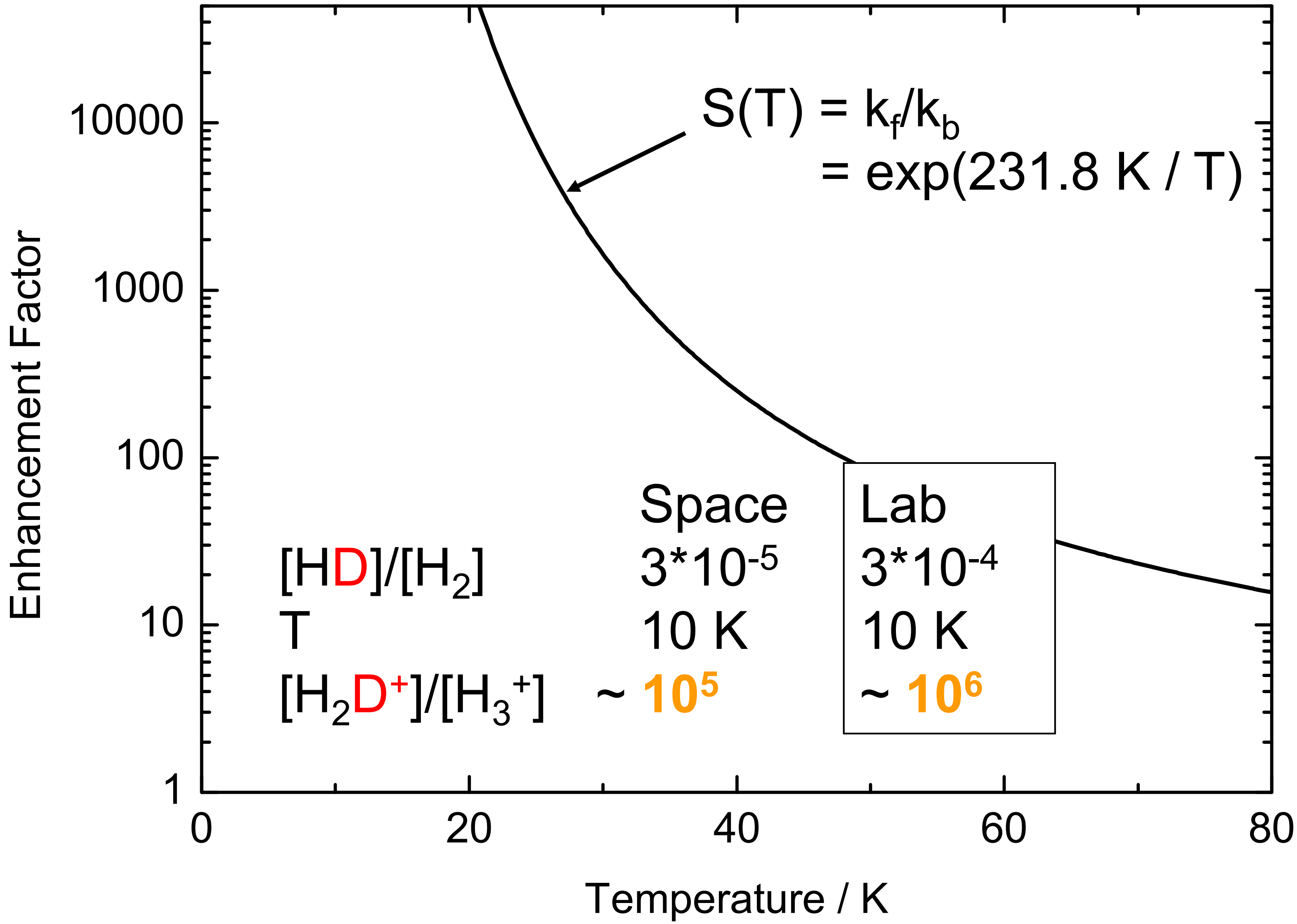


Astrophysical Observations



Bergin et al. The Astrophysical Journal, 557:209-229, 2001

Isotopic Fractionation



Deuteration of H_3^+

$$H_3^+ \underset{H_2}{\overset{HD}{\rightleftharpoons}} H_2D^+$$

Theory (Thermodynamics)

$[HD]/[H_2]$	$3*10^{-4}$
T	10 K
S(T)	$3.6*10^{9}$
$[H_2D^+]/[H_3^+]$	**10^{6}**

Experimental Method:

