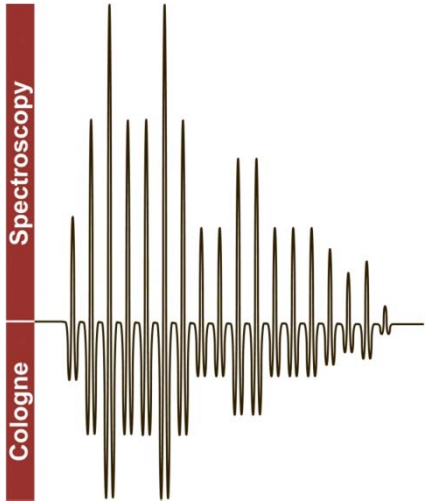
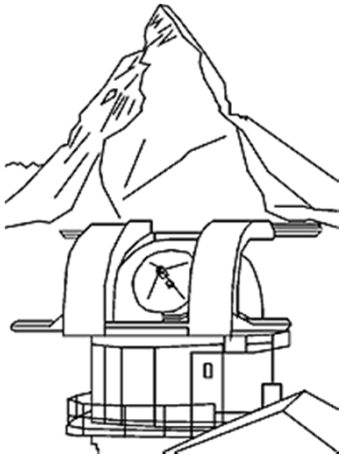
*Chicheley Hall, February 9, 2012*




# Cold trap experiments on $H_3^+ + O_2$ proton transfer

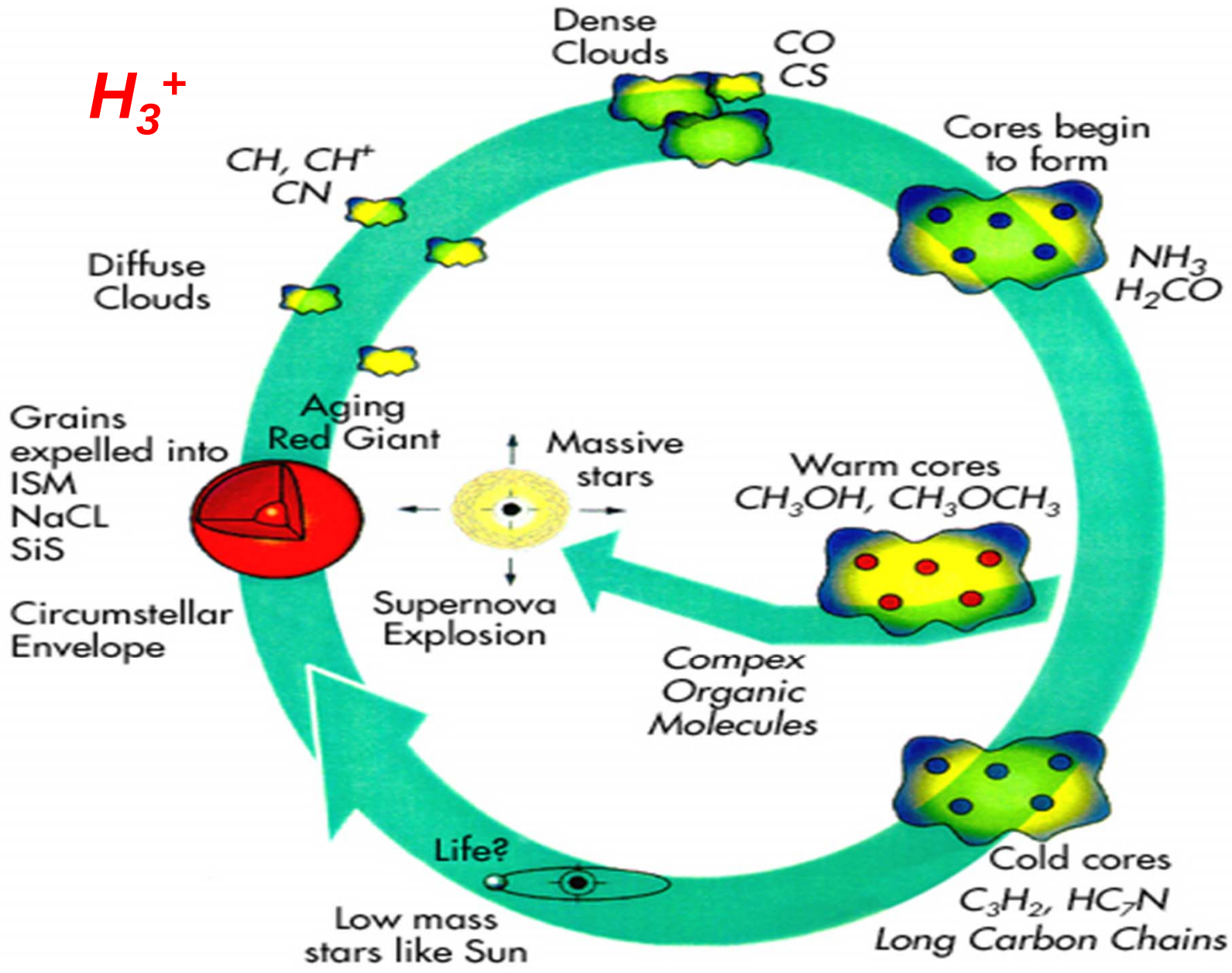


Stephan Schlemmer

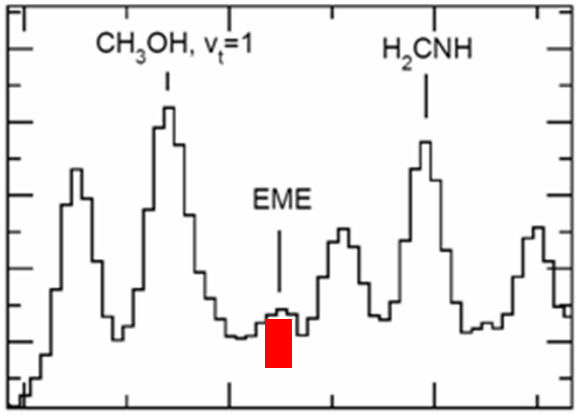
Universität zu Köln

- The THz view into the Sky: Astrophysical Picture
- $H_2D^+$ / $H_3^+$ in Space and Laboratory
- $H_3^+ + O_2$ Proton Transfer
- Preparing a single rotational state of $H_3^+$

# Life cycle of Stars



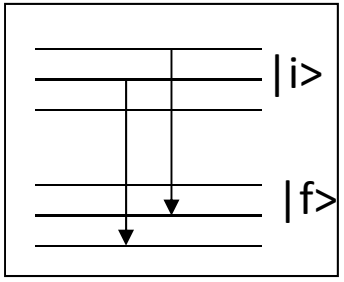
# Understanding the Language of Interstellar Molecules