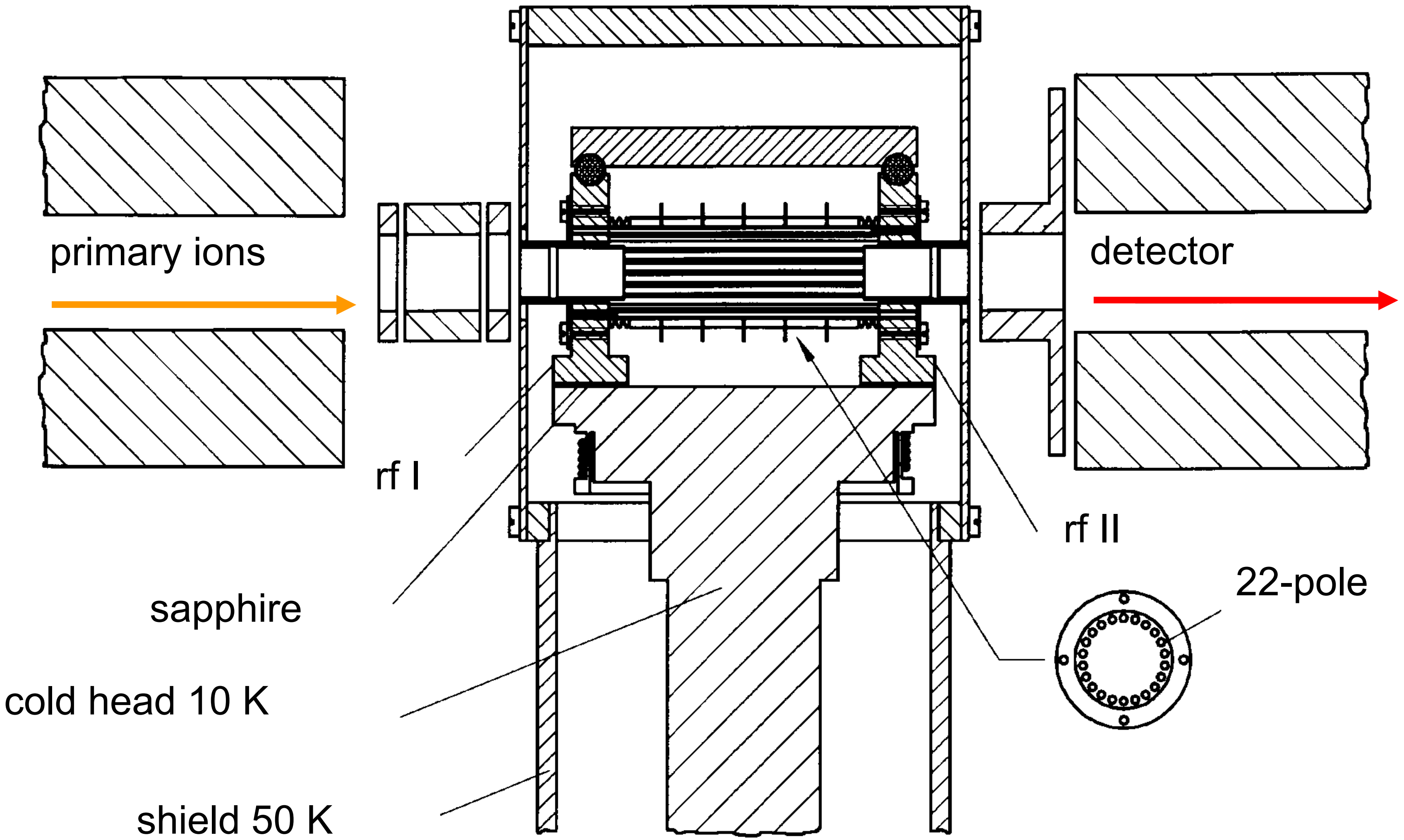
Electrodynamical Trapping

Sandra Brünken

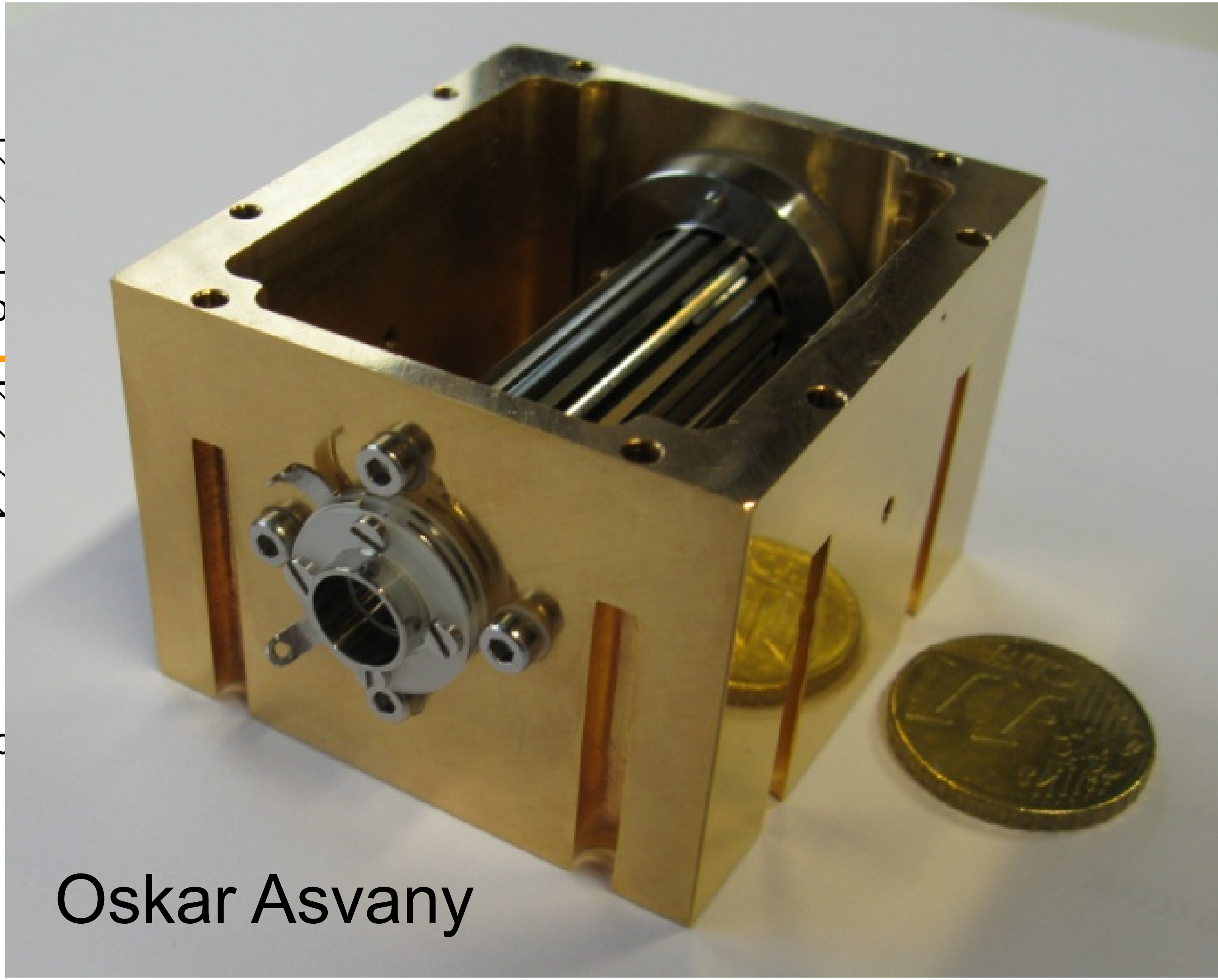
Dieter Gerlich

Oskar Asvany

22-Pole Low Temperature Ion Trap



22-Pole Low Temperature Ion Trap



p

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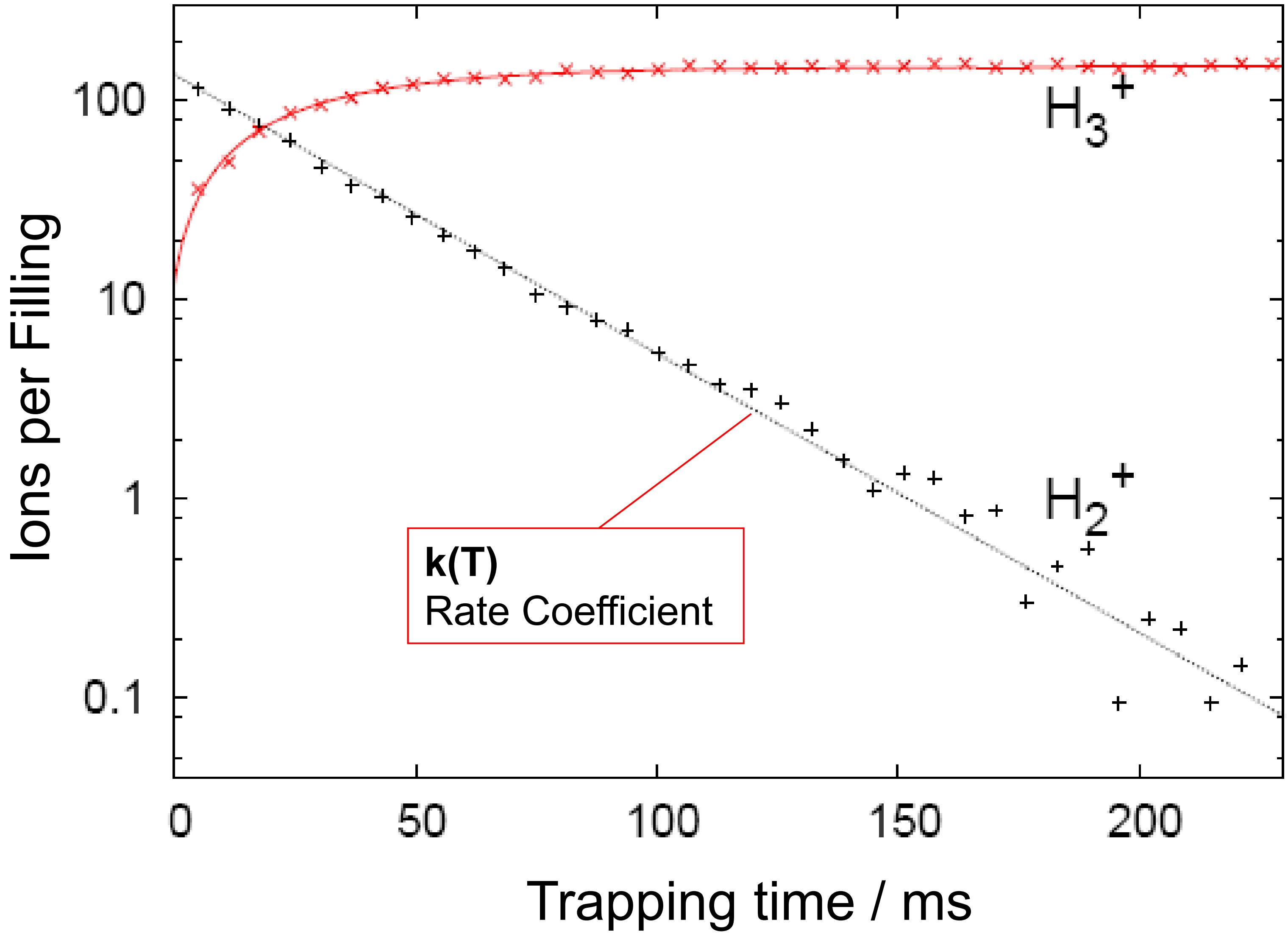
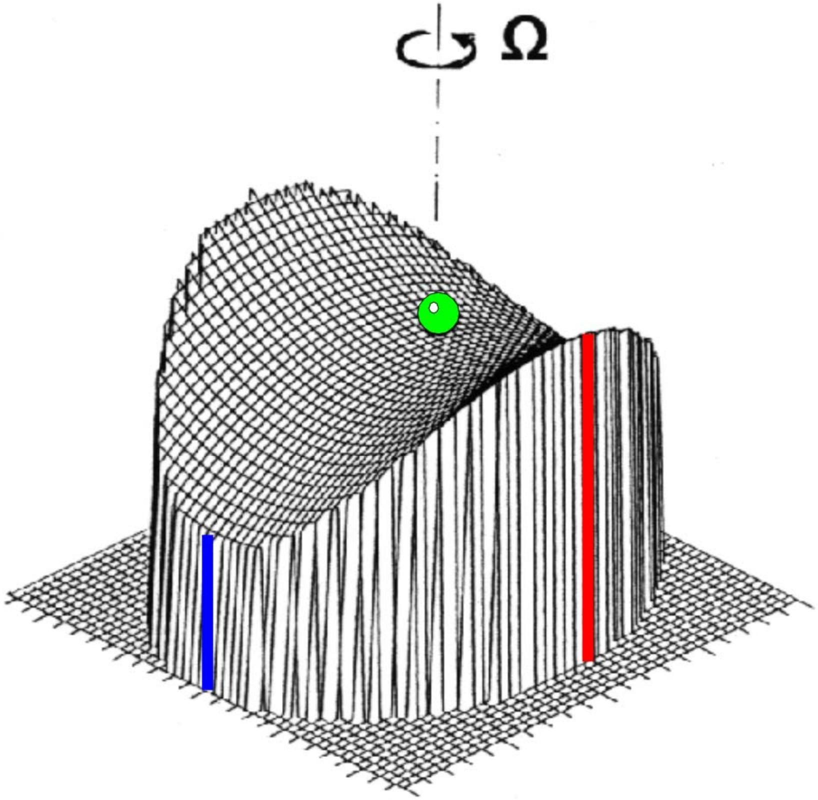
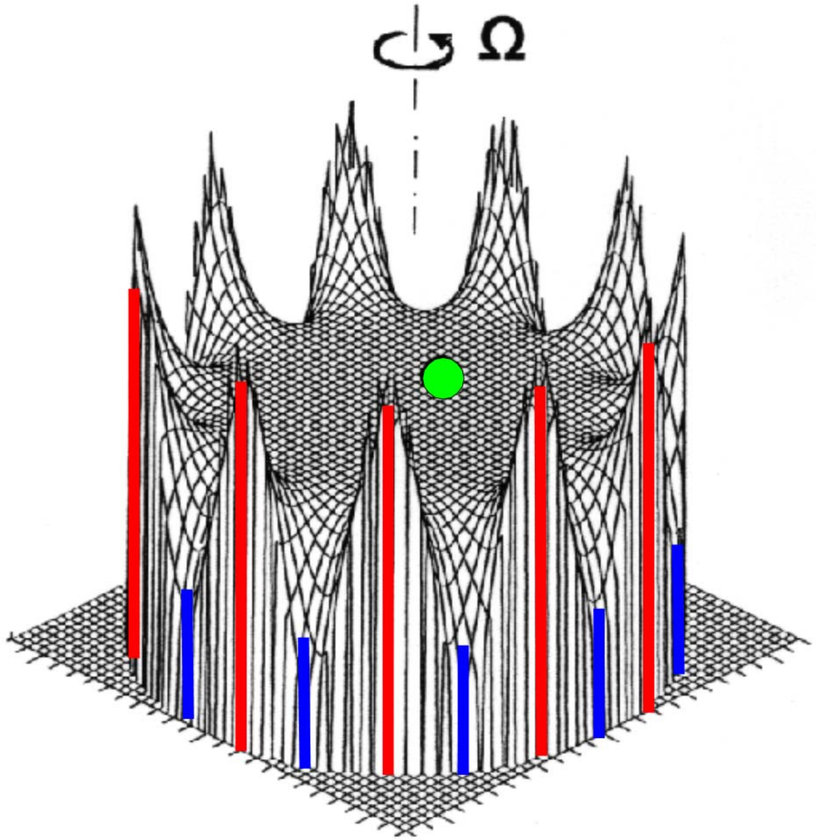
Example: $H_2^+ + H_2 \rightarrow H_3^+ + H$



RF Ion Traps
Mechanical Model



Quadrupole

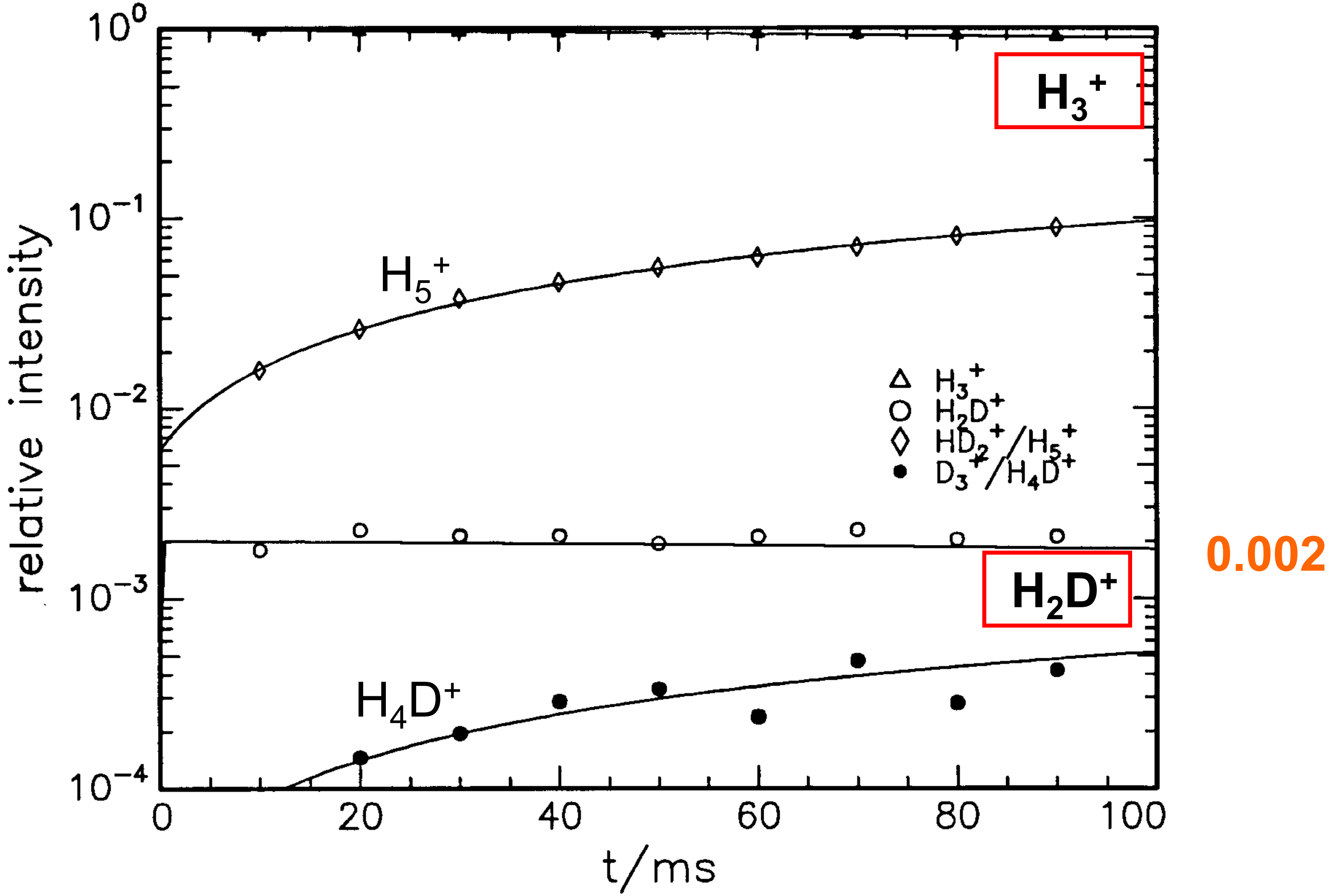


22-Pole

FAQ: Why 22 poles?

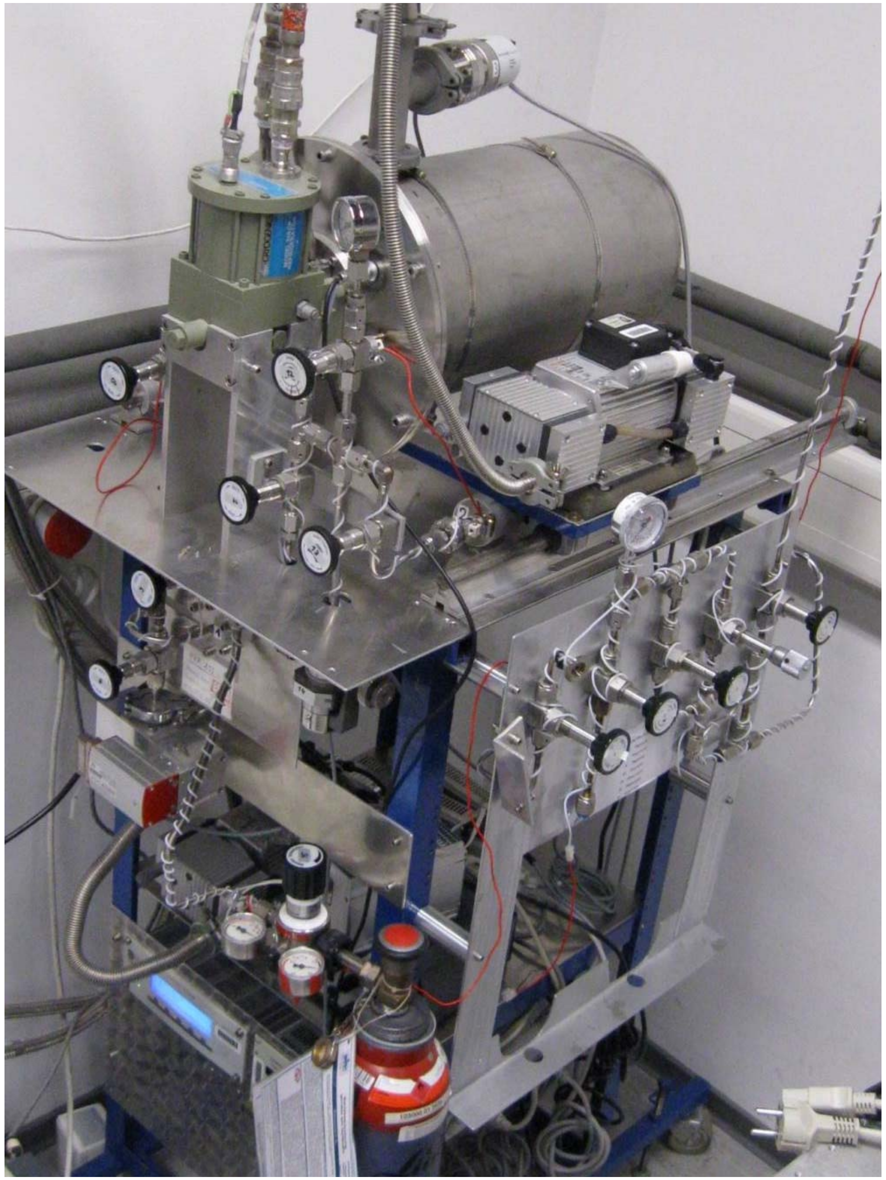
$H_3^+ + HD \Leftrightarrow H_2D^+ + H_2$

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

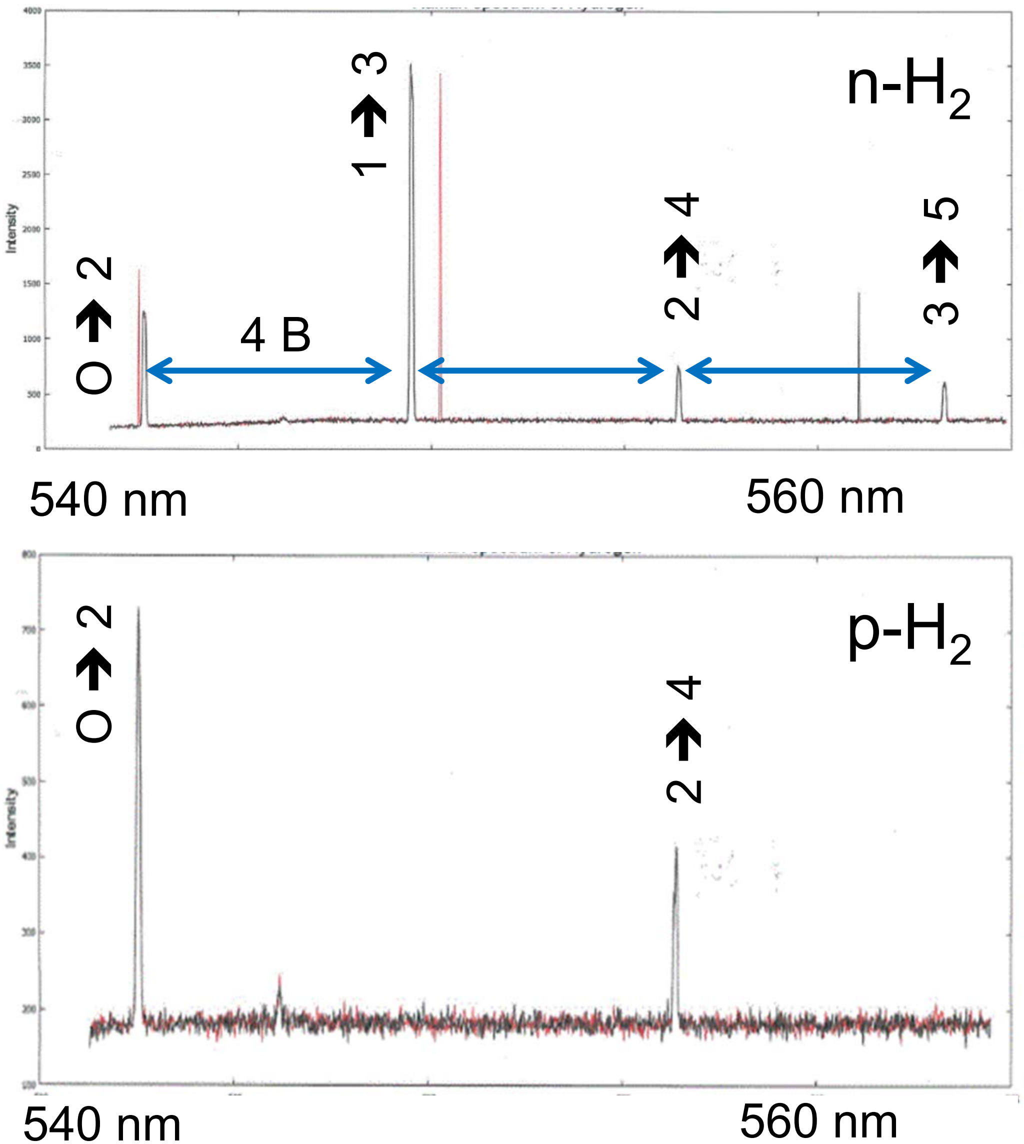


Gerlich, Herbst and Roueff, Planetary and Space Science **50**, 1291 (2002)

Current Experiments with para-H_2 (J=0,2,…)

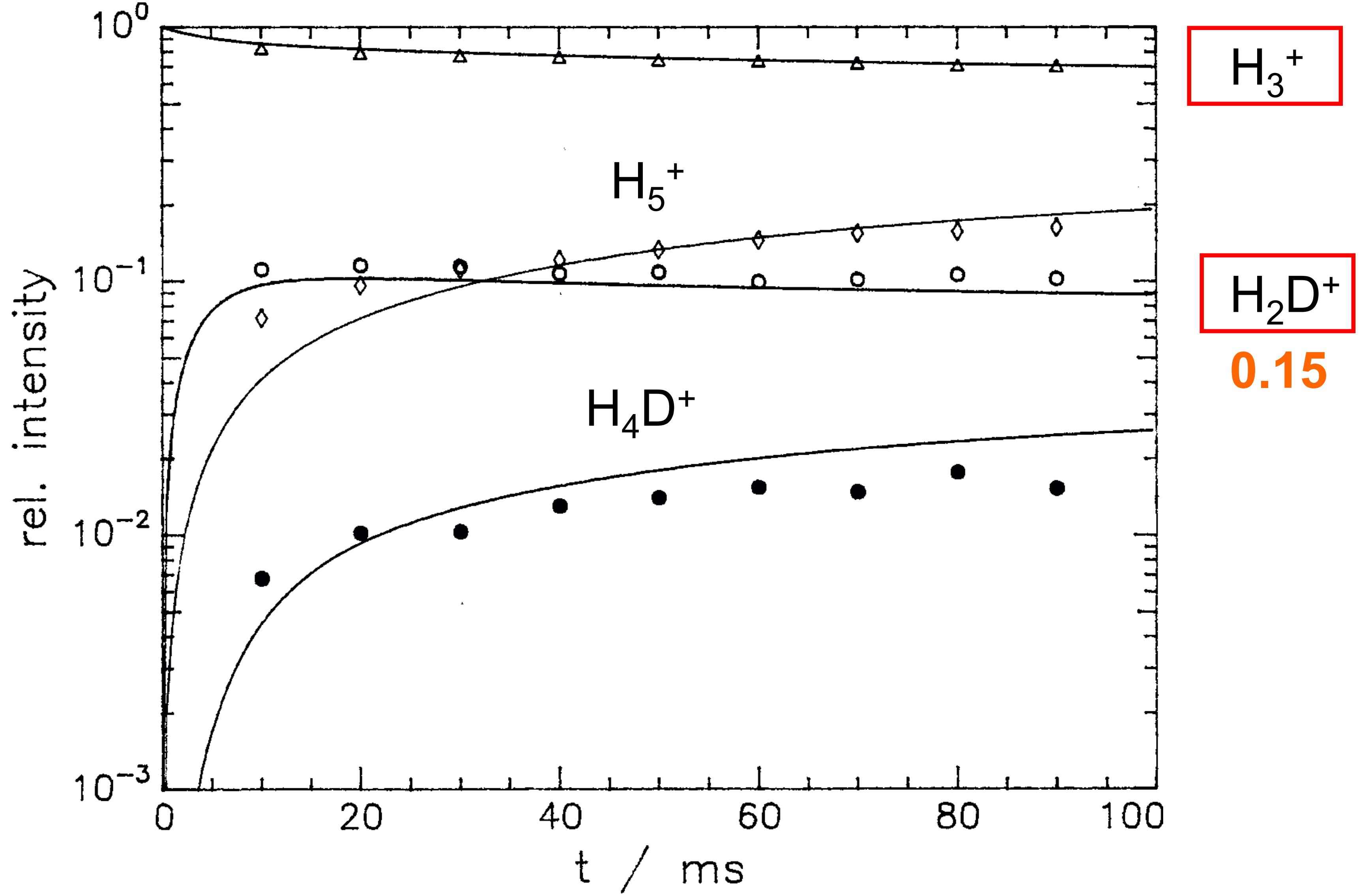


Raman Spectra



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

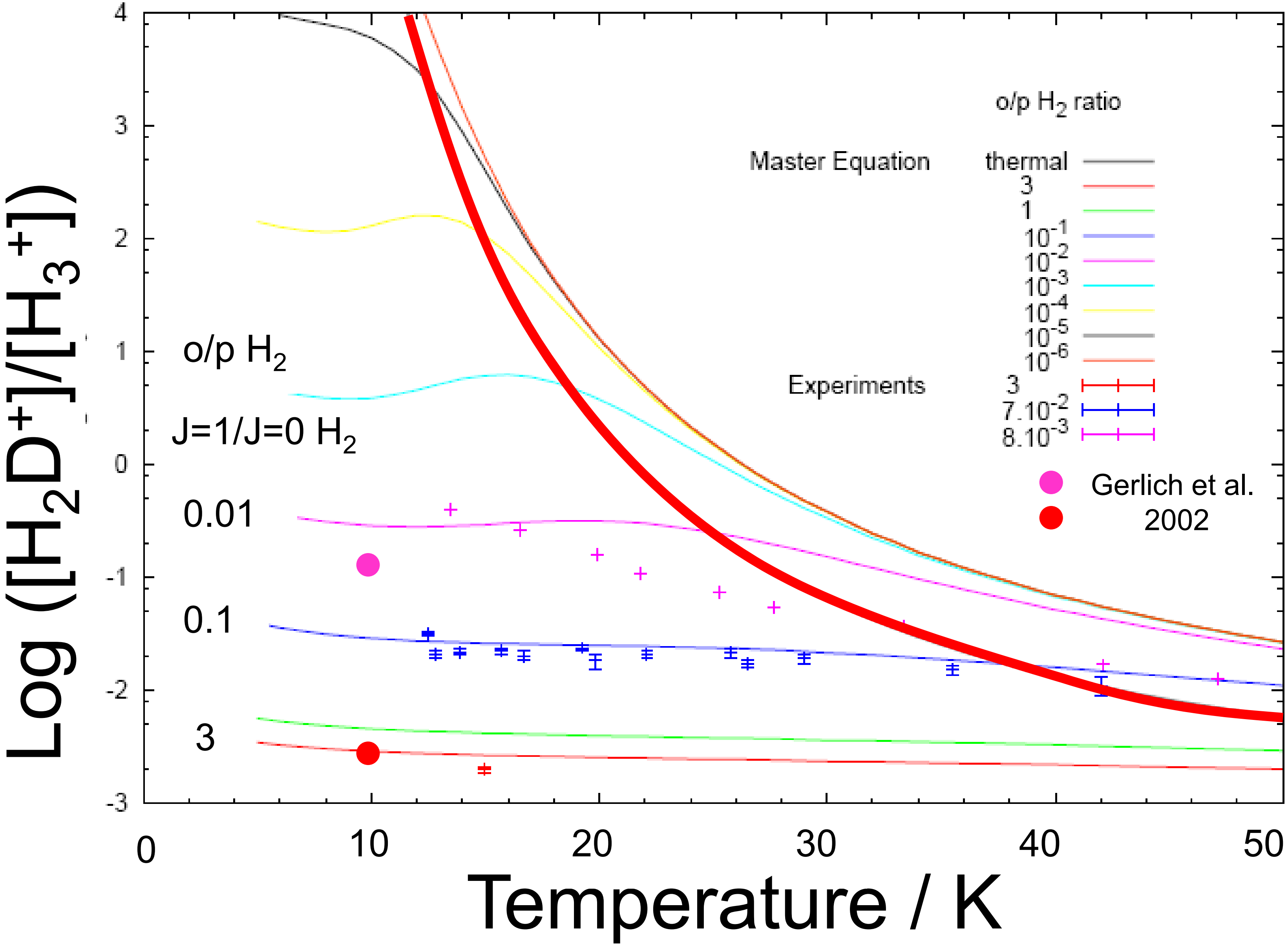
$[p\text{-}H_2] = 1x10^{14}\ cm^{-3}$, $[HD]/[H_2] = 3*10^{-4}$, $T = 10\ K$



Gerlich, Herbst and Roueff, Planetary and Space Science **50**, 1291 (2002)