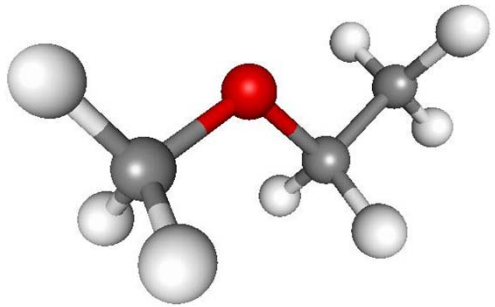

Observations
+
Modelling

**C**ologne **D**atabase for
**M**olecular **S**pectroscopy

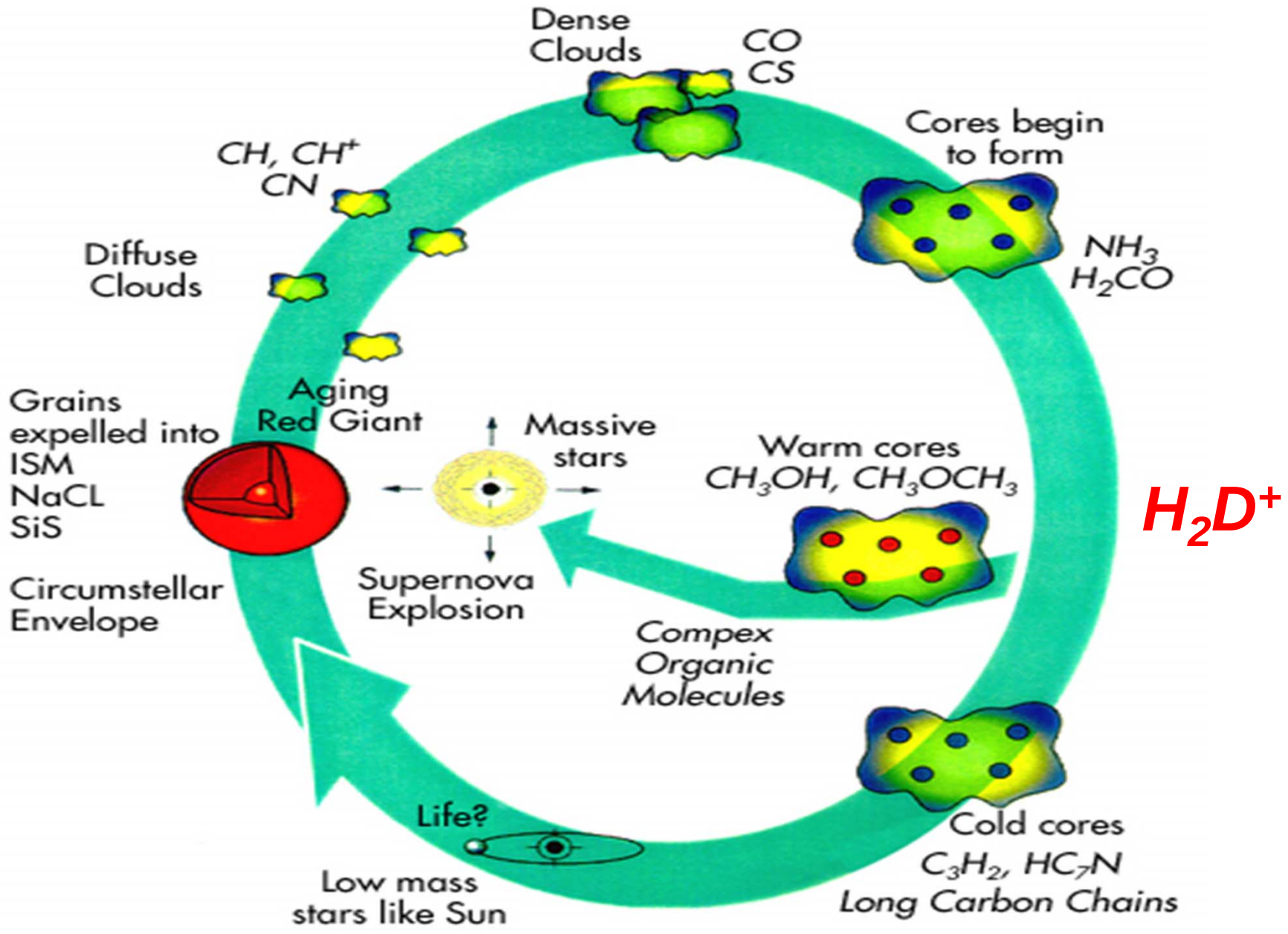
Laboratory Astrophysics

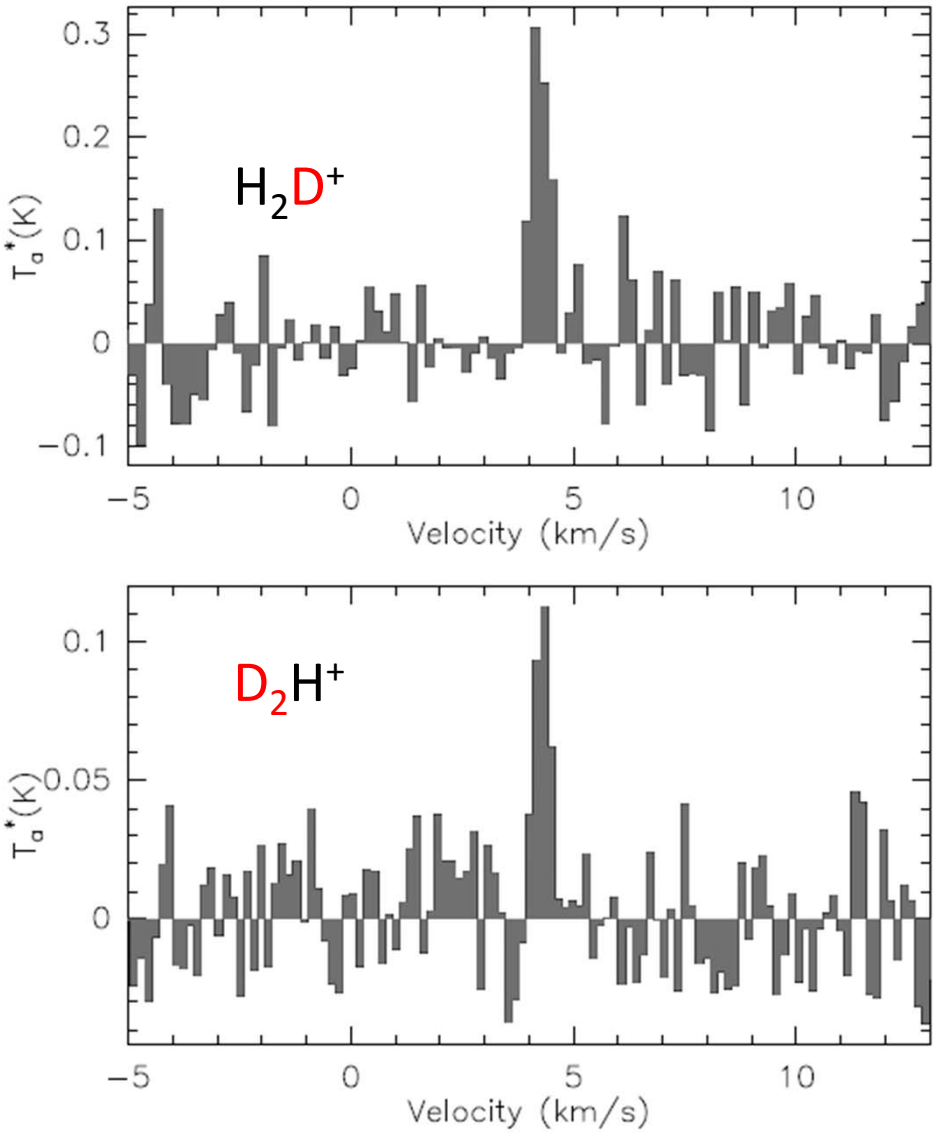



Quantum Chemistry



# Molecules: Chemical Clocks






# **Deuterated Molecules** in Interstellar Medium

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

Deuteriumreservoir

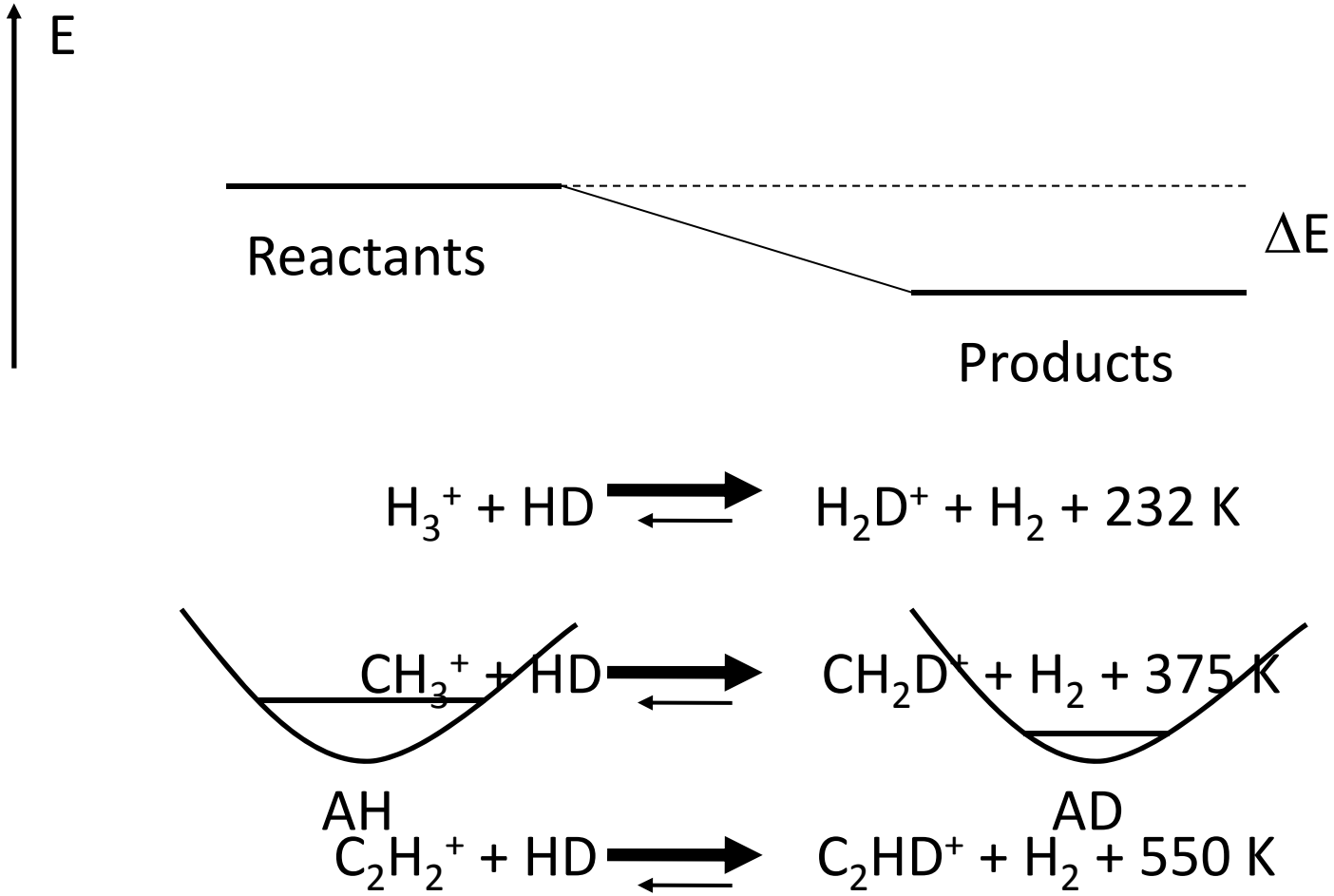
$[HD]/[H_2] \sim 3.0 \cdot 10^{-5}$

Isotope Enrichment

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

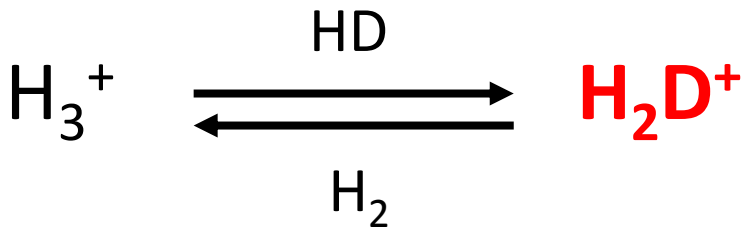
B. Parise, A. Belloche, F. Du, R. Güsten and K. Menten
A&A, 526, A31 (2011)