Experimental Results & Modelling

Hugo et al., J.Chem.Phys. 2009, **130,** 164302

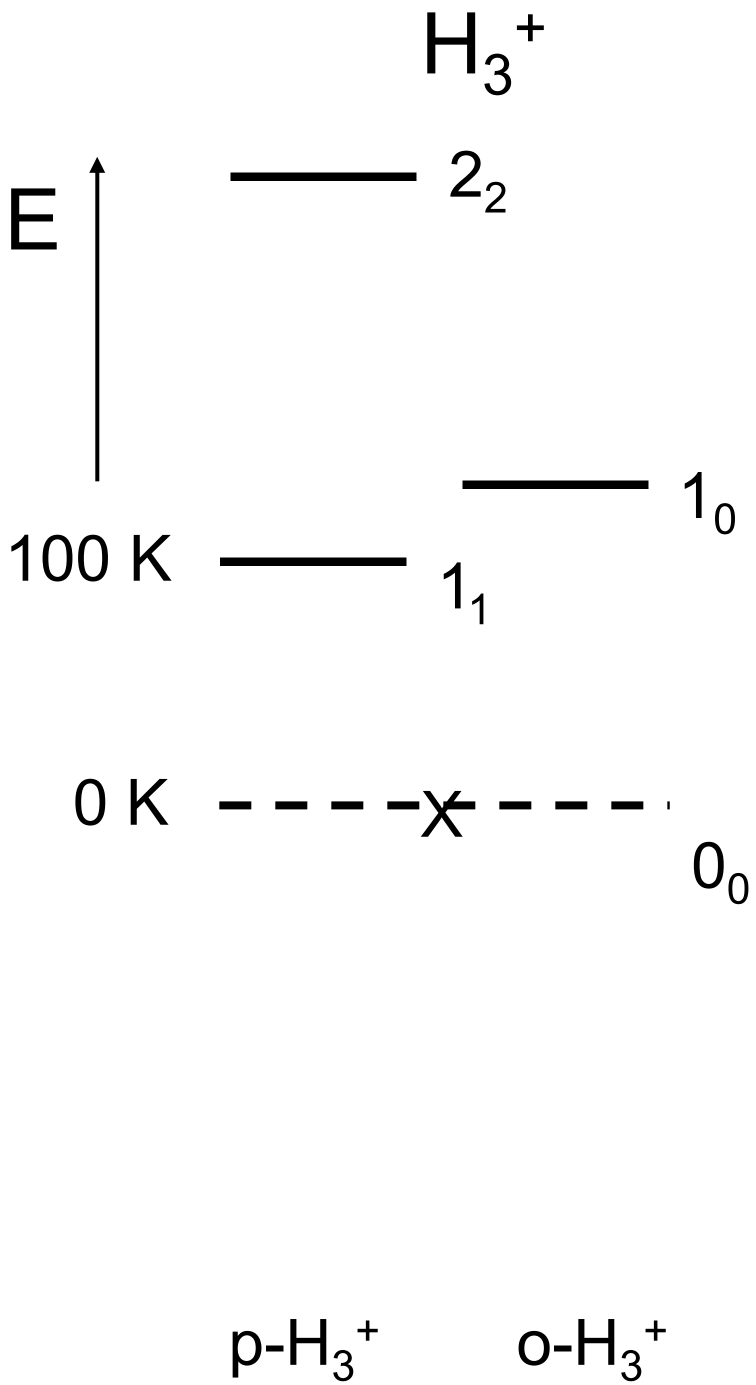


Isotopic Fractionation

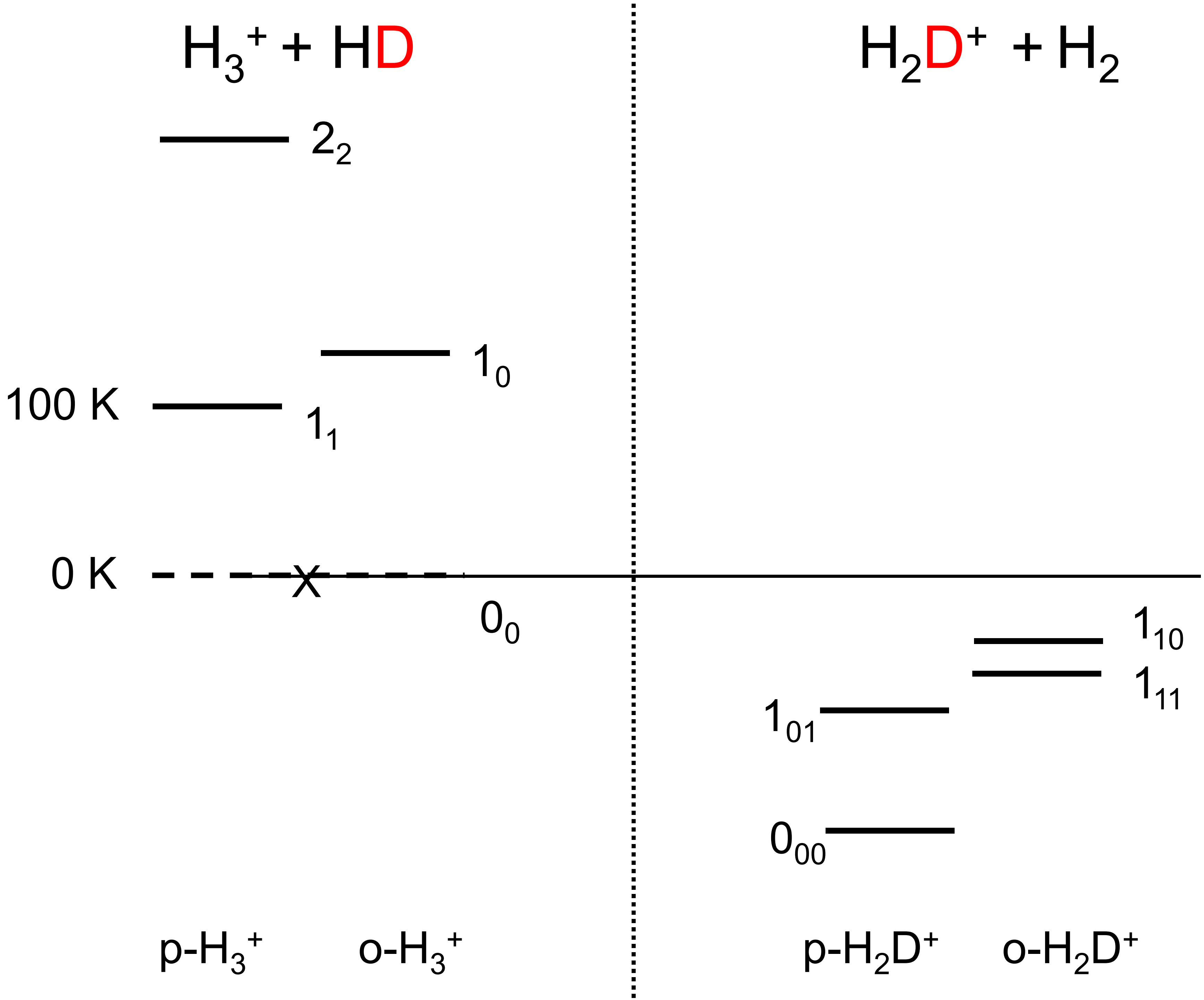
$H_3^+ + HD \rightarrow H_2D^+ + H_2$

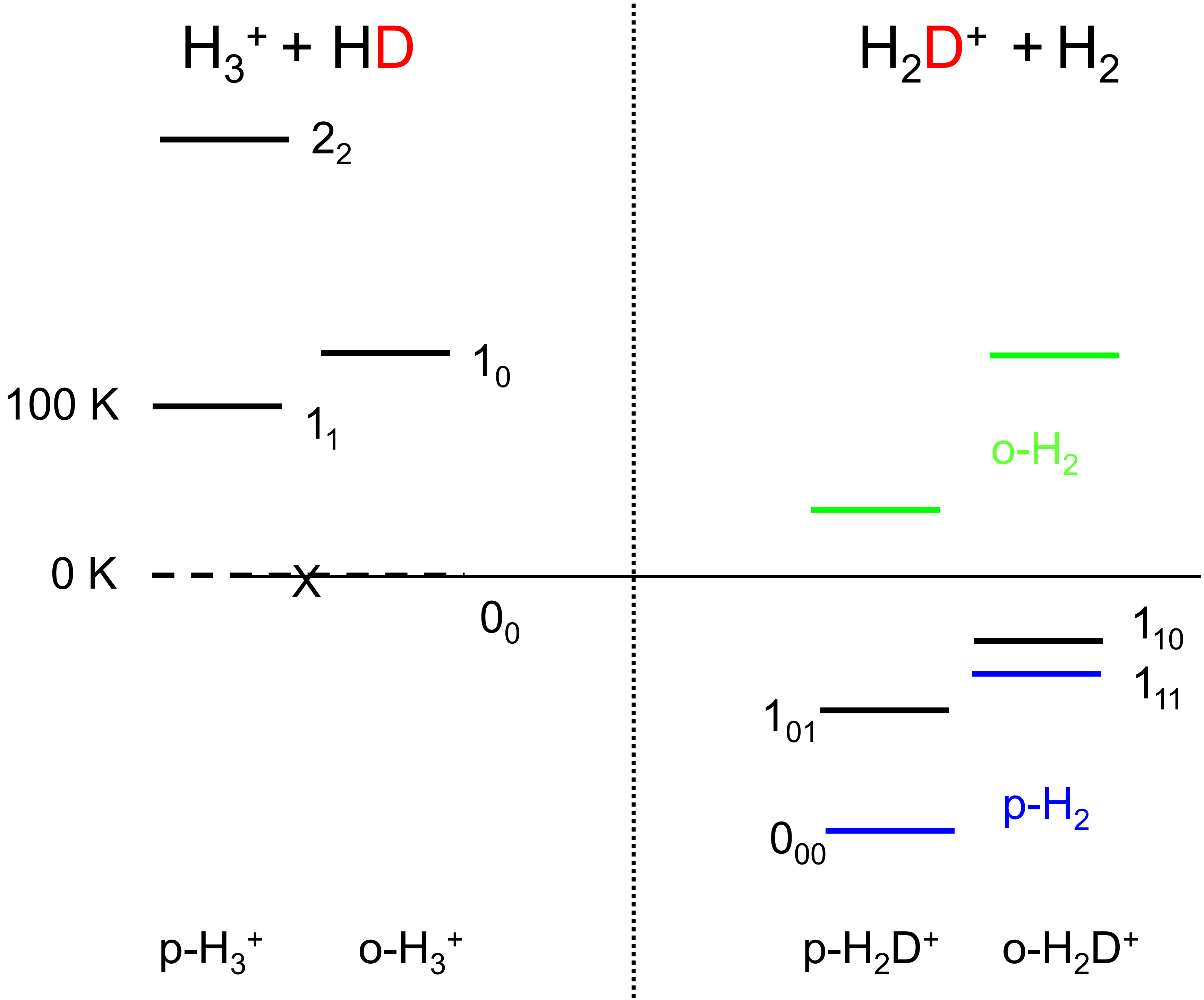
and the H_2 / H_2D^+ OPR

$o/p\text{-}H_2D^+ + o/p\text{-}H_2 \rightarrow o/p\text{-}H_2D^+ + o/p\text{-}H_2$



Lowest energy levels of H_3^+

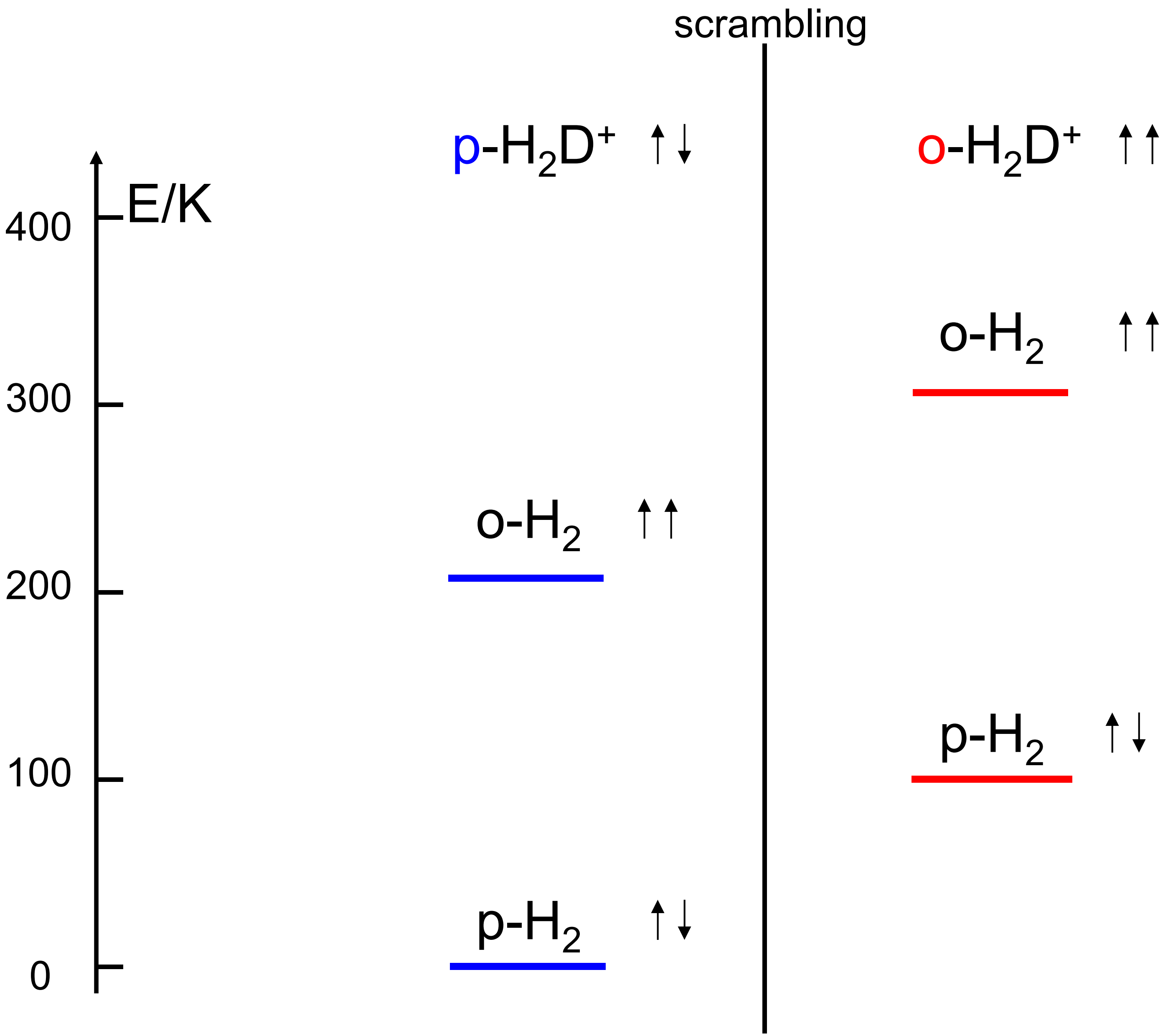

$H_3^+ + HD$
$H_2D^+ + H_2$
2_2
1_0
100 K
1_1
0 K
0_0
1_{10}
1_{11}
1_{01}
0_{00}
p-H_3^+
o-H_3^+
p-H_2D^+
o-H_2D^+


$H_3^+ + HD$
$H_2D^+ + H_2$
2_2
1_0
100 K
1_1
o-H_2
0 K
0_0
1_{10}
1_{11}
1_{01}
p-H_2
0_{00}
p-H_3^+
o-H_3^+
p-H_2D^+
o-H_2D^+

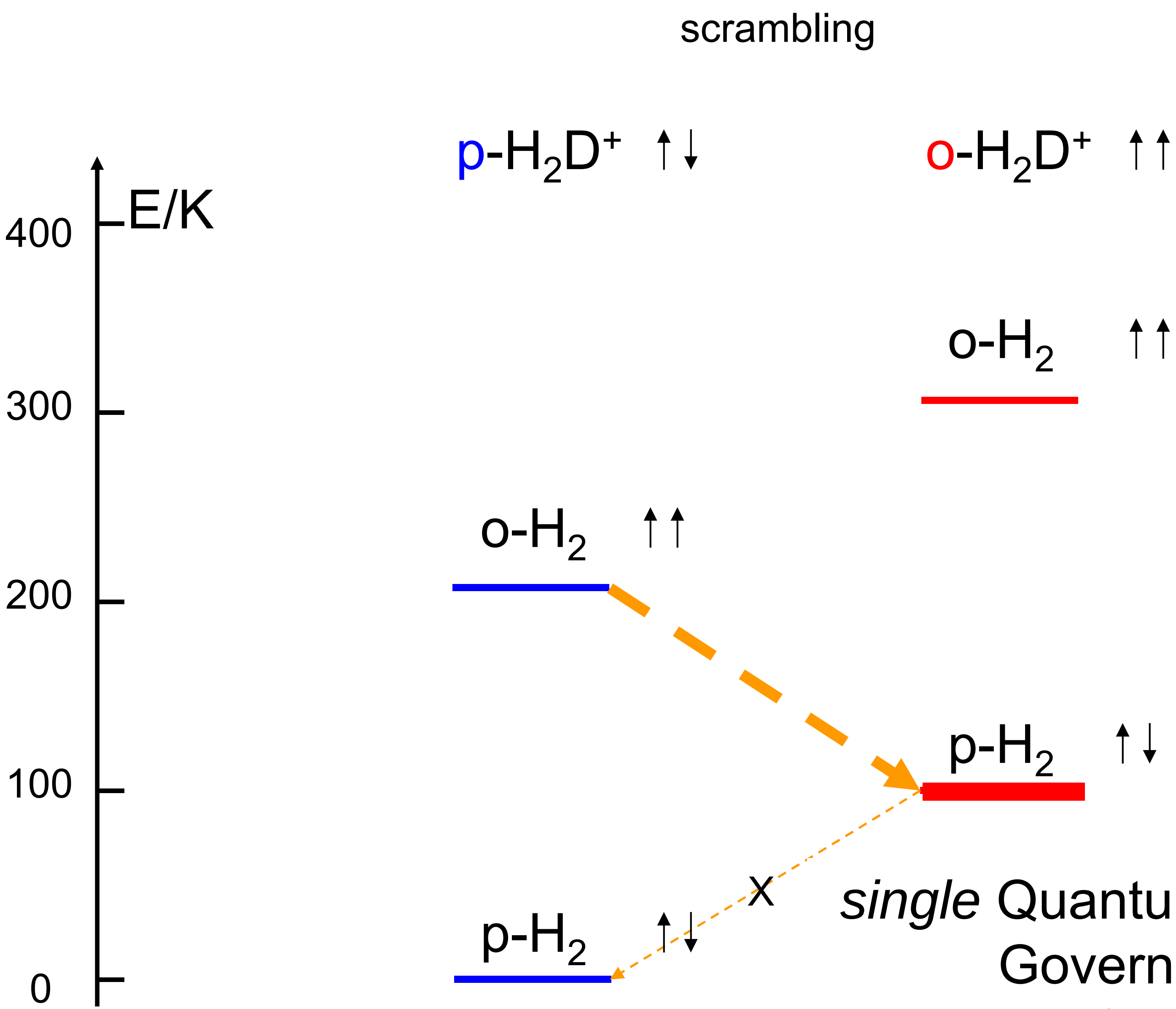
Role of Nuclear Spin?