# Primary Deuteration Reactions



# Isotopic Fractionation

## Ideal Case – Laboratory Situation

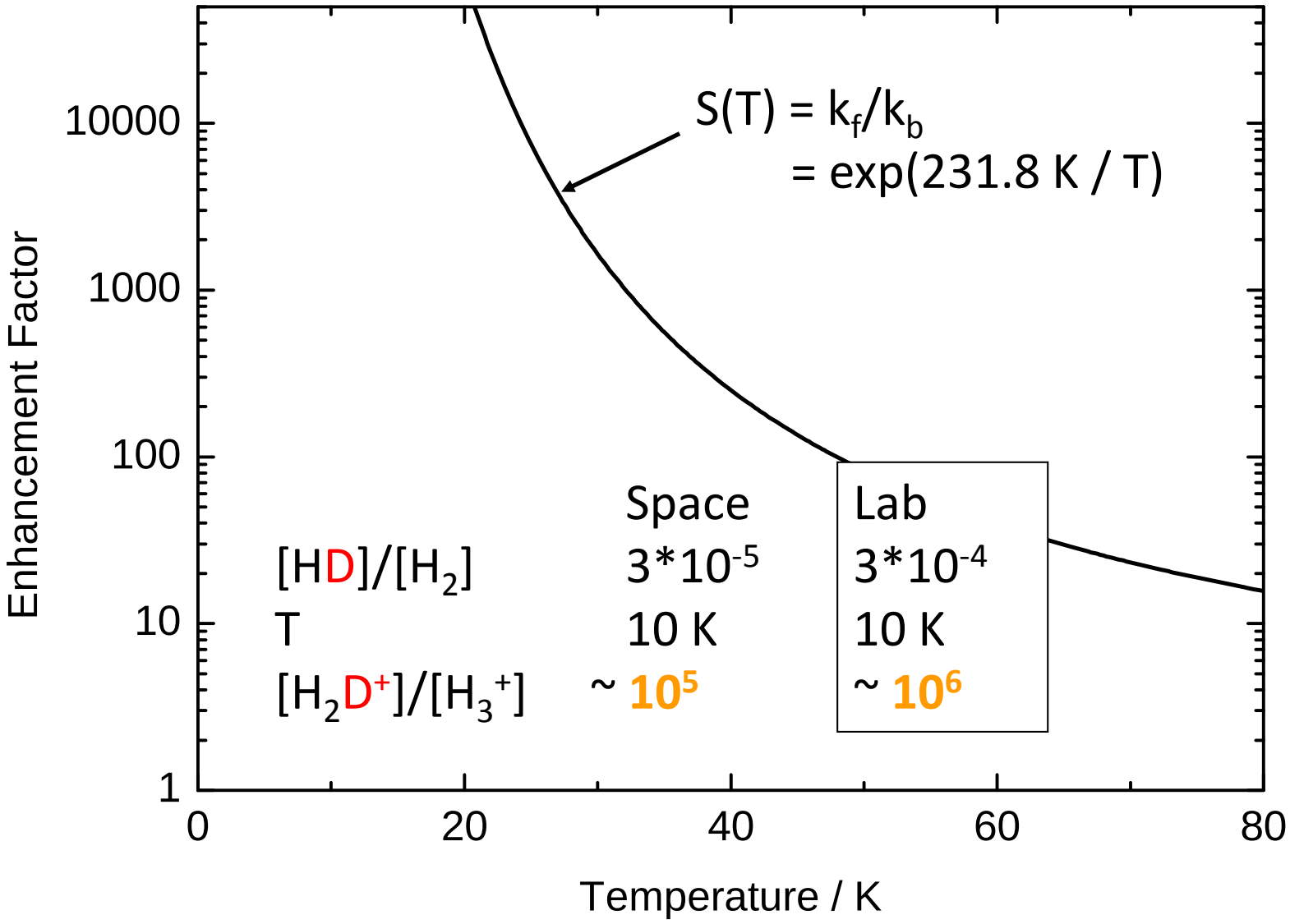



Equilibrium

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

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

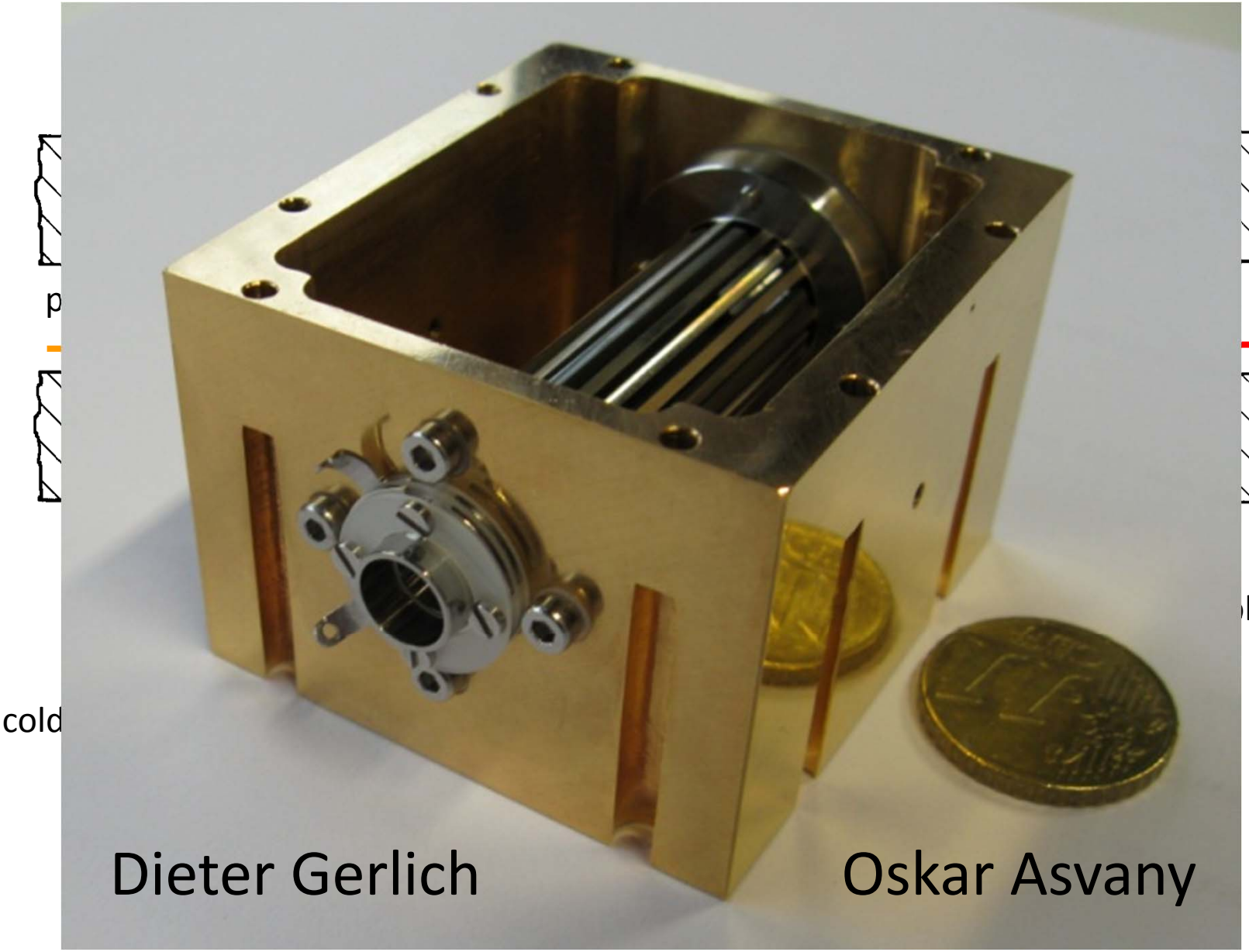
# Isotopic Fractionation



# Experimental Method:

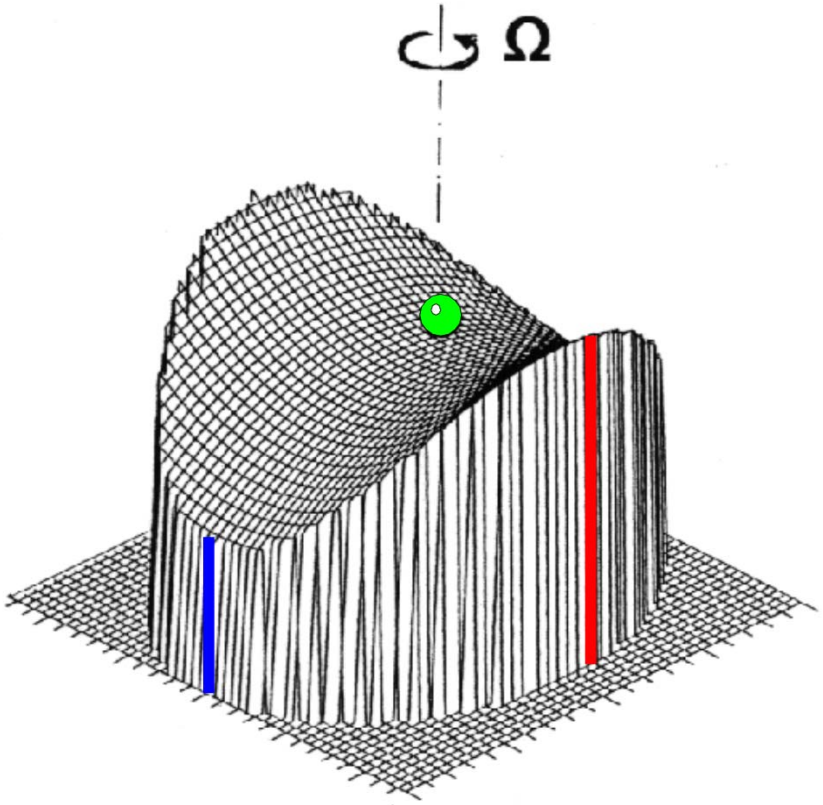
# Electrodynamical Trapping

# 22-Pole Low Temperature Ion Trap

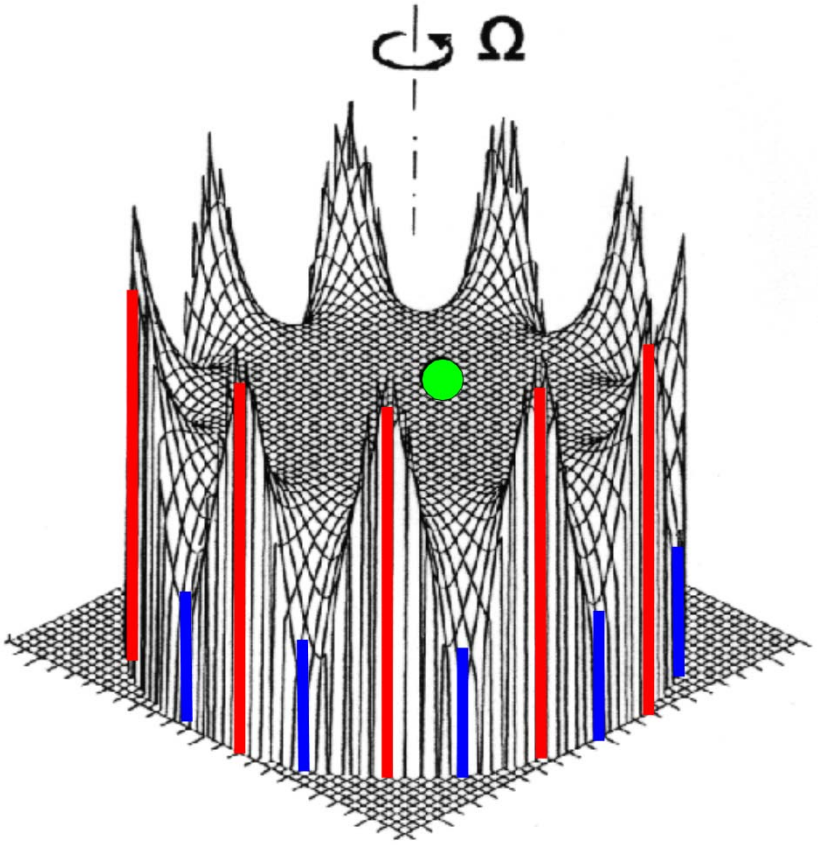


# RF Ion Trap

## Mechanical Model

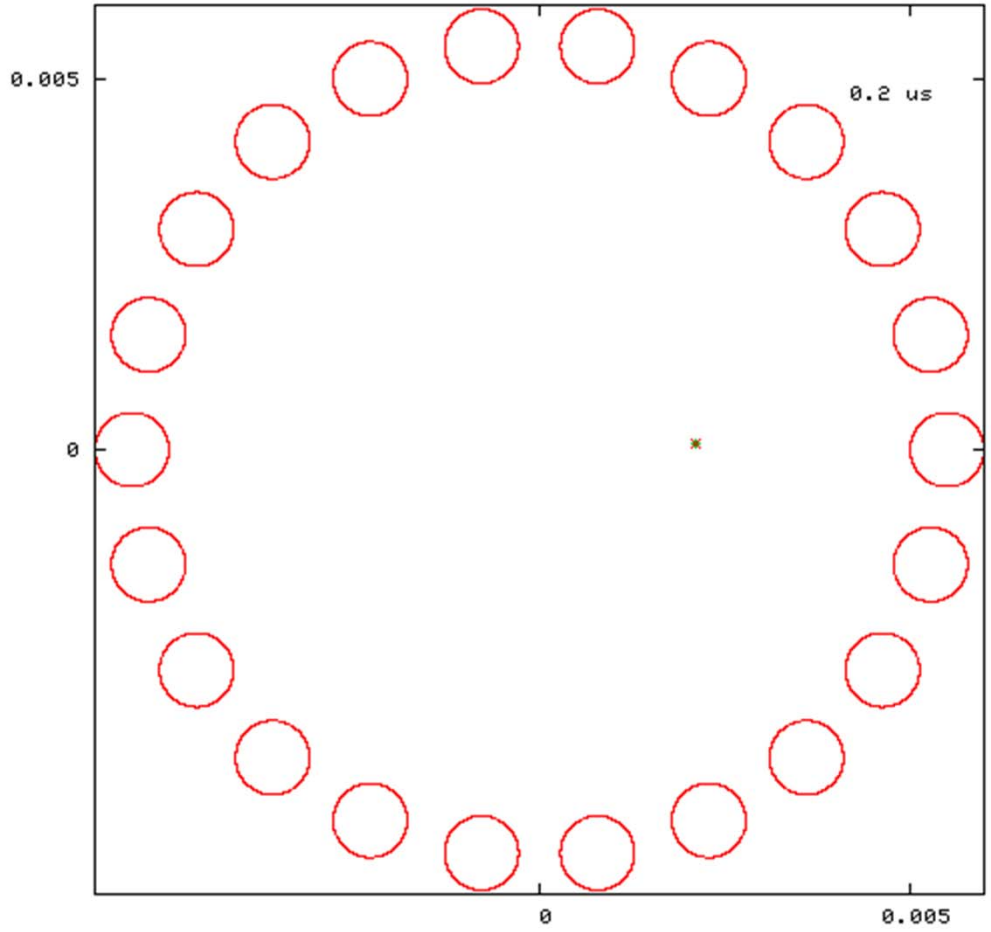



Quadrupole




22-Pole

# Trajectories of ions in 22-pole trap



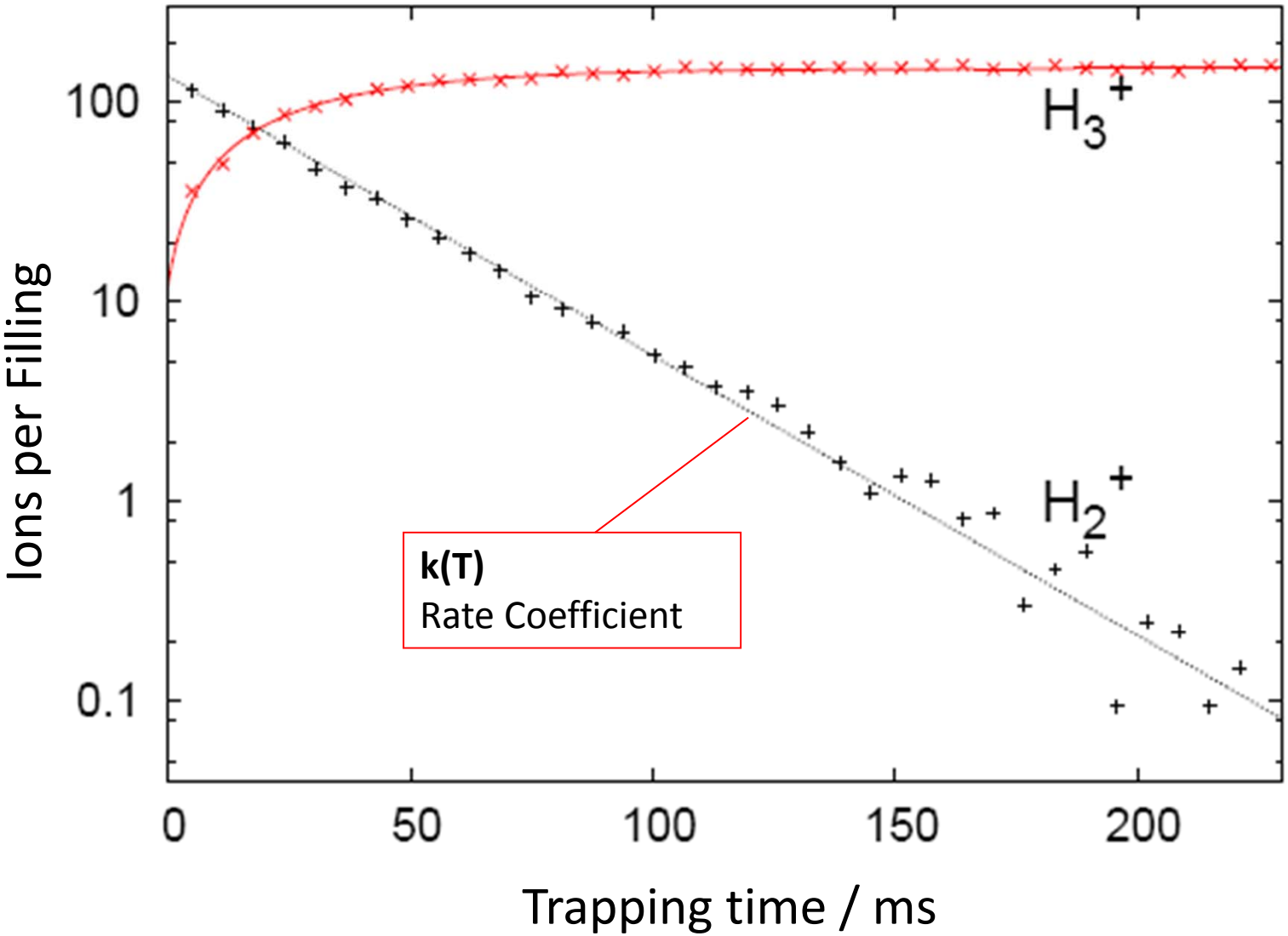

f= 17MHz

$V_0$=20V

\+ m=20u

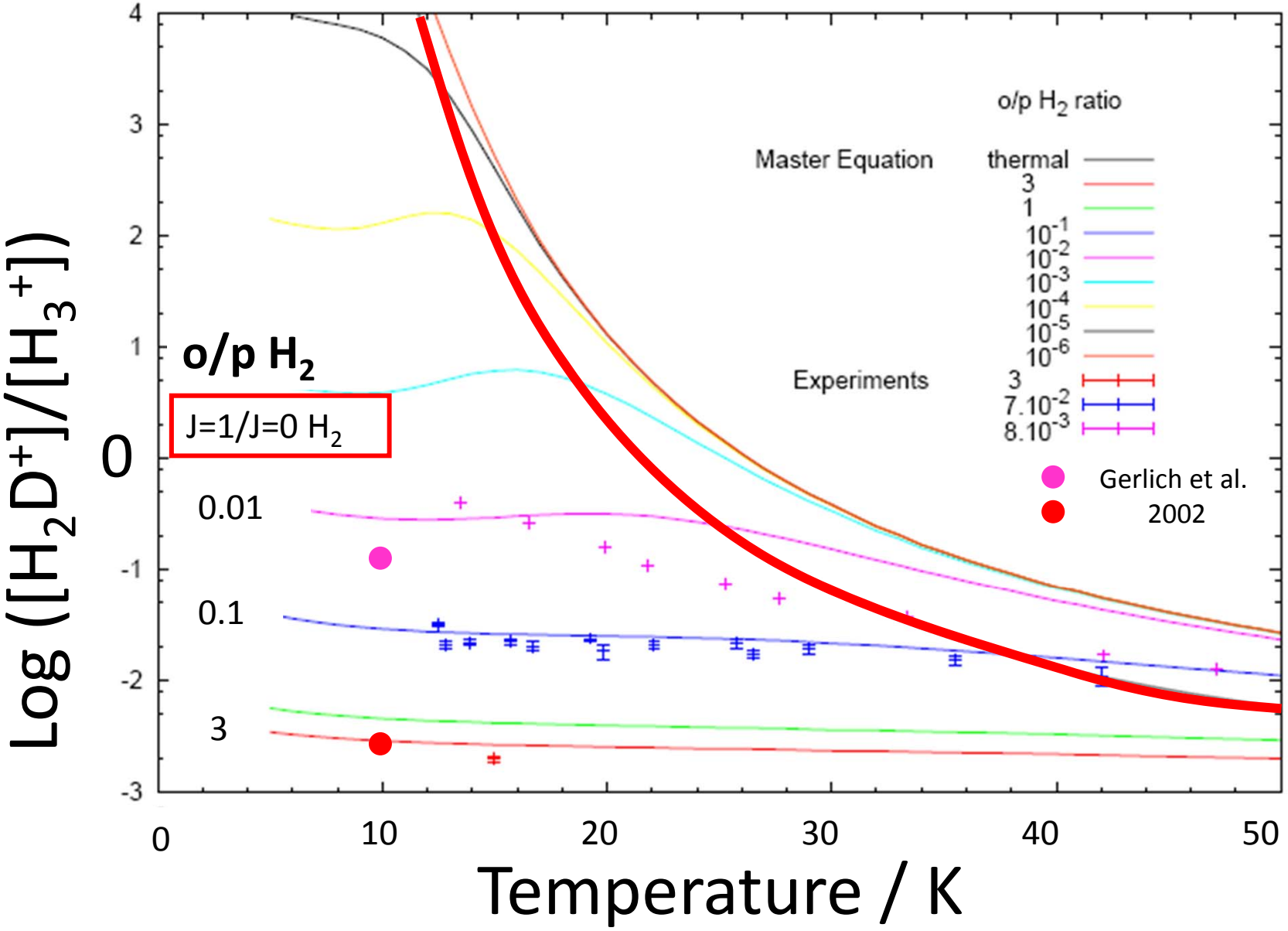
× m=2u

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

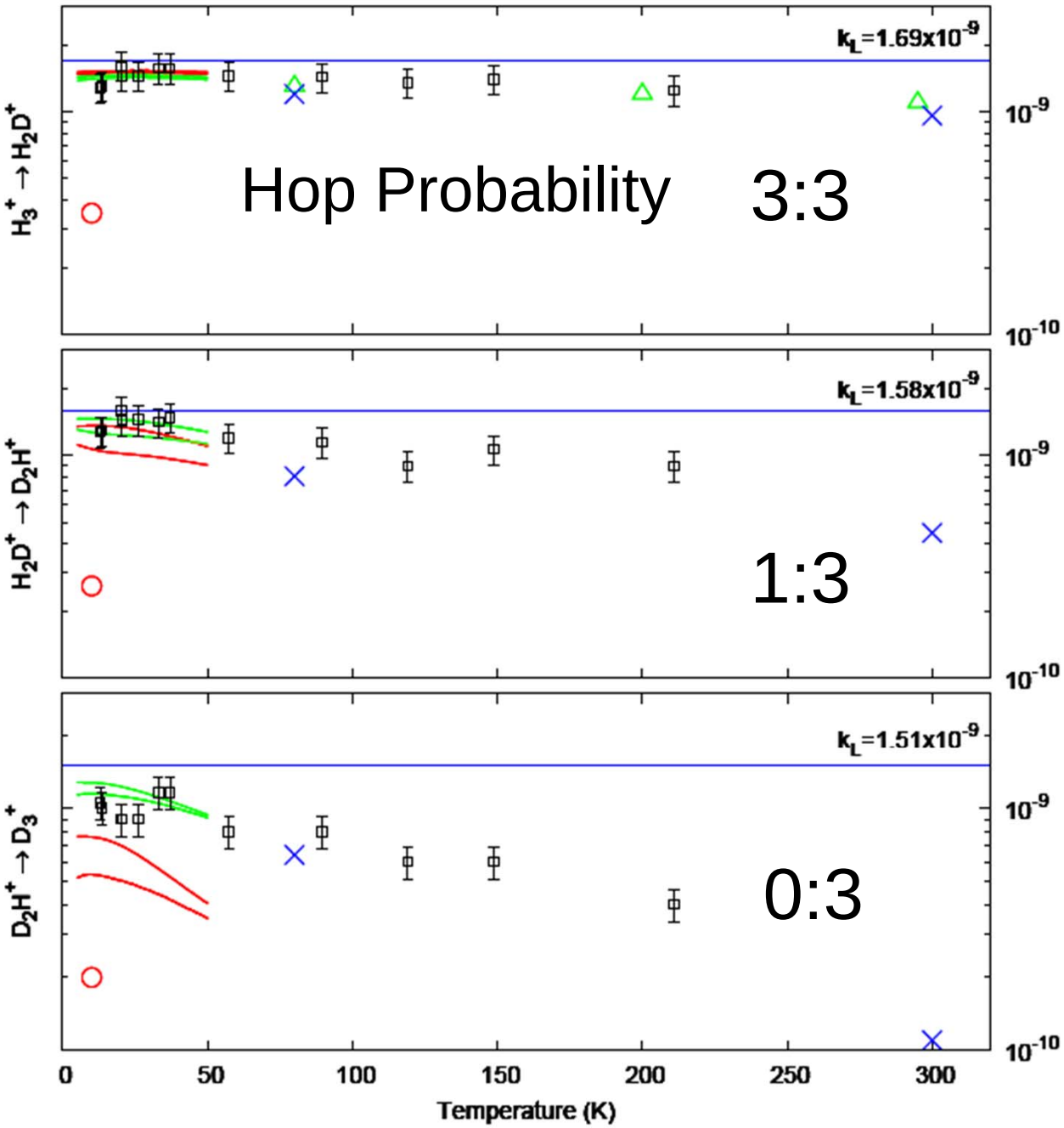


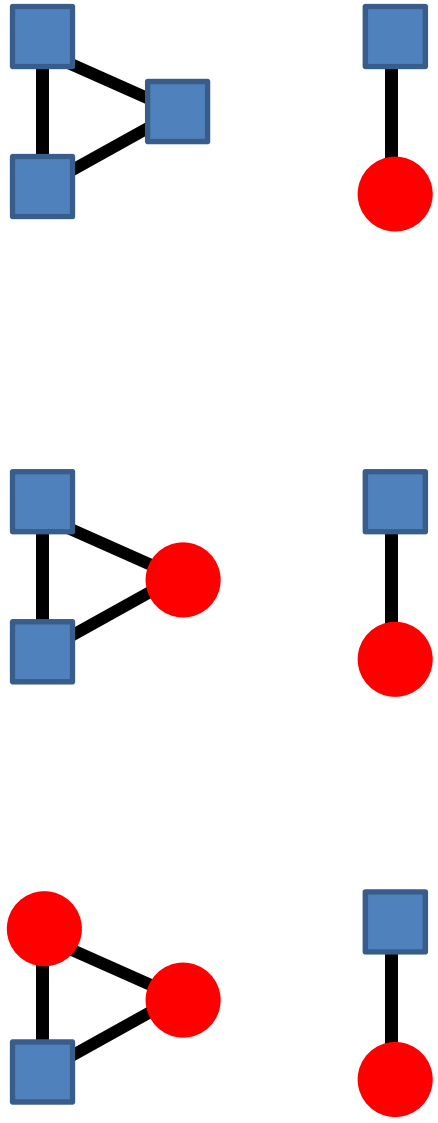
# New Experimental Results & Modelling

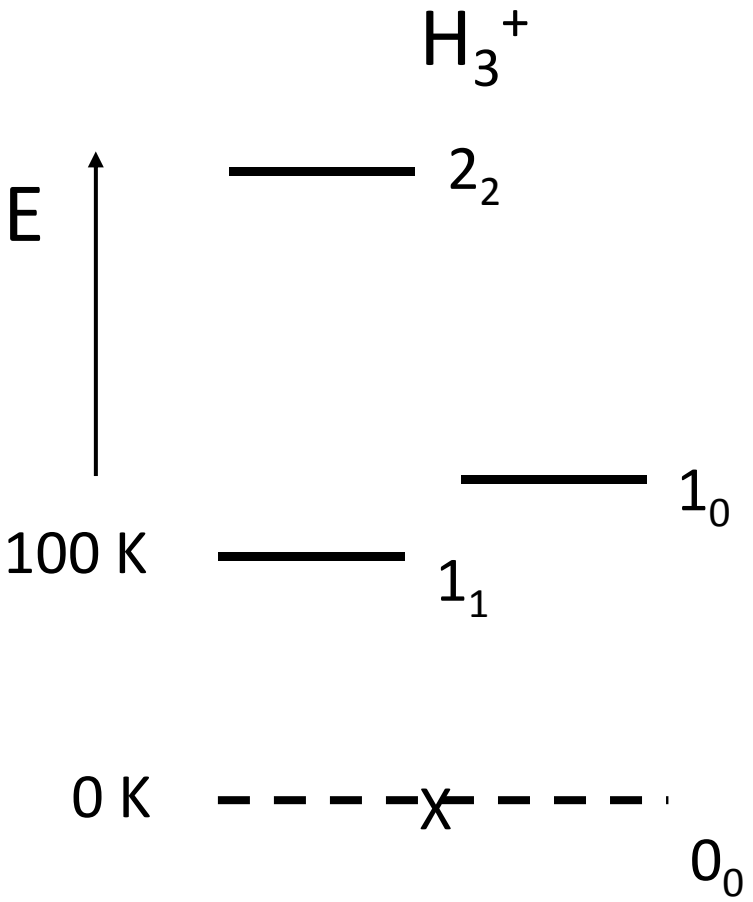
Hugo et al., J.Chem.Phys. 2009, **130,** 164302