Conservation laws: E, J, P, I, …

Para – Ortho Conversion



Para – Ortho Conversion

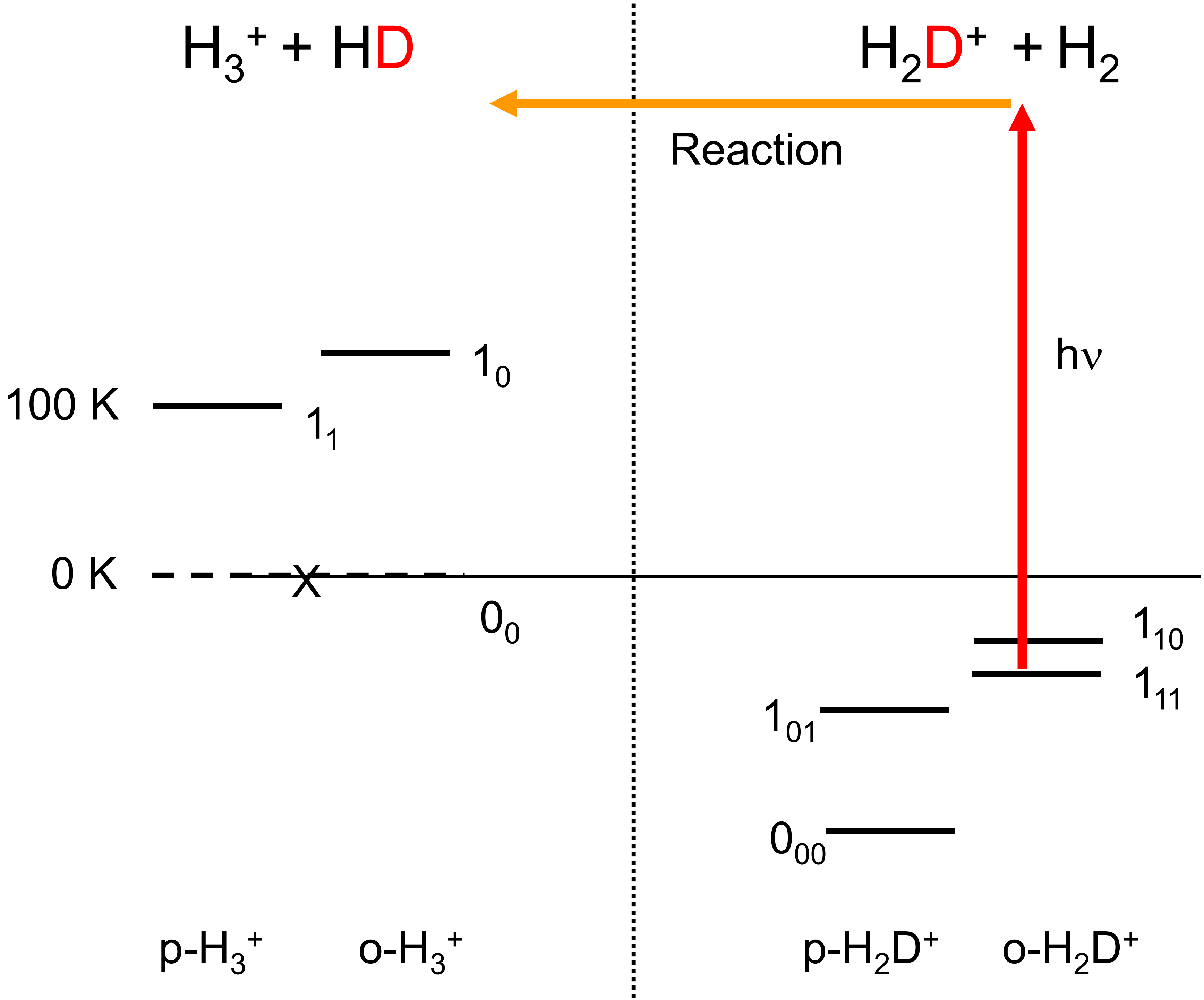


single Quantum State Governs Deuterium Chemistry?

Laboratory Approach

H_2D^+ State Distributions

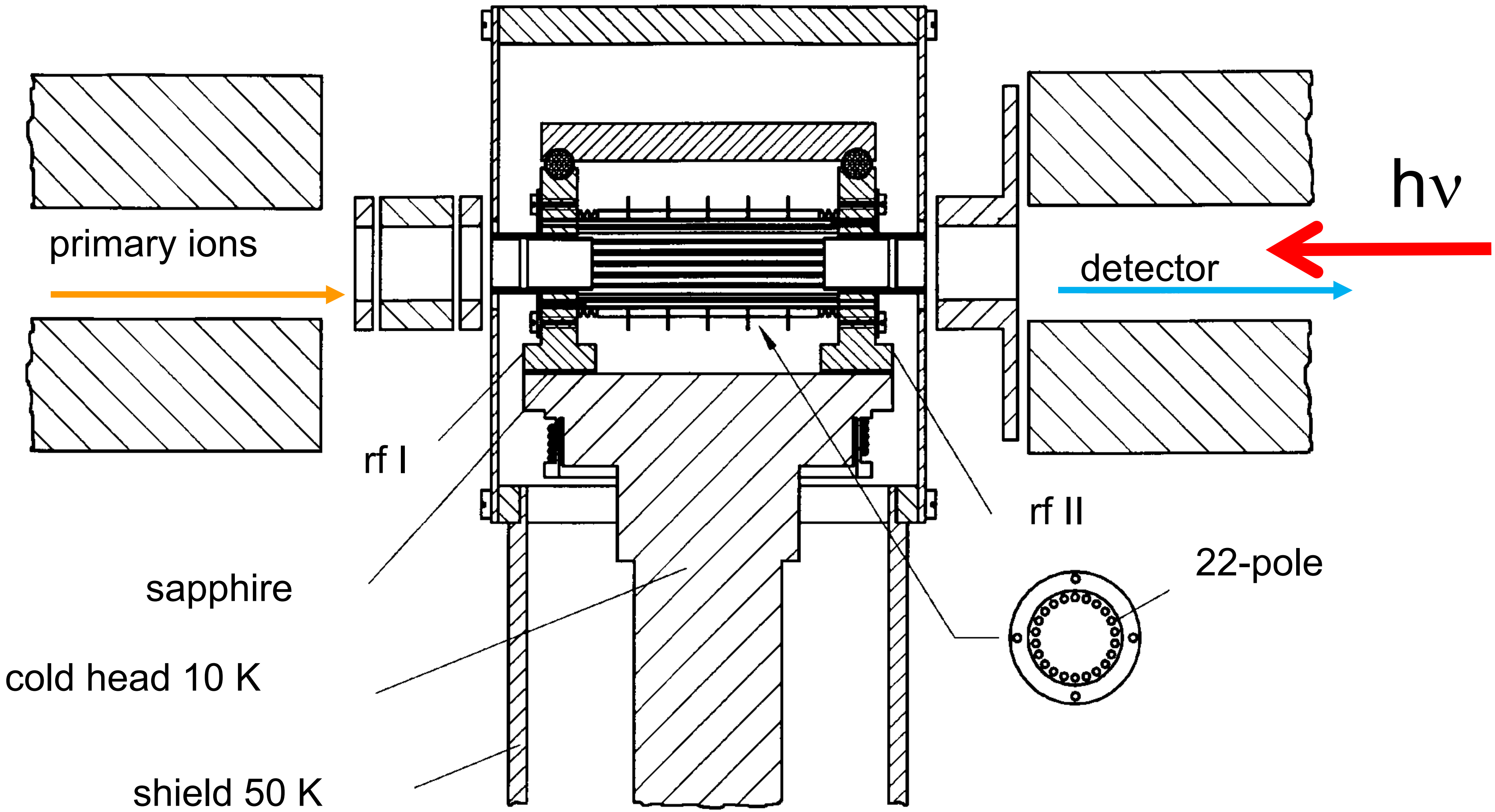
Translation
Rotation
Nuclear Spin



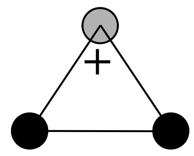
H3+ + HD
H2D+ + H2
Reaction
hν
1_0
100 K
1_1
0 K
0_0
1_10
1_11
1_01
0_00
p-H3+
o-H3+
p-H2D+
o-H2D+

Light Induced Reactions

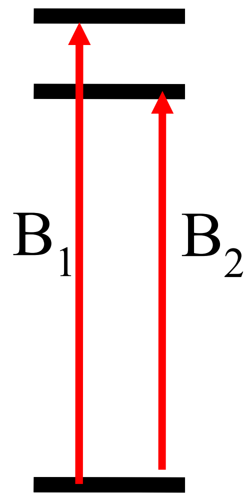
Spectroscopy in Traps



relative B coefficients



transition	line position / cm^{-1}	laser power / mW	meas B_{rel}	calc B_{rel}
		H_2D^+		
$0_{00} \rightarrow 1_{11}$	6466.532	1.8	1	1
$0_{00} \rightarrow 1_{01}$	6330.973	4.0	0.32±0.02	0.31
$1_{11} \rightarrow 1_{10}$	6303.784	5.0	0.29	0.29
$1_{11} \rightarrow 0_{00}$	6340.688	5.3	0.27 ±0.03	0.27
$1_{11} \rightarrow 2_{02}$	6459.036	4.1	0.35 ±0.04	0.34
		D_2H^+		
$0_{00} \rightarrow 1_{11}$	6536.319	1.6	1	1
$0_{00} \rightarrow 1_{11}$	6482.033	3.8	0.33±0.02	0.32



signal~B·pop·P·k*

conclusions:

1) *ab initio* predicted (relative) B coefficients reliable

2) reaction probability independent of rovib. overtone excitation

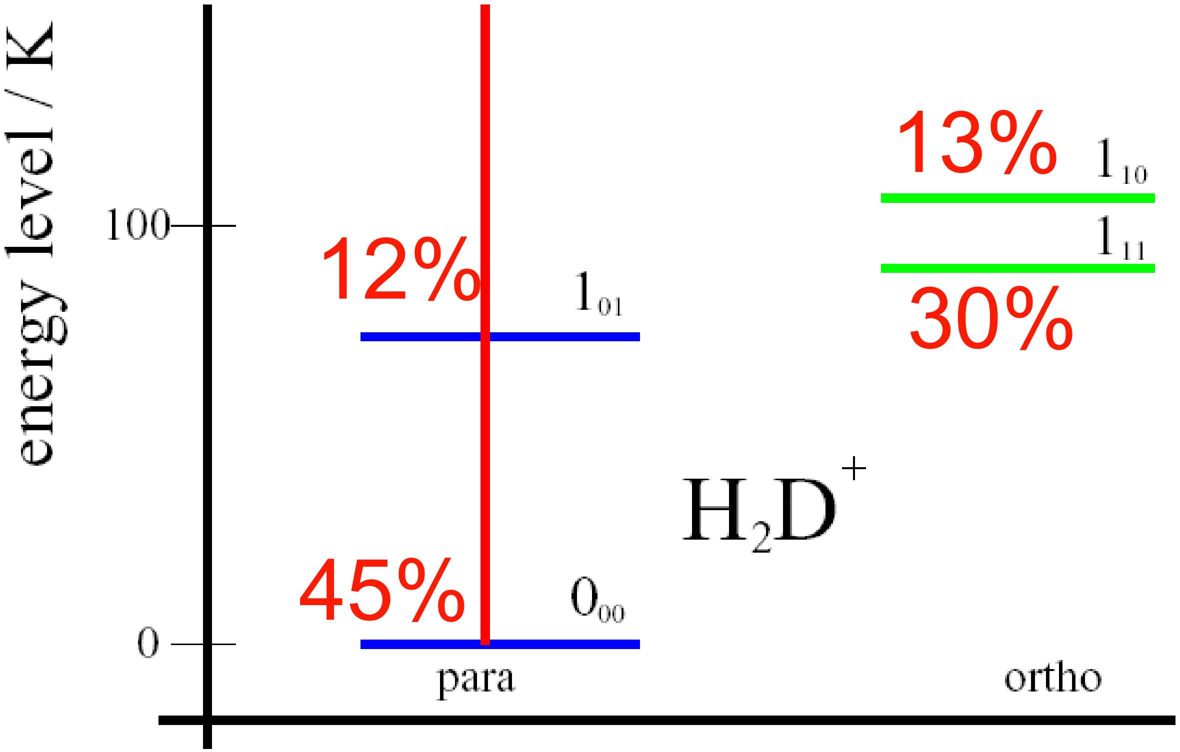
Rotational Level Populations of H_2D^+

$$\text{pop} \sim \frac{[H_3^+]}{B \cdot P}$$

$T_{Doppler}=(27\pm2)K$

$T_{rot,para}=(27\pm2)K$

$T_{ortho/para}=(35)K$



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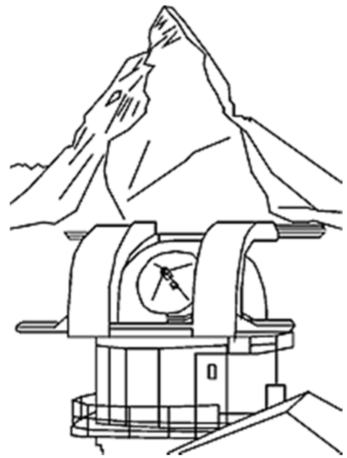