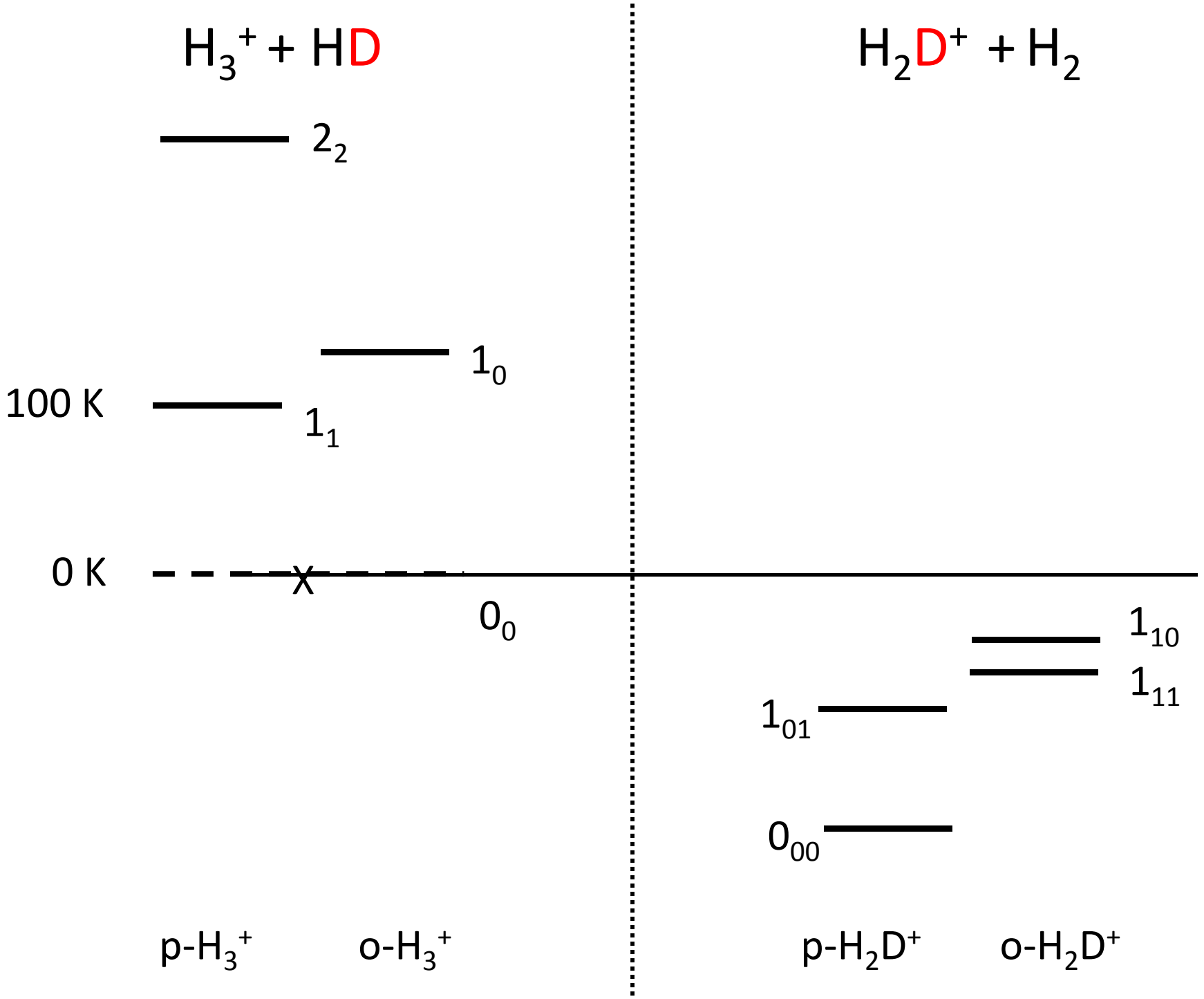
# Reaction Mechanism: Proton Hop

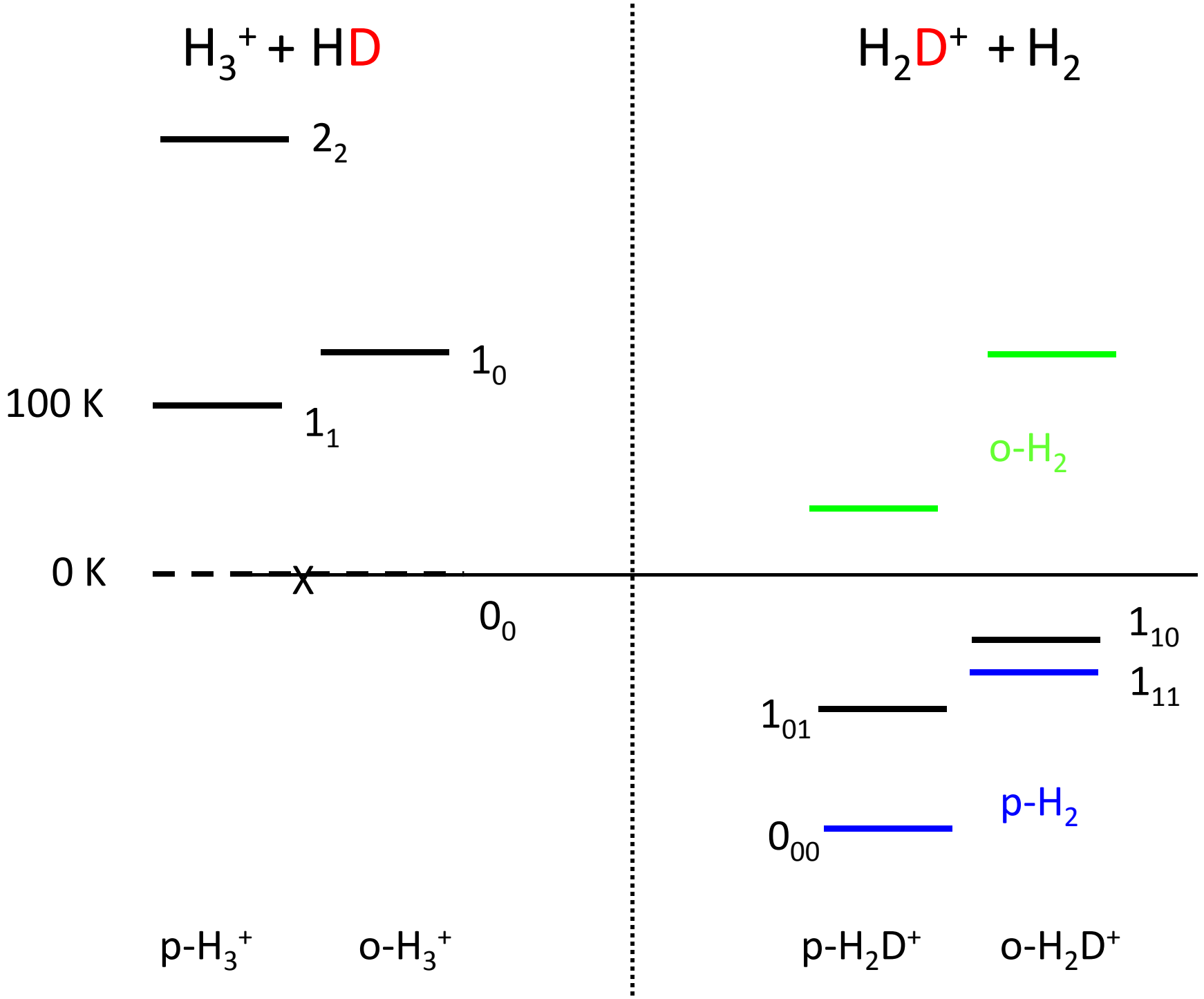


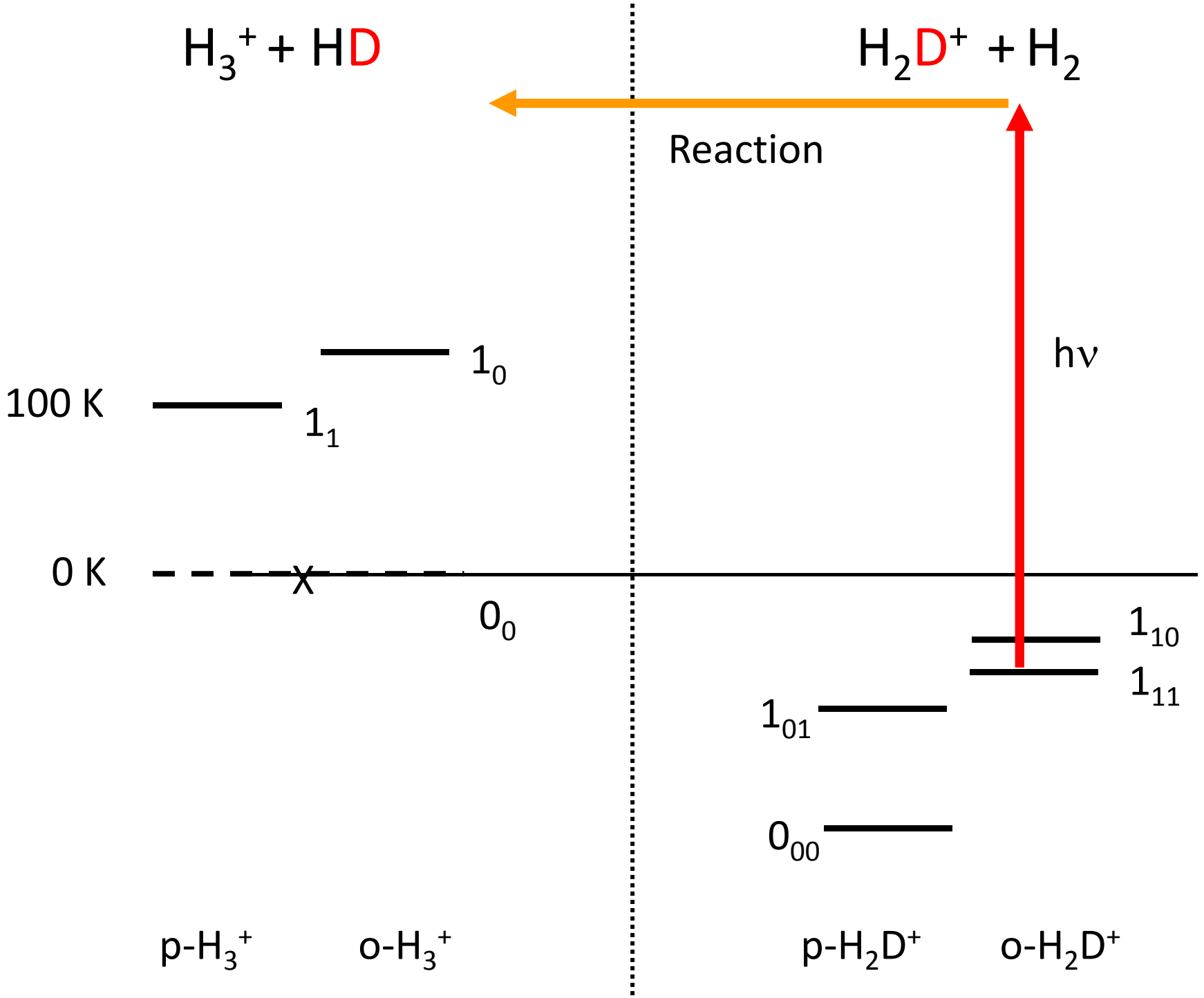



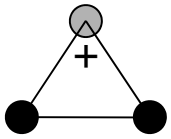



Lowest energy levels of $H_3^+$

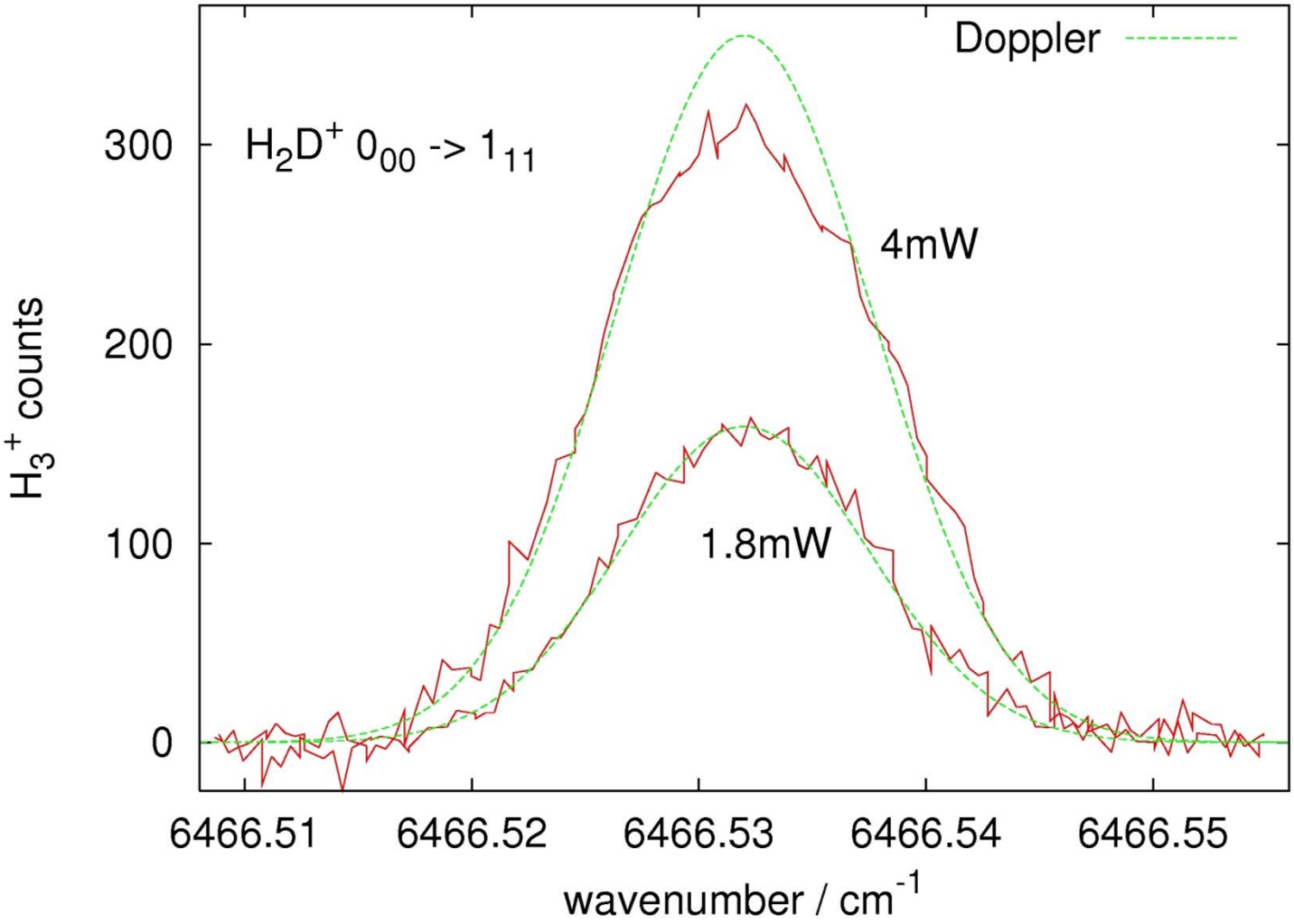

$H_3^+ + HD$
$H_2D^+ + H_2$
$2_2$
$1_0$
100 K
$1_1$
0 K
$0_0$
$1_{10}$
$1_{11}$
$1_{01}$
$0_{00}$
p-$H_3^+$
o-$H_3^+$
p-$H_2D^+$
o-$H_2D^+$


$H_3^+ + HD$
$H_2D^+ + H_2$
$2_2$
$1_0$
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-$H_2D^+$


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



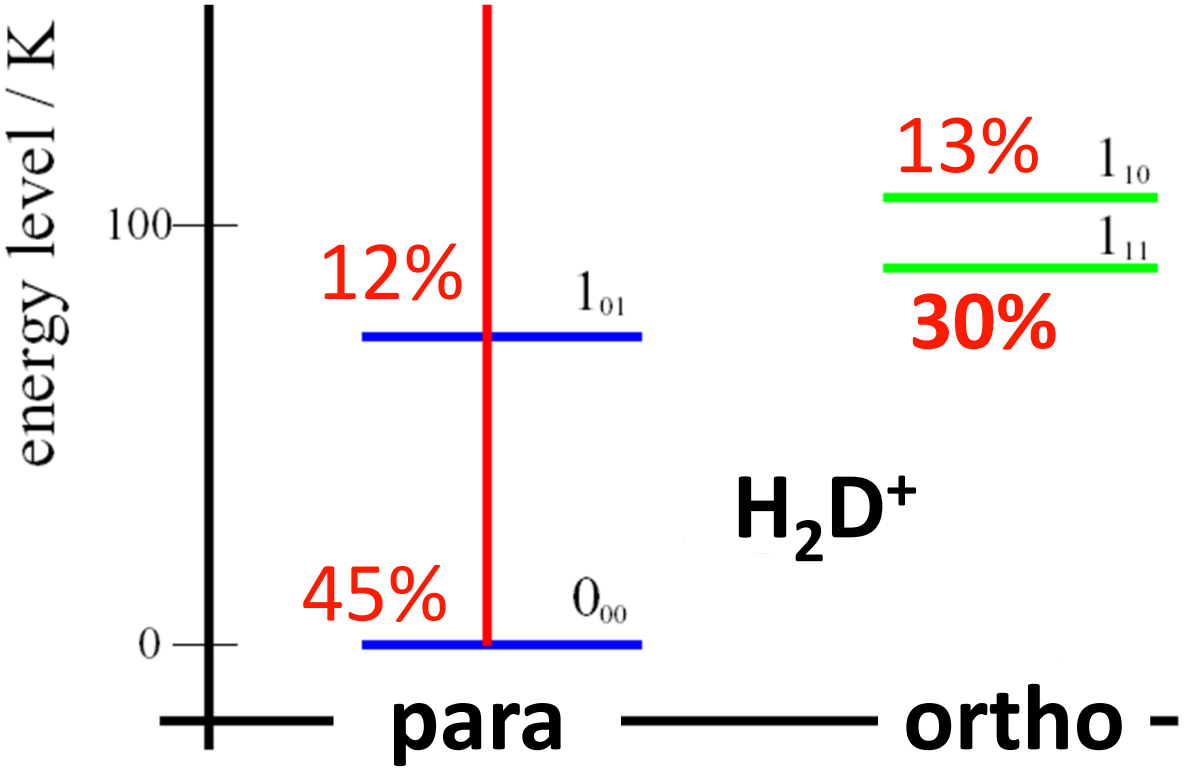
# Spectroscopic results for $H_2D^+$




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

# rotational level populations of $H_2D^+$

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



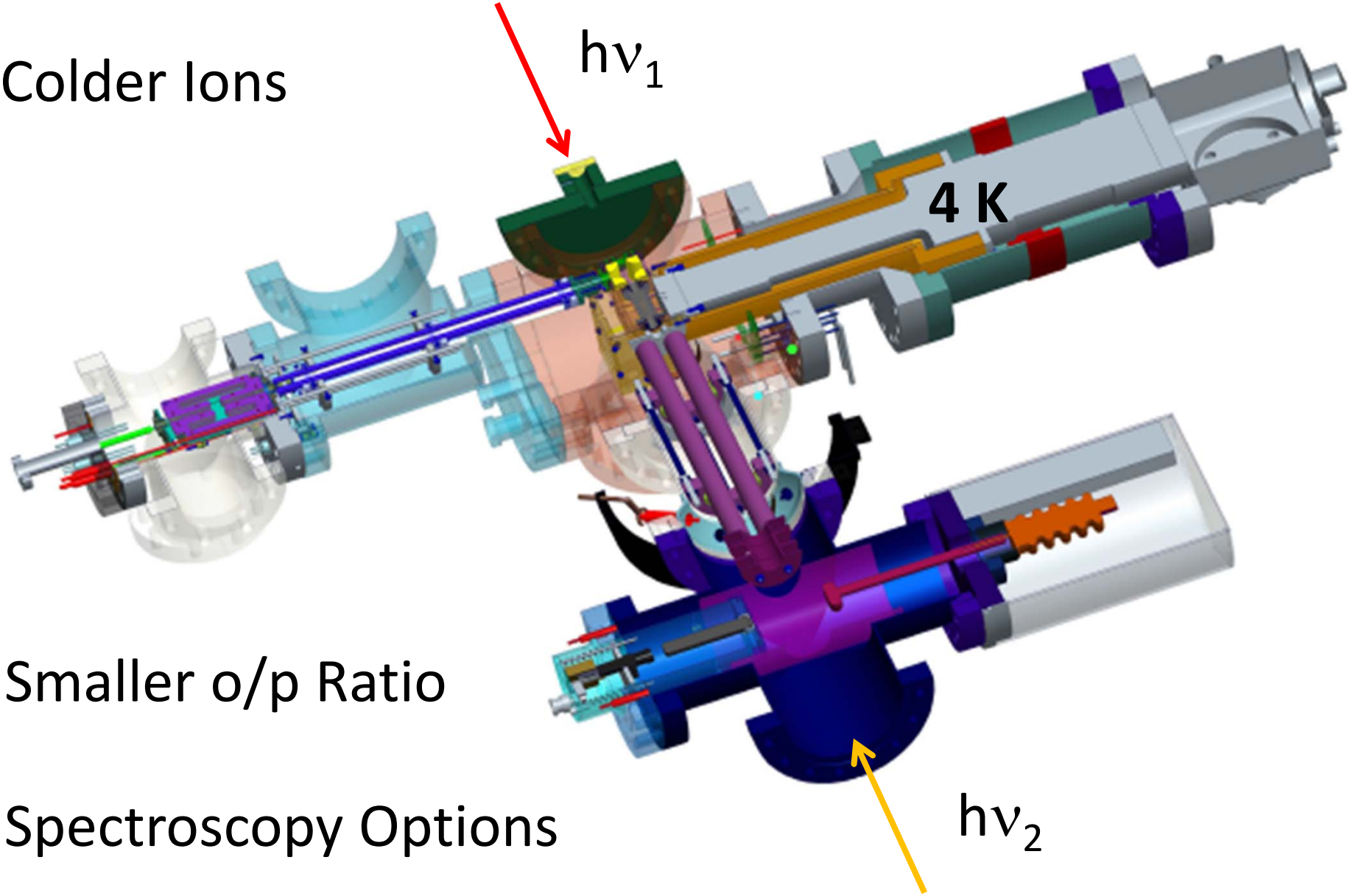

$T_{Doppler}=(27\pm2)K$

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

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

# COLTRAP: Future $H_3^+$ / $H_2D^+$ Experiments

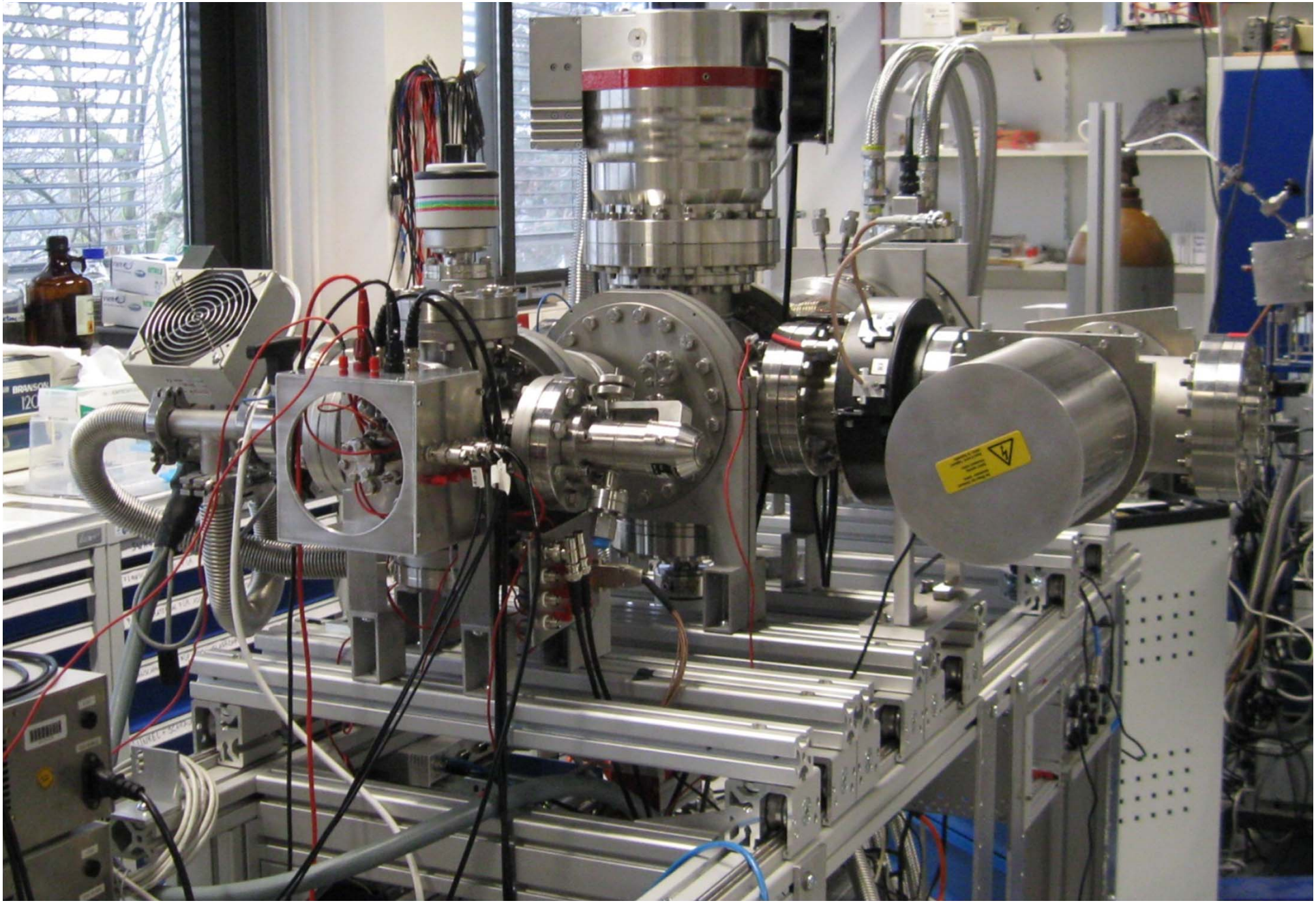
Colder Ions




Smaller o/p Ratio

Spectroscopy Options

# FELION: Spectroscopy Trap for FELIX

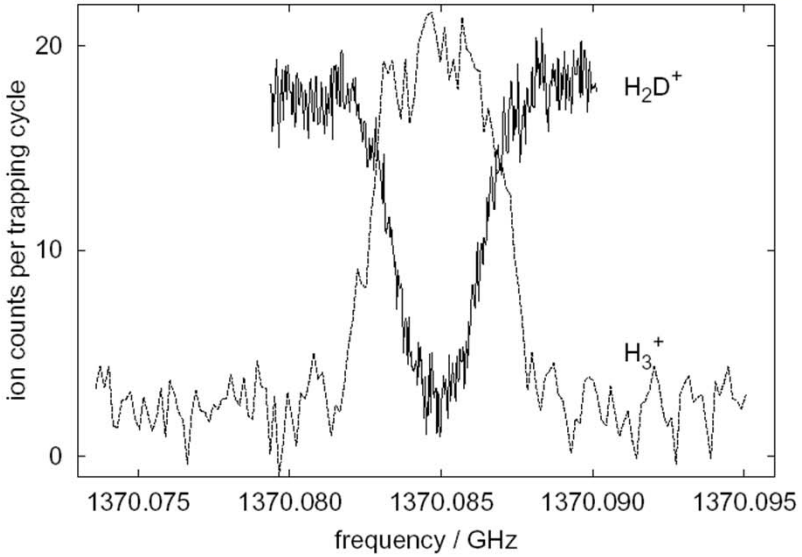


**Li**

100 K

0 K


SOFIA
NASA
DLR


20
10
0
ion counts per trapping cycle
$H_2D^+$
$H_3^+$
1370.075
1370.080
1370.085
1370.090
1370.095
frequency / GHz


GREAT
Receiver

The Astrophysical Journal, 697:601–609, 2009

# IS $HO_2^+$ A DETECTABLE INTERSTELLAR MOLECULE?

Susanna L. Widicus Weaver[1,4], David E. Woon[2], Branko Ruscic[3], and Benjamin J. McCall

$$H_3^+ + O_2 \rightleftharpoons H_2 + O_2H^+$$

Tracer for $O_2$?

Chemistry of near thermoneutral Reaction

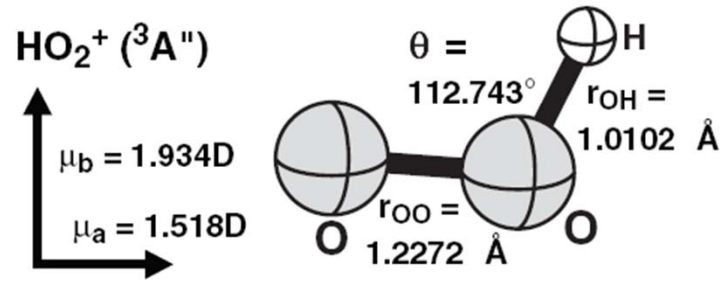


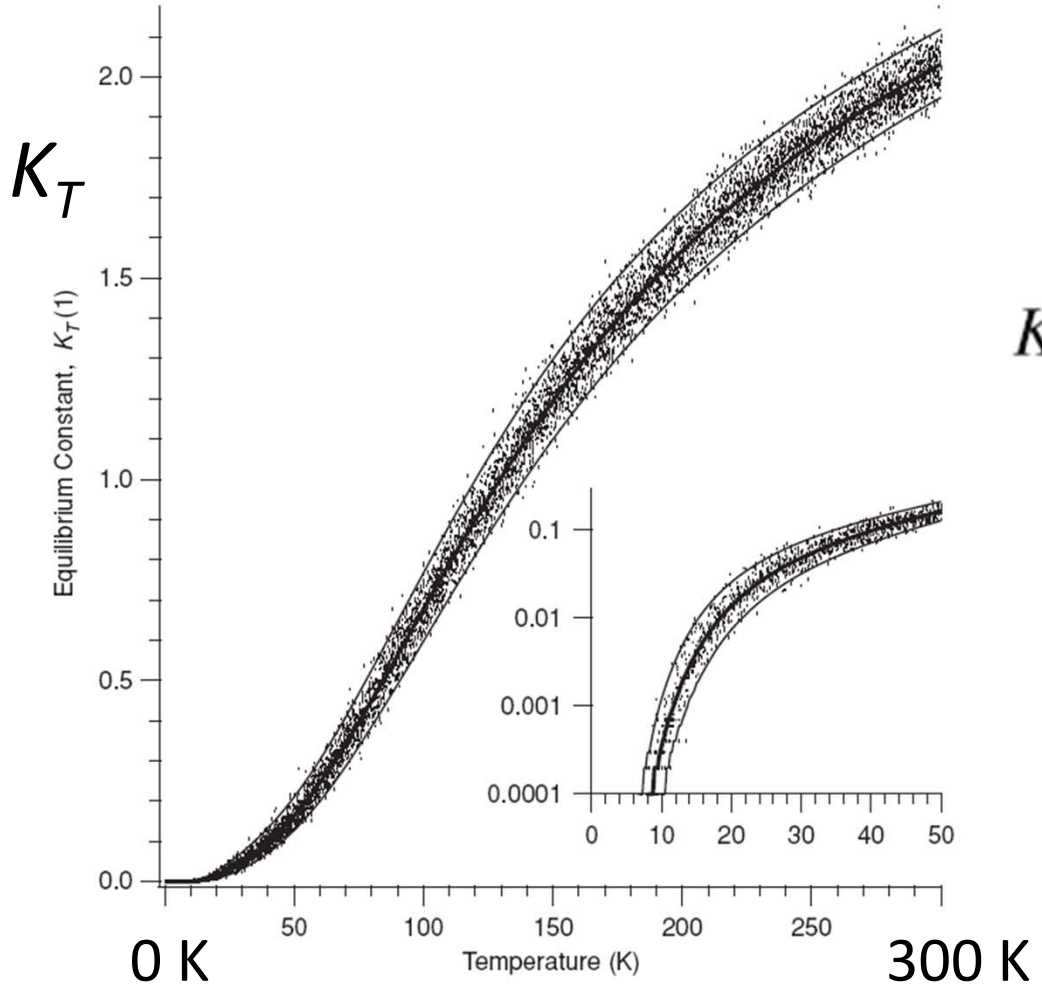

**Figure 1.** Equilibrium structural parameters for $HO_2^+$ (RCCSD(T) at the valence complete basis set limit with core–valence corrections) and dipole moment components (MRCI/AV5Z).

Molecular Parameters Determined for $HO_2$ and $HO_2^+$

| Spectroscopic Constant | $HO_2$ Calculated[a] | $HO_2$ Experimental[b] | $HO_2^+$ Calculated[a] |
|---|---|---|---|
| $A_0$ (GHz) | 615.997 | 610.2733 | 659.301 |
| $B_0$ (GHz) | 33.604 | 33.5178 | 38.344 |
| $C_0$ (GHz) | 31.643 | 31.6677 | 35.885 |
| $\nu_1$ ($cm^{-1}$) | 3457 | 3436.2 | 3028 |
| $\nu_2$ ($cm^{-1}$) | 1406 | 1391.8 | 1440 |
| $\nu_3$ ($cm^{-1}$) | 1128 | 1097.6 | 1068 |
| $\Delta_N$ (MHz) | 0.1127 | 0.116908 | 0.1075 |
| $\Delta_{NK}$ (MHz) | 3.303 | 3.44572 | 5.515 |
| $\Delta_K$ (MHz) | 115.02 | 123.5906 | 299.03 |
| $\mu_a$ (D) | 1.405 | 1.412 | 1.518 |
| $\mu_b$ (D) | 1.572 | 1.541 | 1.934 |
| $D$ ($cm^{-1}$) | | | 6.870 |
| $E$ ($cm^{-1}$) | | | 0.033 |
| $\epsilon_{aa}$ (MHz) | −46730 | −49572 | −1182 |
| $\epsilon_{bb}$ (MHz) | −432 | −422.9 | −481 |
| $\epsilon_{cc}$ (MHz) | −159 | 8.748 | −476 |