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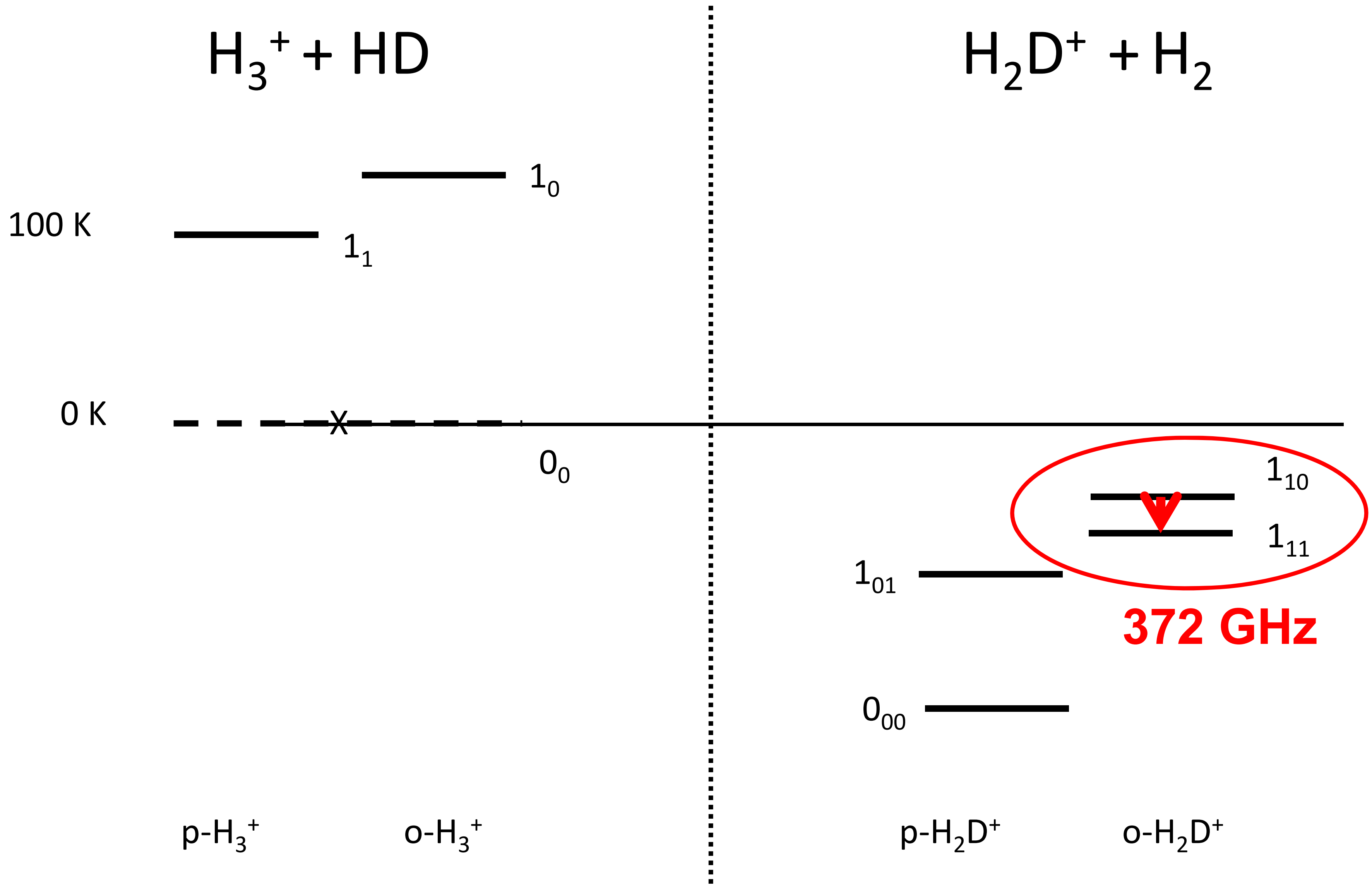
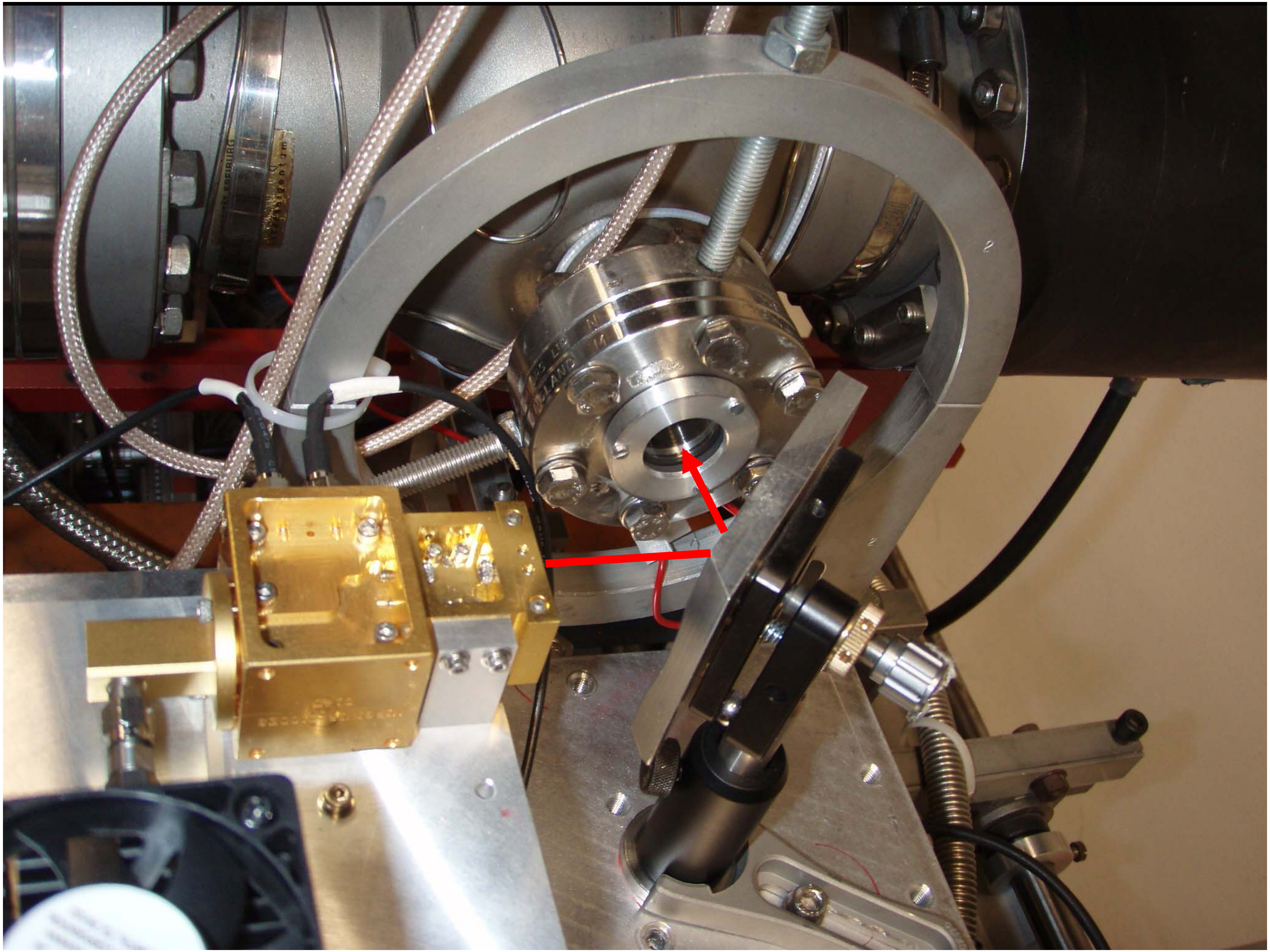
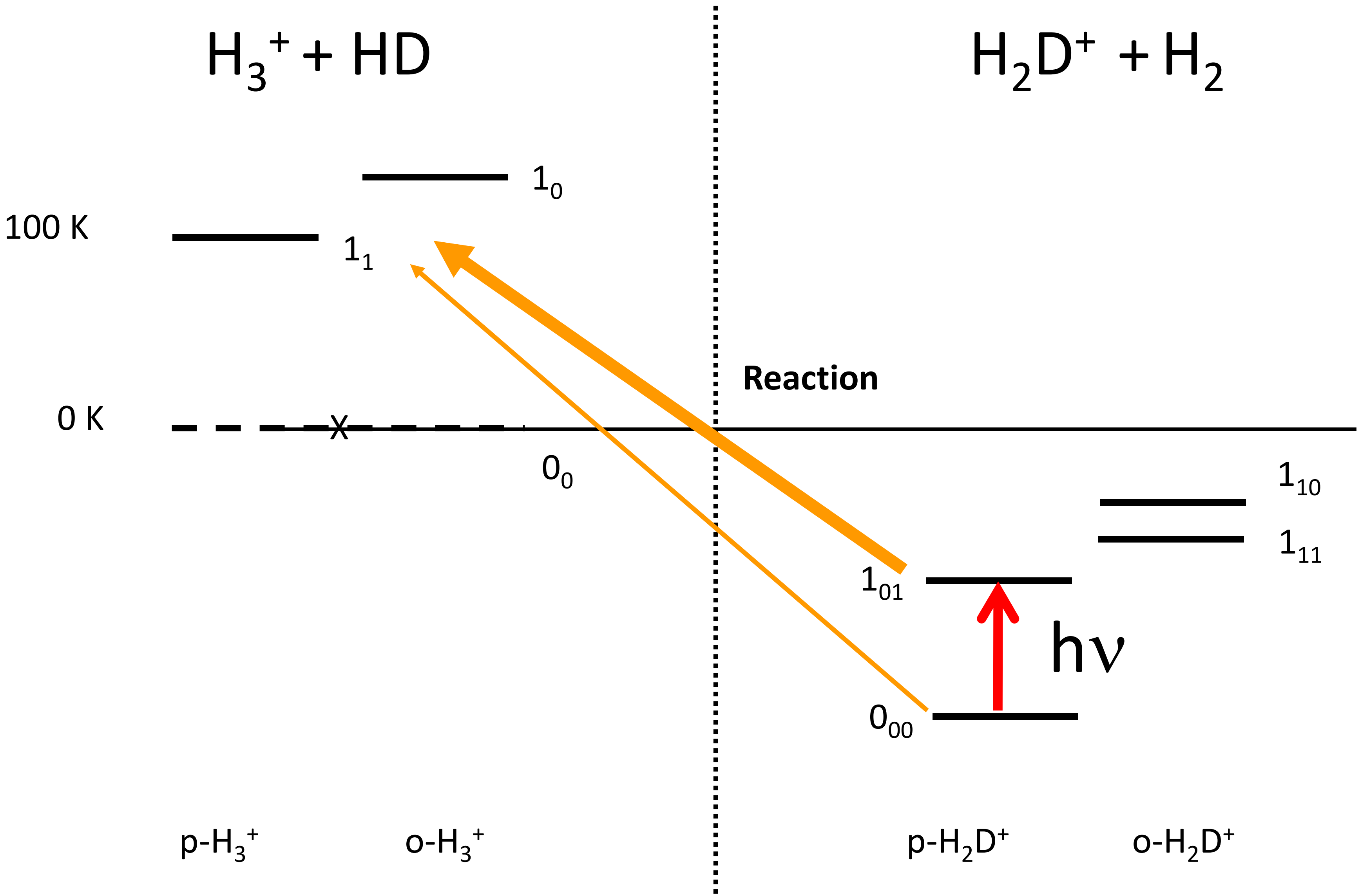
H_2D^+ Detection in Space



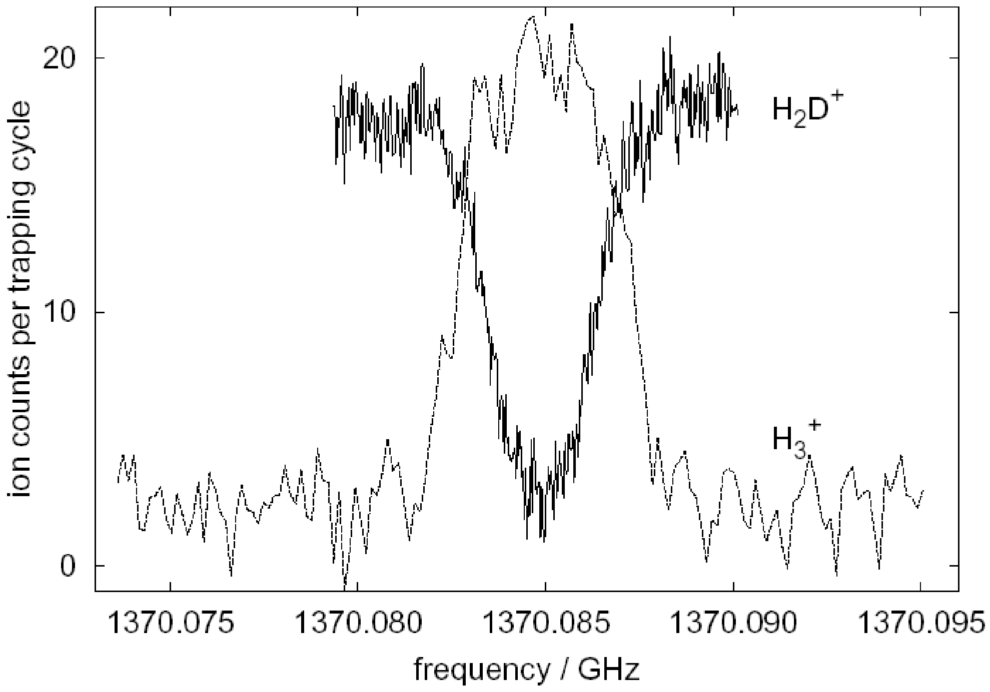


*Light I*nduced *R*eactions probing H_2D^+



Results

H_2D^+



	$H_2D^+\ 1_{01} \leftarrow 0_{00}$
this work	1370084.880(20)
ab initio[a]	1369991.8
unpublished value[b]	1370146.0(3)

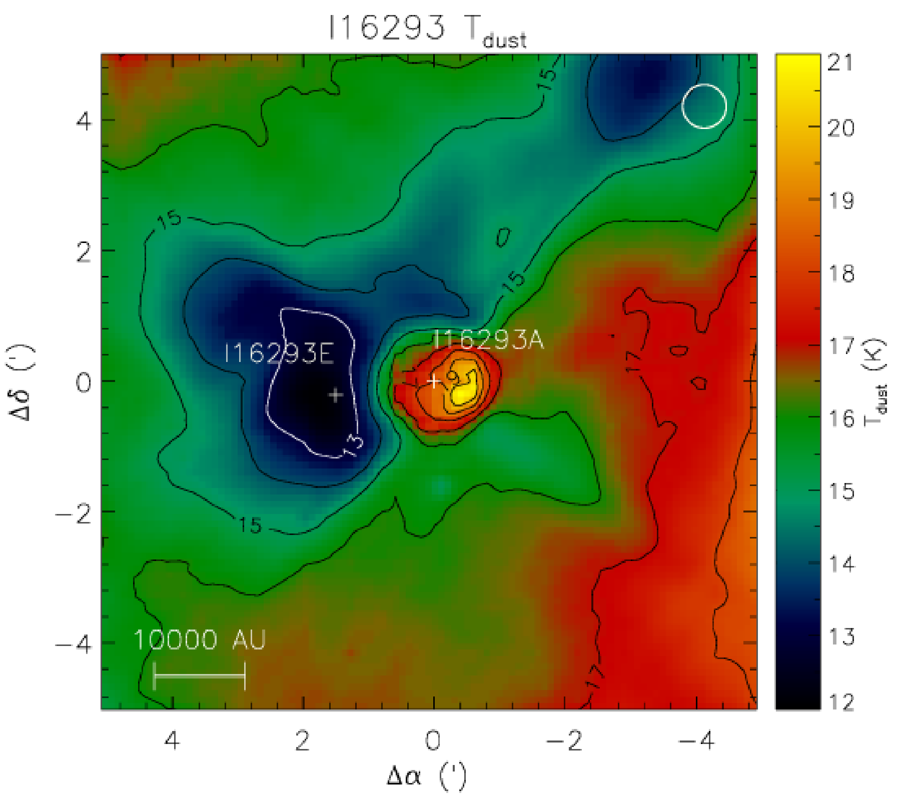
O. Asvany et al., PRL 100, 233004 (2008)

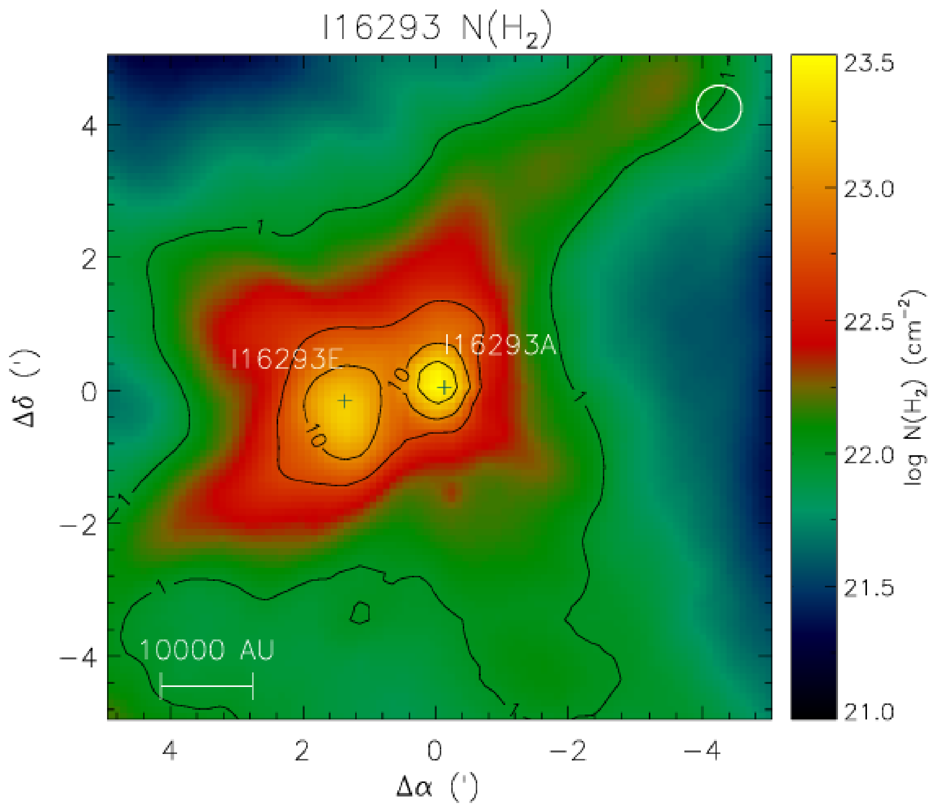
Δ = 62 MHz (!)

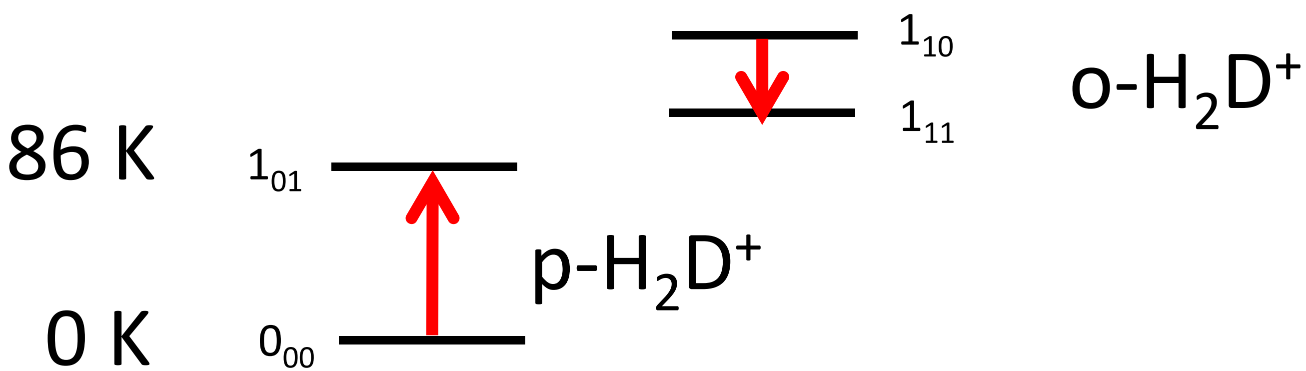
O. Asvany et al.

Δ = 62 MHz (!)

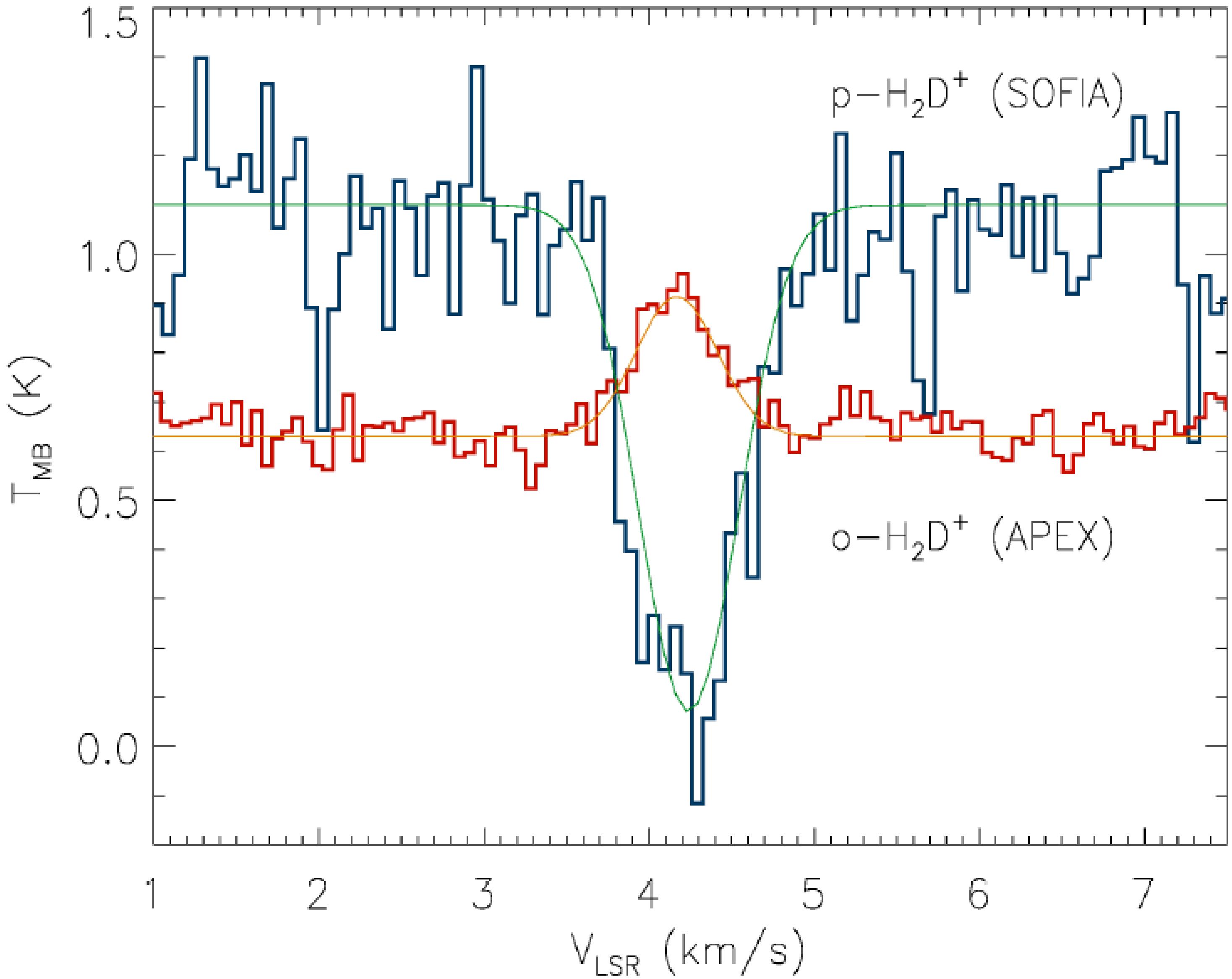
Protostellar Cloud Core I16293A



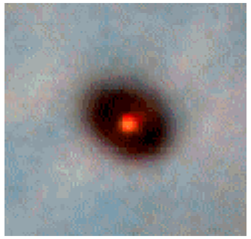




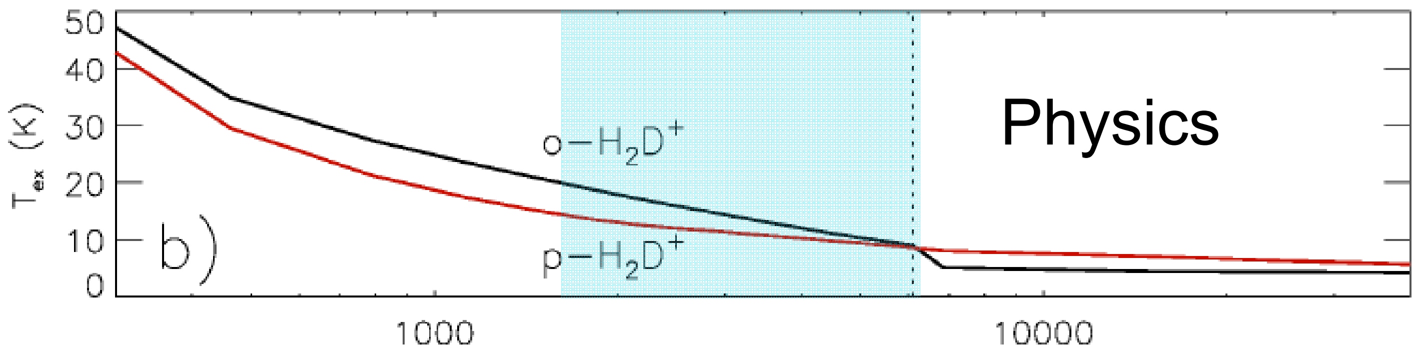
Para-H_2D^+ found in Space



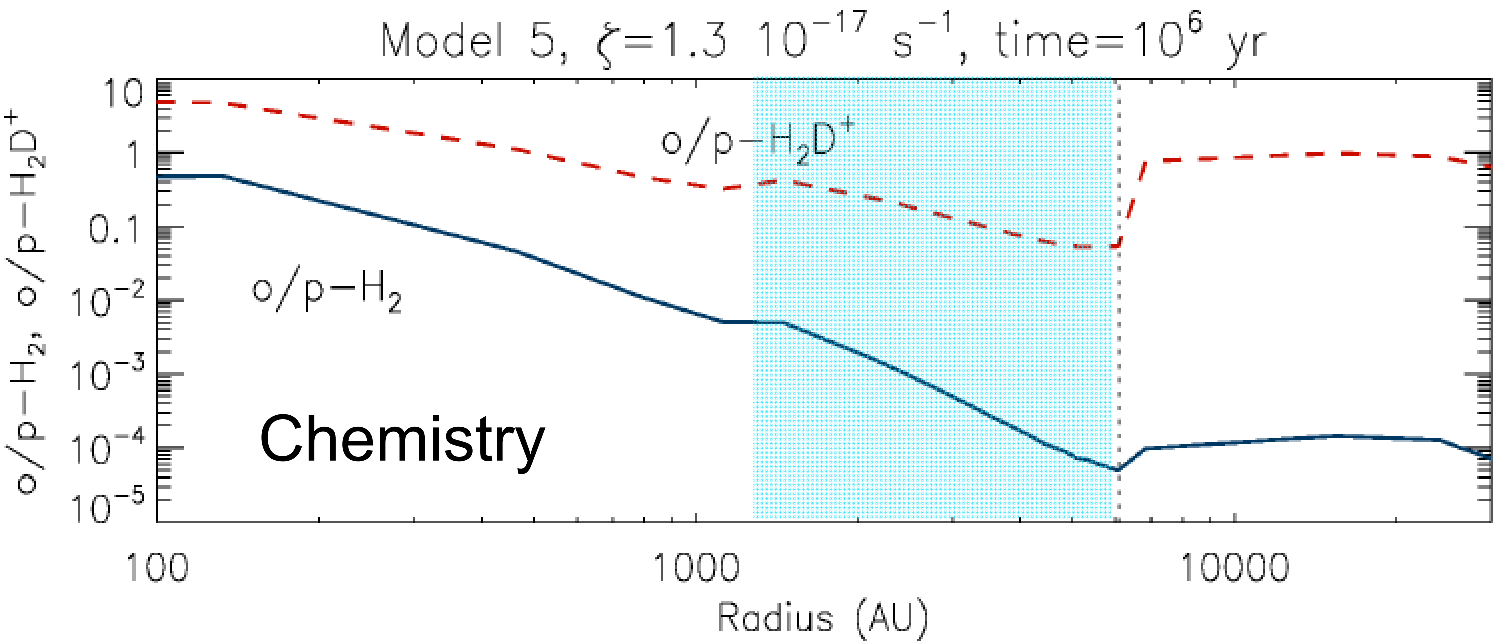
Astrochemical Modelling



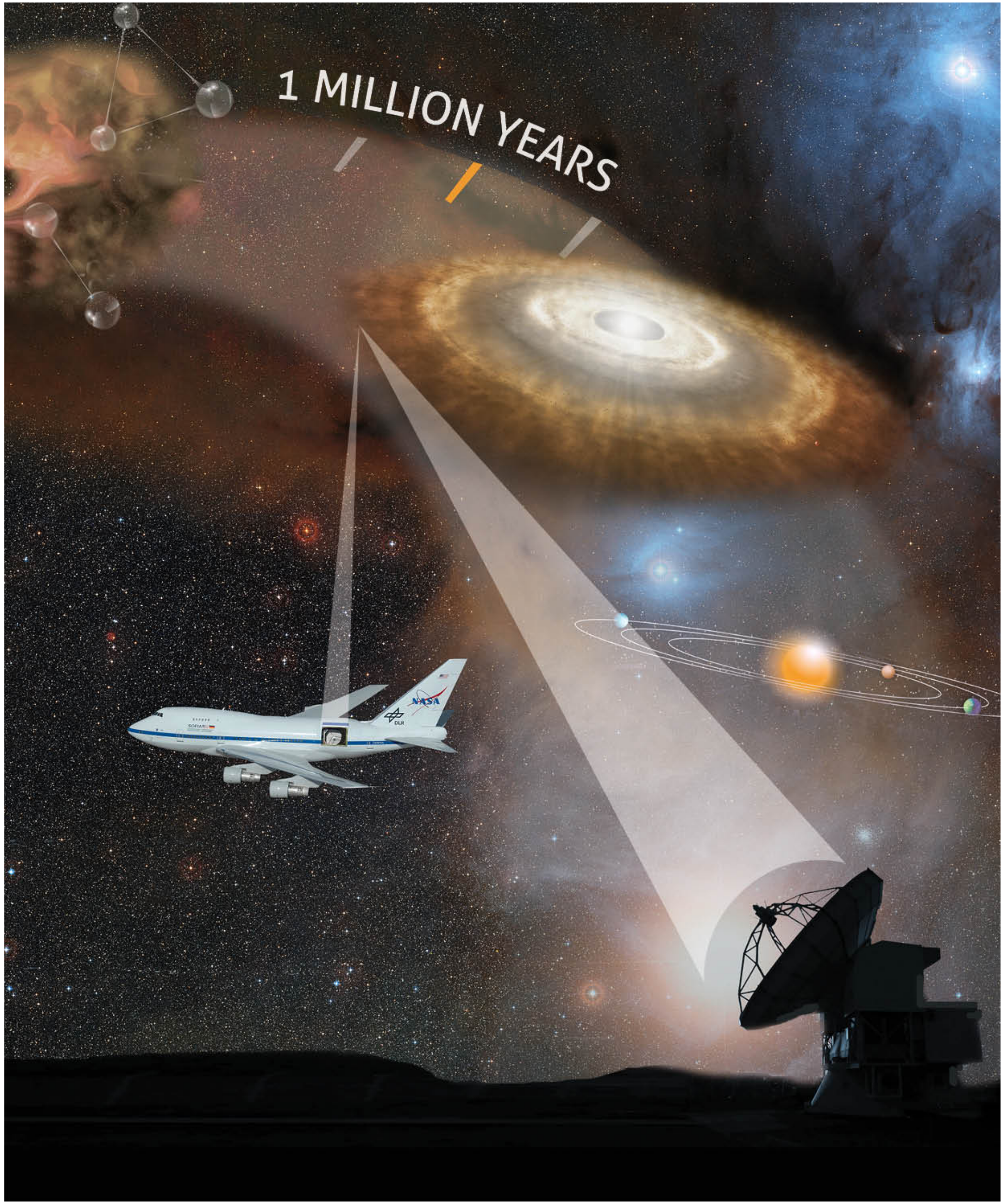
T



o/p

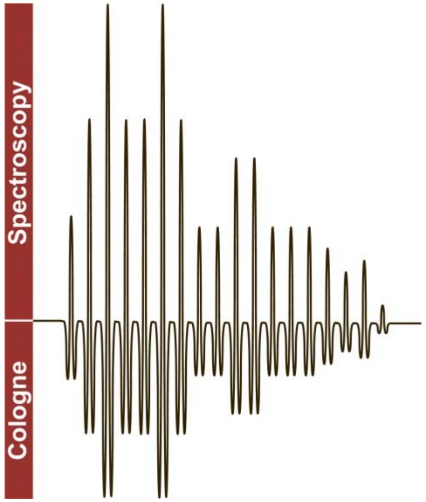


Collaboration: Jorma Harju, Olli Sipilä, Paola Caselli

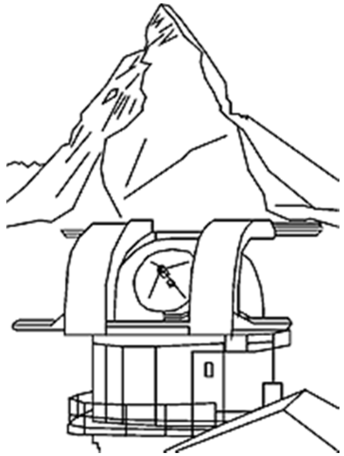


H_2D^+ observations give an age of at least one million years for a cloud core forming Sun-like stars