# Predictions: Equilibrium Constant

$$H_3^+ + O_2 \rightleftharpoons H_2 + O_2H^+$$

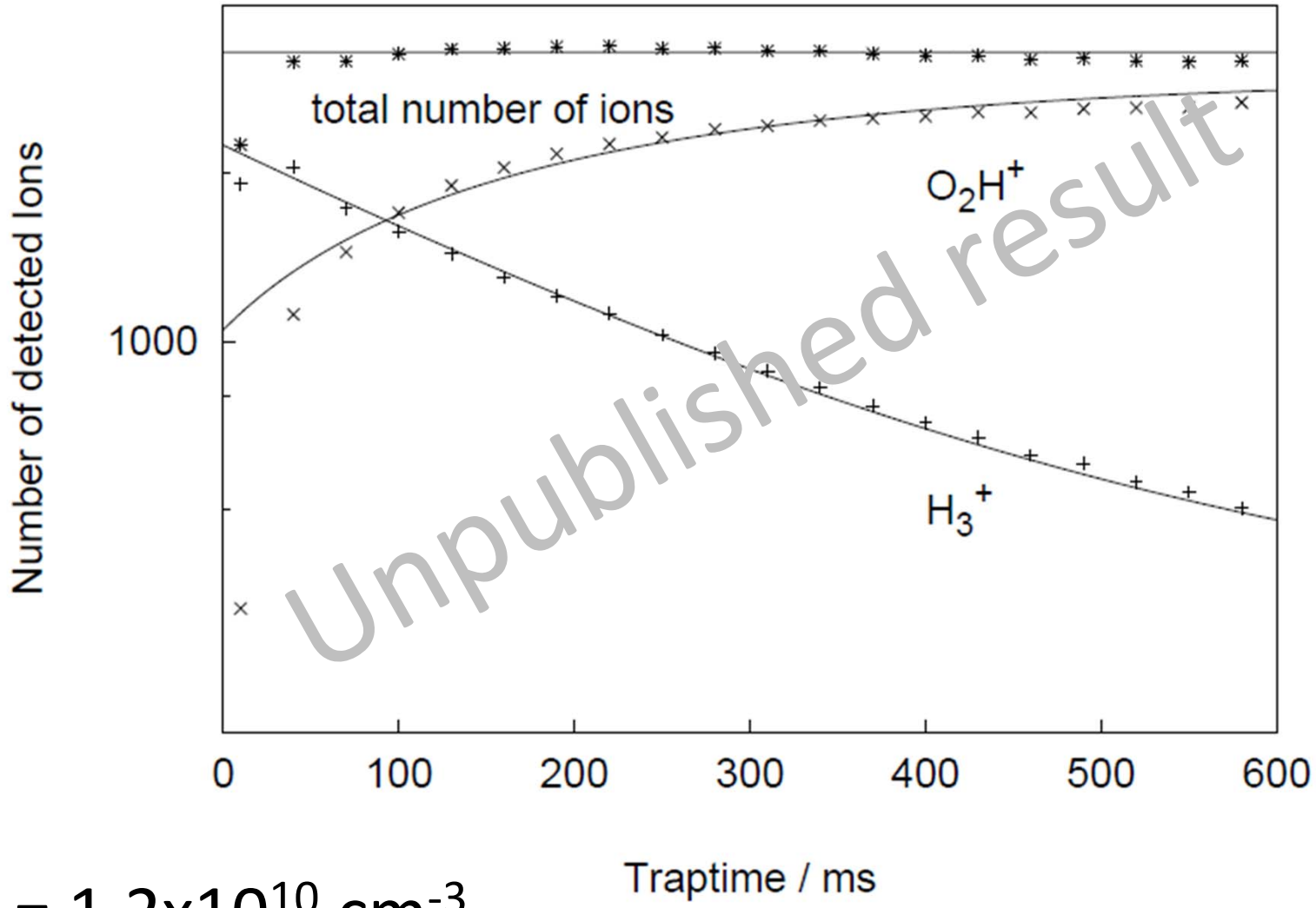



$$K_T(1) = e^{-\frac{E_0(1)}{kT}} \frac{q(HO_2^+)q(H_2)}{q(H_3^+)q(O_2)}$$

Formation of $O_2H^+$ endothermic: $E_a/k = 72 +/- 13$ K

# Trap Experiments

$$H_3^+ + O_2 \rightleftharpoons H_2 + O_2H^+$$

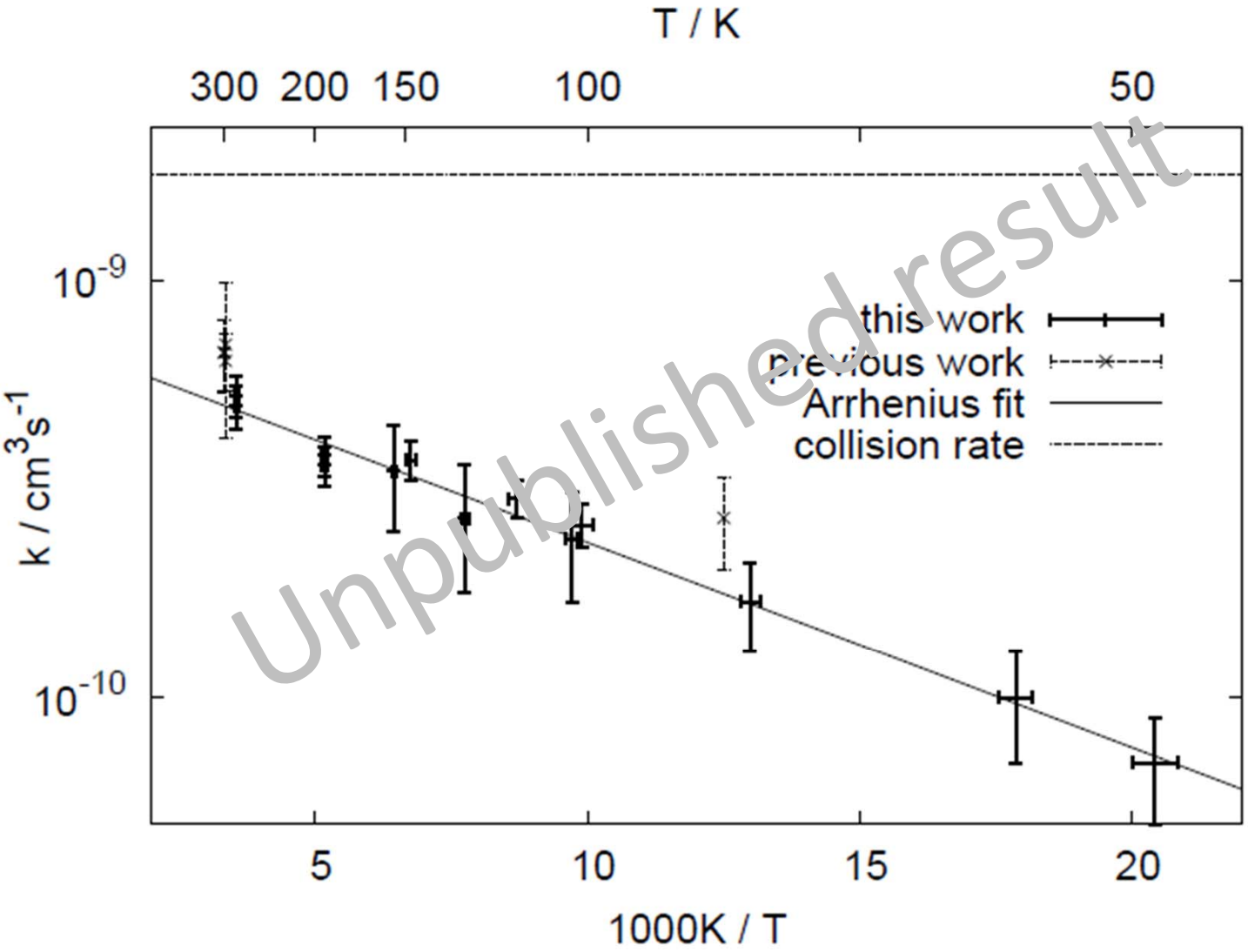



$[O_2] = 1.2 \times 10^{10}$ cm$^{-3}$

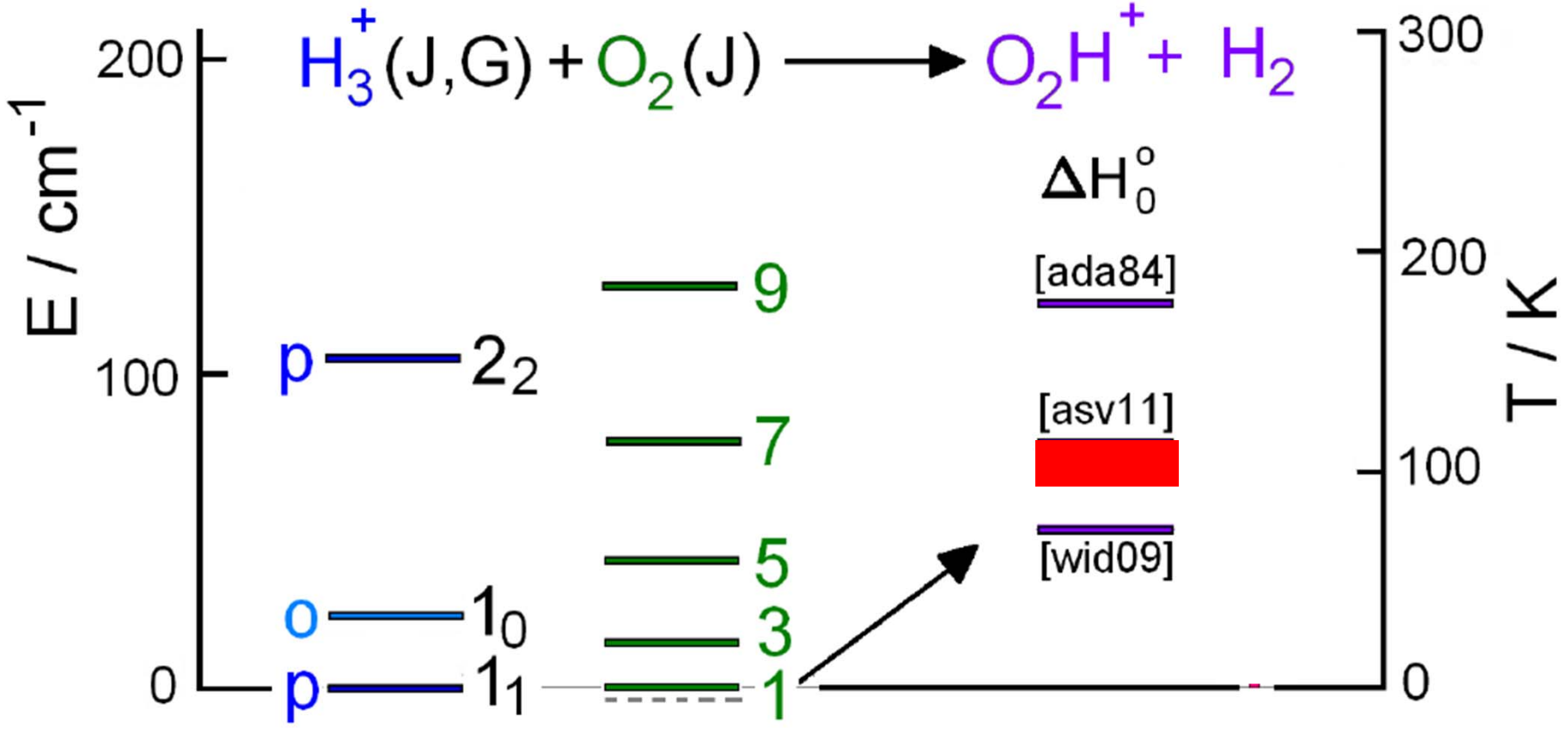
T = 129 K

# Arrhenius Plot

$E_a/k = 113+/-4$ K

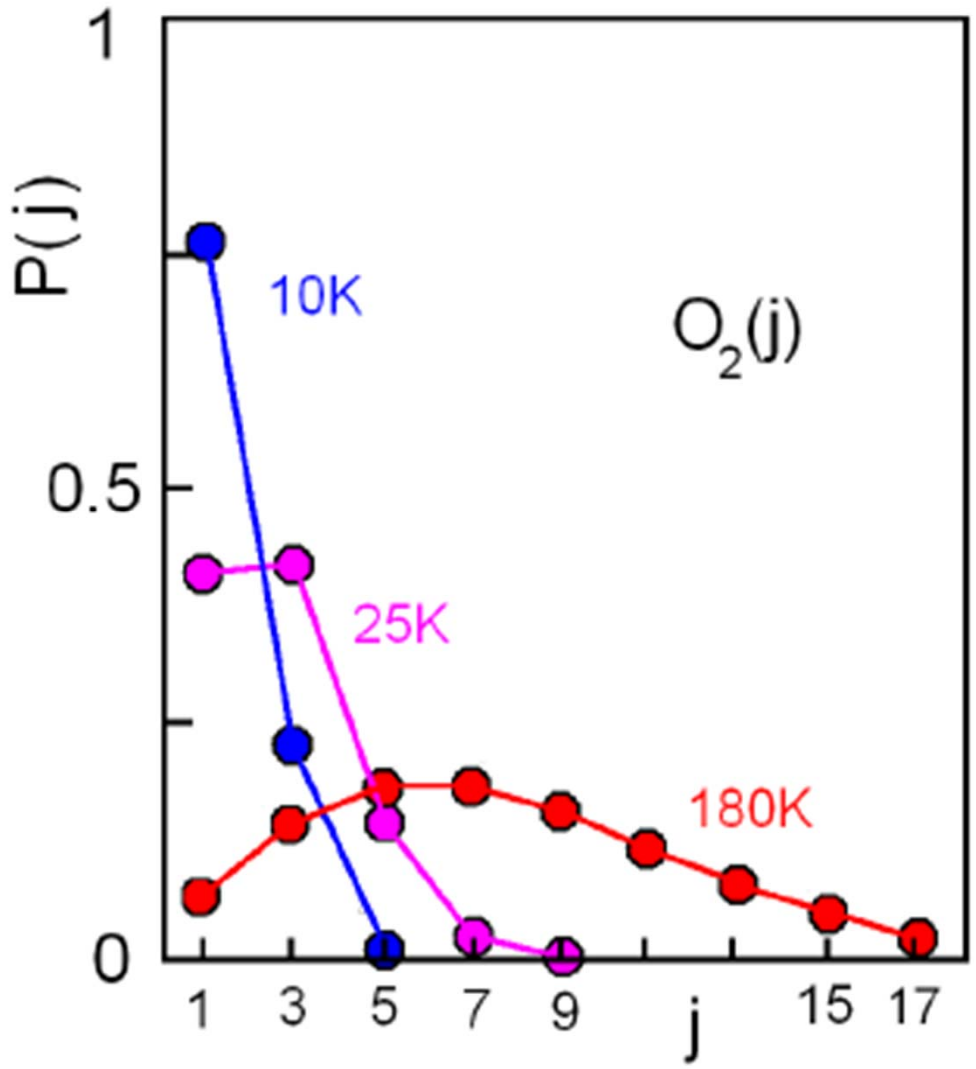


# Energetics of $H_3^+ + O_2$ Collision



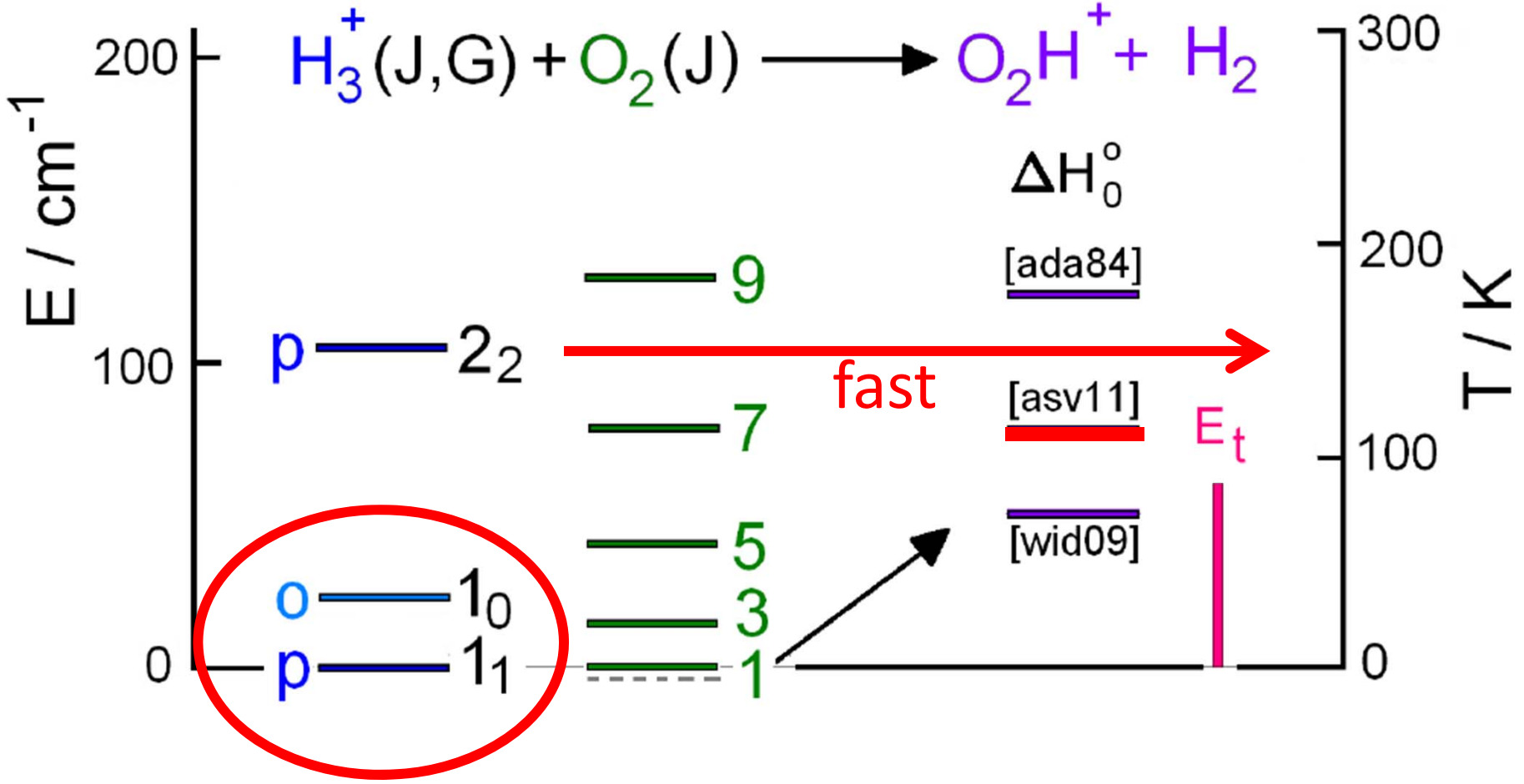

Dieter Gerlich at 2011 COST Meeting

# $O_2$ Rotational State Distribution



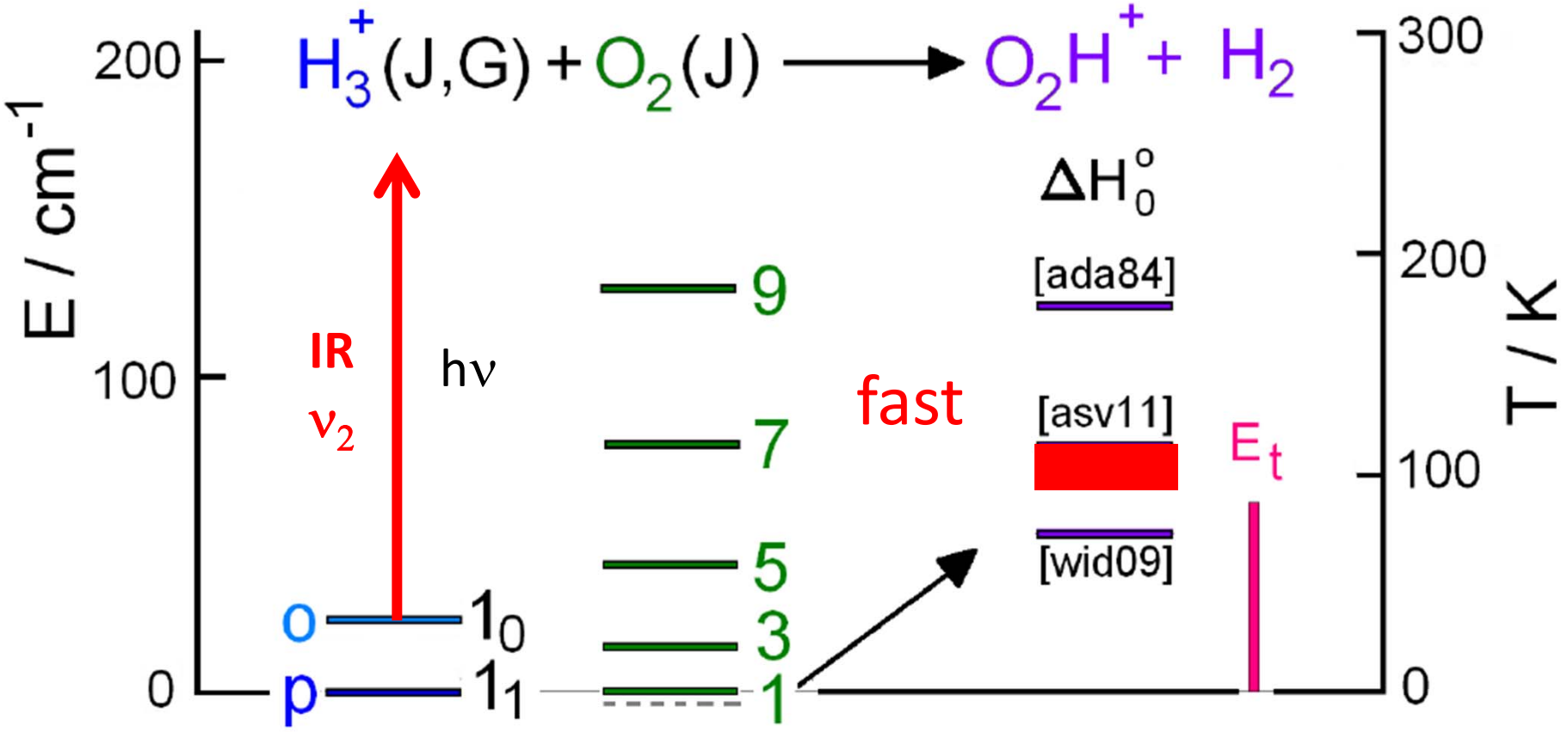