S. Brünken et al.
Nature
doi:10.1038/nature13924



Cold Chemistry in Space and Laboratory



Stephan Schlemmer

Universität zu Köln

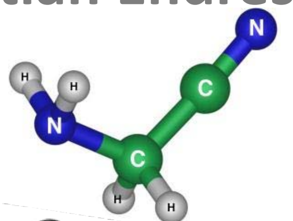
- H_2 Formation, OPR and Chemical Clocks
- H_3^+ / H_2D^+ Isotopic Fractionation, H_3^+/H_2D^+, OPR
- $H_2D^+ + H_2$ THz Spectroscopy in Lab and Space

High-Resolution Spectroscopy of Interstellar Molecules

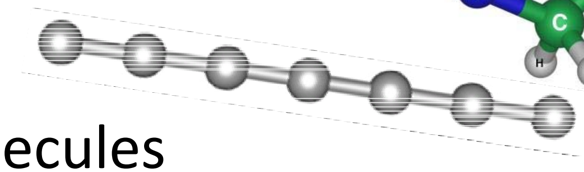
Cologne Astrophysics Group

Universität zu Köln

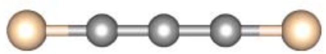
- Complex Molecules in Laboratory and Space
  Frank Lewen, Holger Müller, Christian Endres

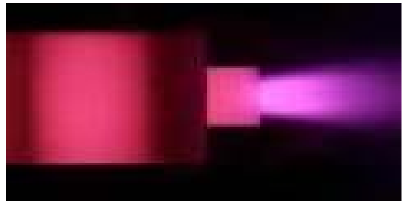


- Carbon Chain Molecules
  Thomas Giesen

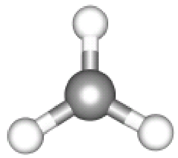


- Silcon Carbon Molecules
  Sven Thorwirth

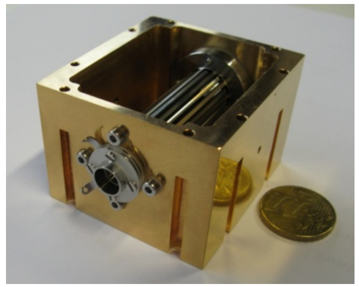




- He-Clusters **Leonid Surin**

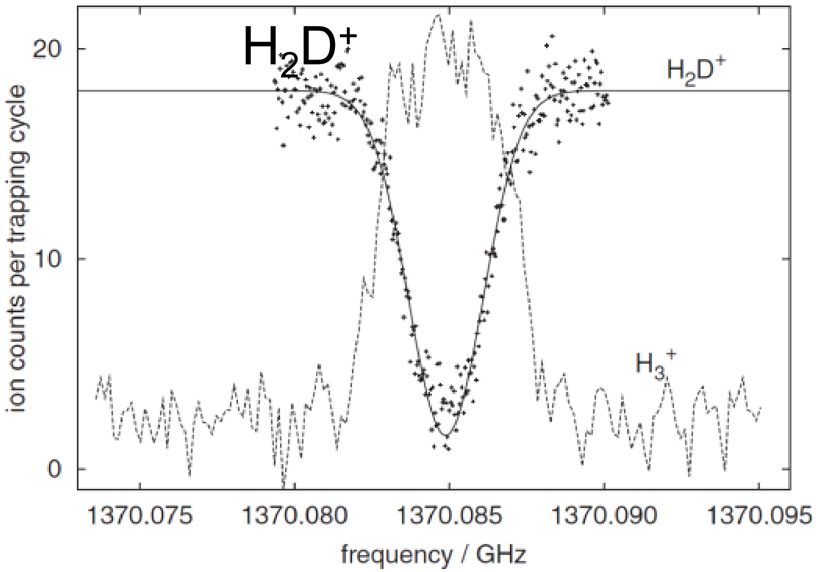


- Trap Experiments
  Sandra Brünken, Oskar Asvany, Pavol Jusko



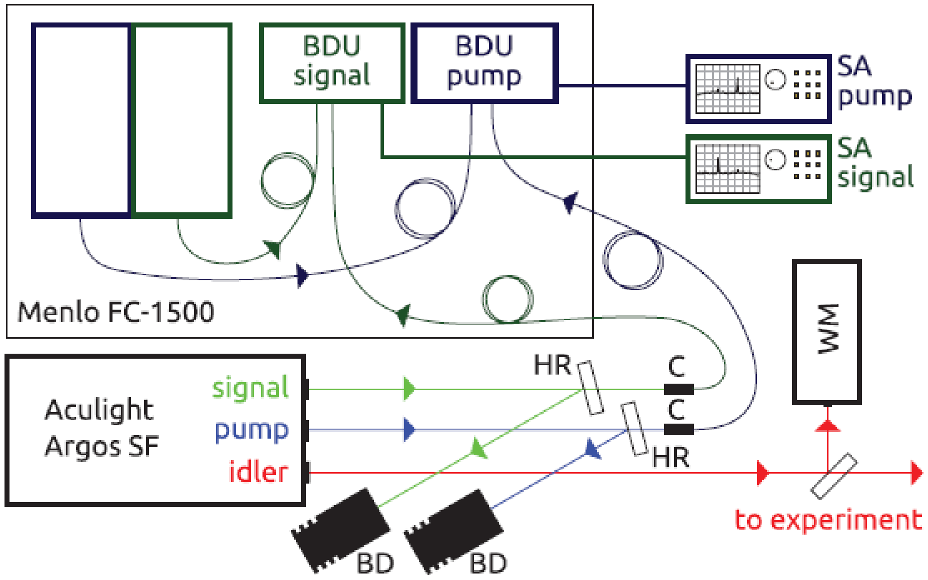
THz Action Spectroscopy

LIR



Asvany et al. 2008, Phys Rev Lett

Frequency Comb

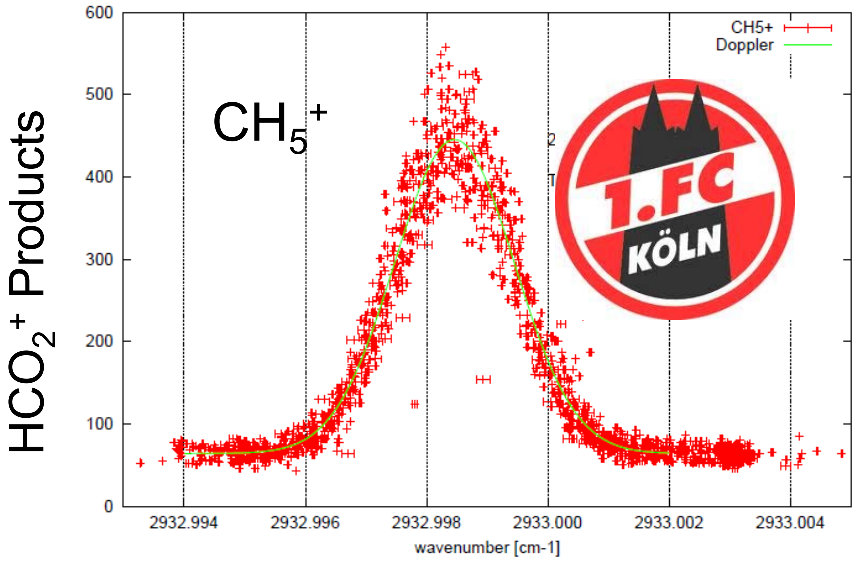


Gärtner et al. 2013, J. Phys. Chem. A

Asvany et al. 2012, Rev Sci Instr

Infrared Action Spectroscopy

LIR

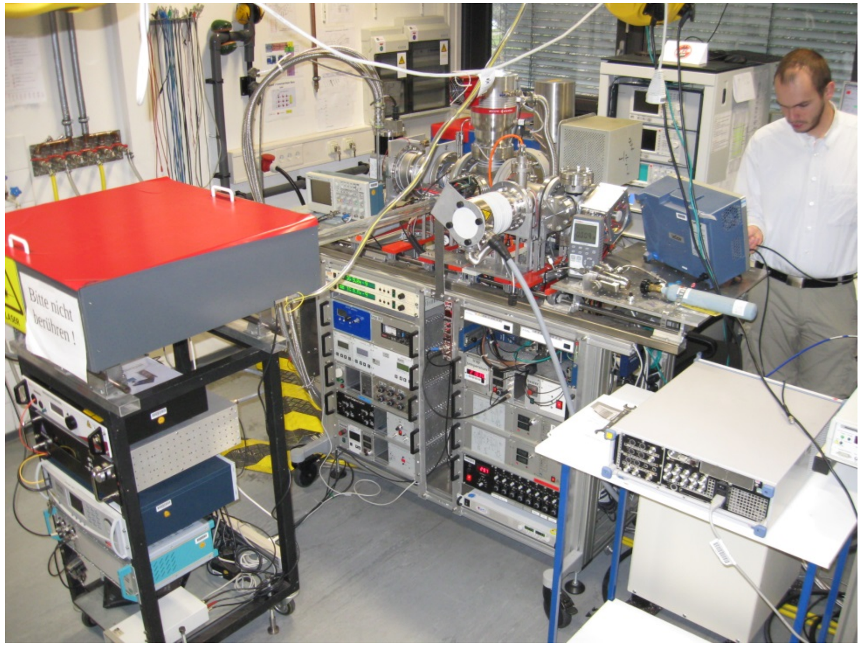


2932.998459(7) cm^{-1}

T = 20.9 +/- 0.4 K

Asvany et al. 2012, Rev Sci Instr

COLogne **TRAP**



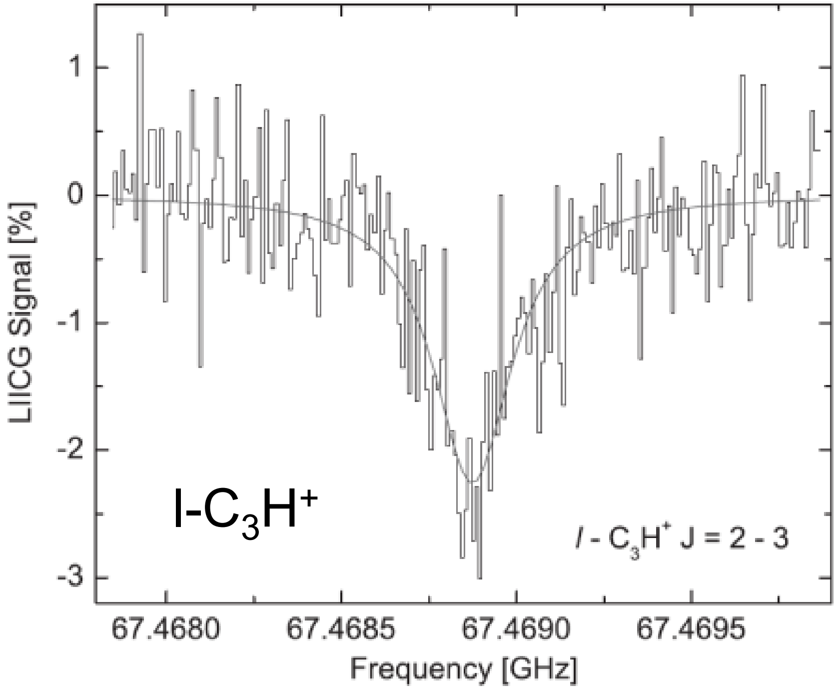
Accuracy: 0.2 MHz

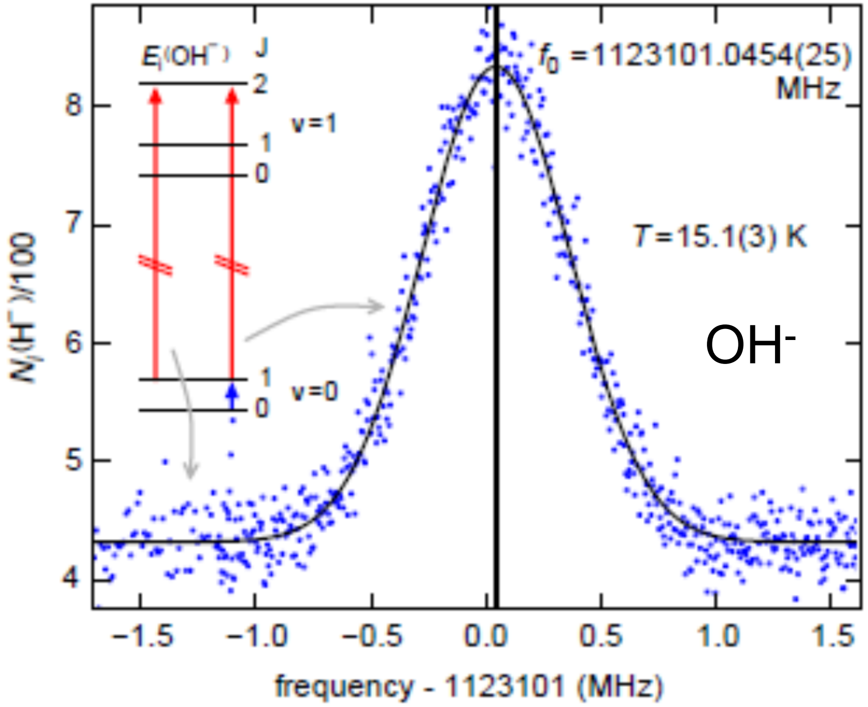
Asvany et al. 2013, Appl Phys B

THz Action Spectroscopy

LIICG

2-photon LIR





Asvany et al. 2013, Appl Phys B

Brünken et al. 2014, ApJL

Jusko et al. 2014, Phys Rev Lett