Dieter Gerlich at 2011 COST Meeting

# Towards State Preparation: Collaboration with Dieter Gerlich




o-$H_3^+$ + $O_2$ ⟶ X ⟶ o-$H_2$ + $O_2H^+$

# State Popoulation: Light Induced Reactions




$H_3^+ + O_2 \not\rightarrow H_2 + O_2H^+$

$H_3^+ + h\nu + O_2 \rightarrow H_2 + O_2H^+$

VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

# Observation of the Infrared Spectrum of $H_3^+$

Takeshi Oka

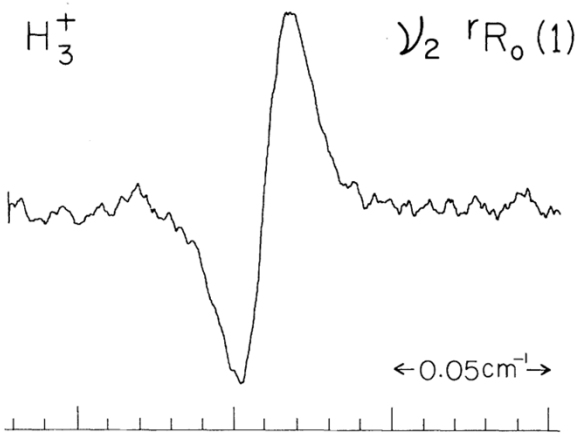
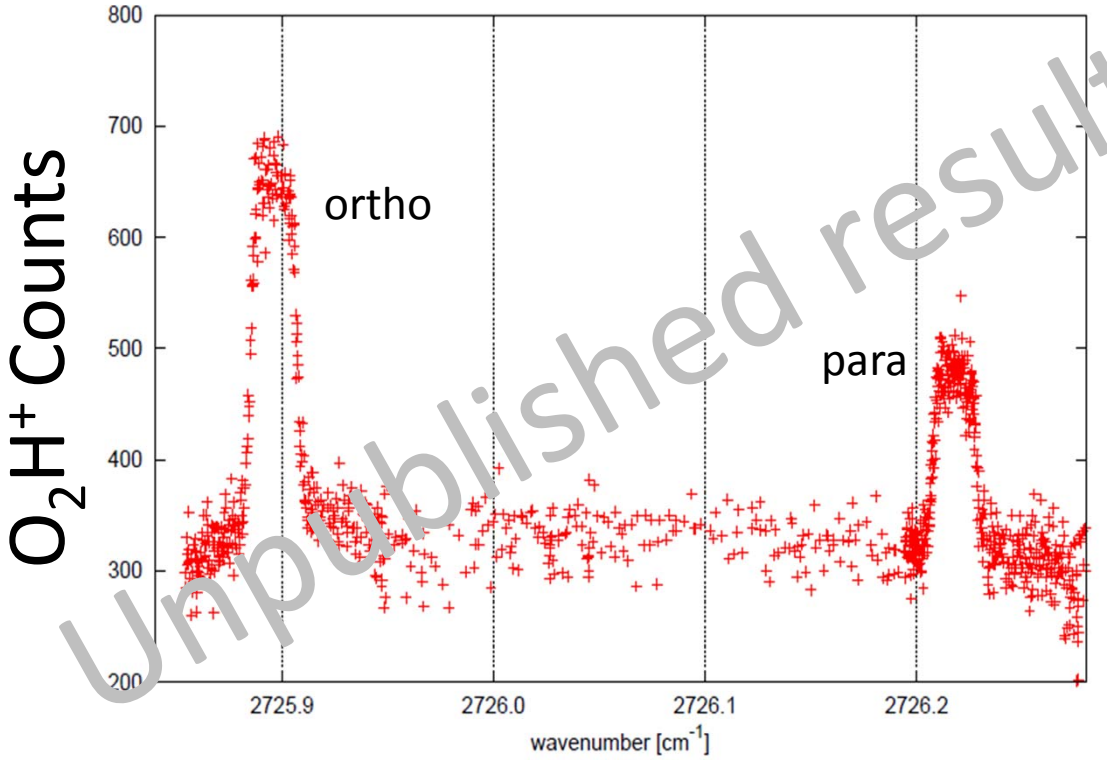
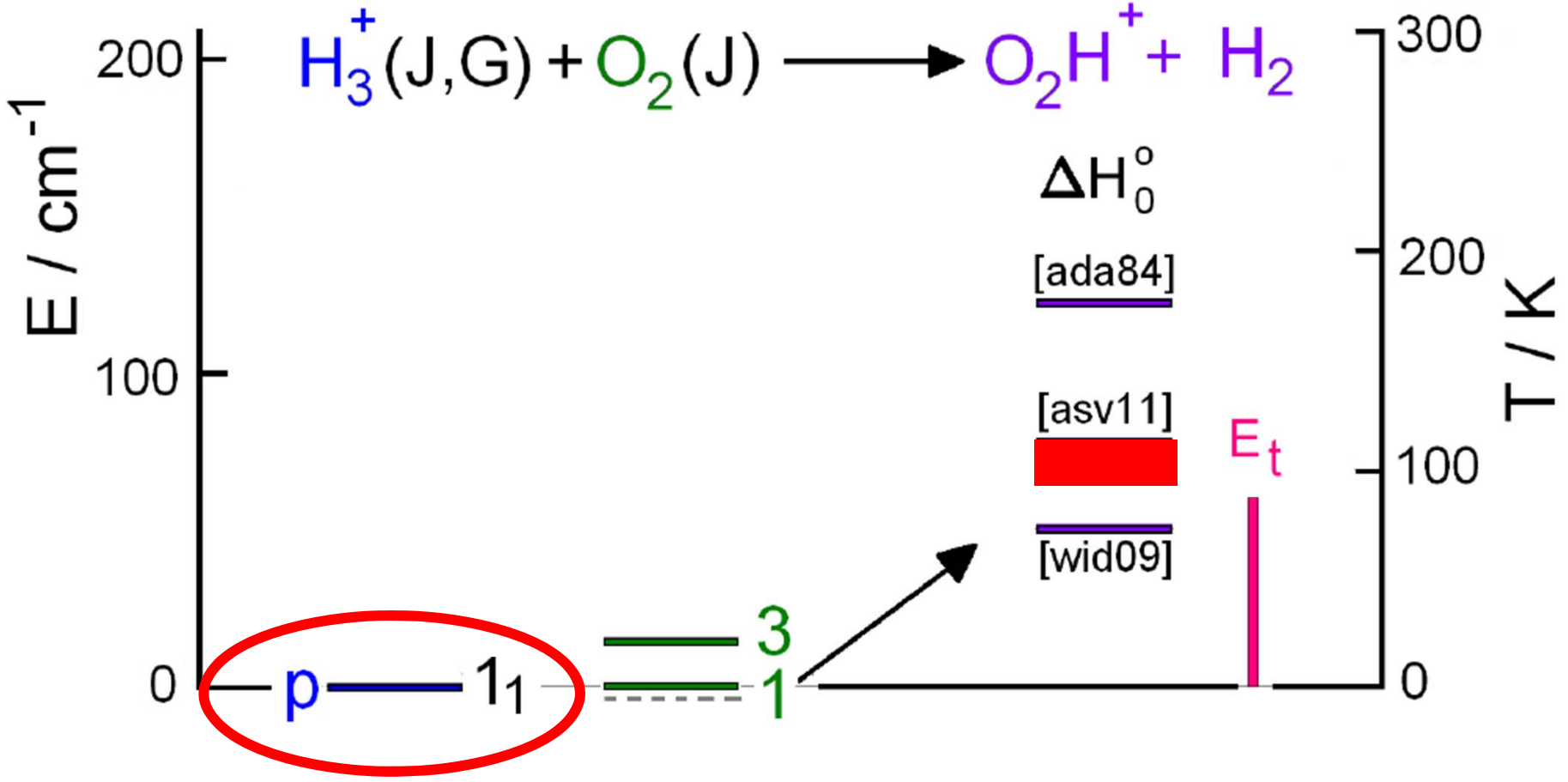



FIG. 1. The observed $^rR_0(1)$ transition ($J=2$, $k=\pm 1$, $l=\pm 1$)← ($J=1$, $k=0$) of $H_3^+$ at 2725.885 $cm^{-1}$. Discharge current, 140 mA; pressure, 0.5 Torr; the time constant for detection, 400 msec.

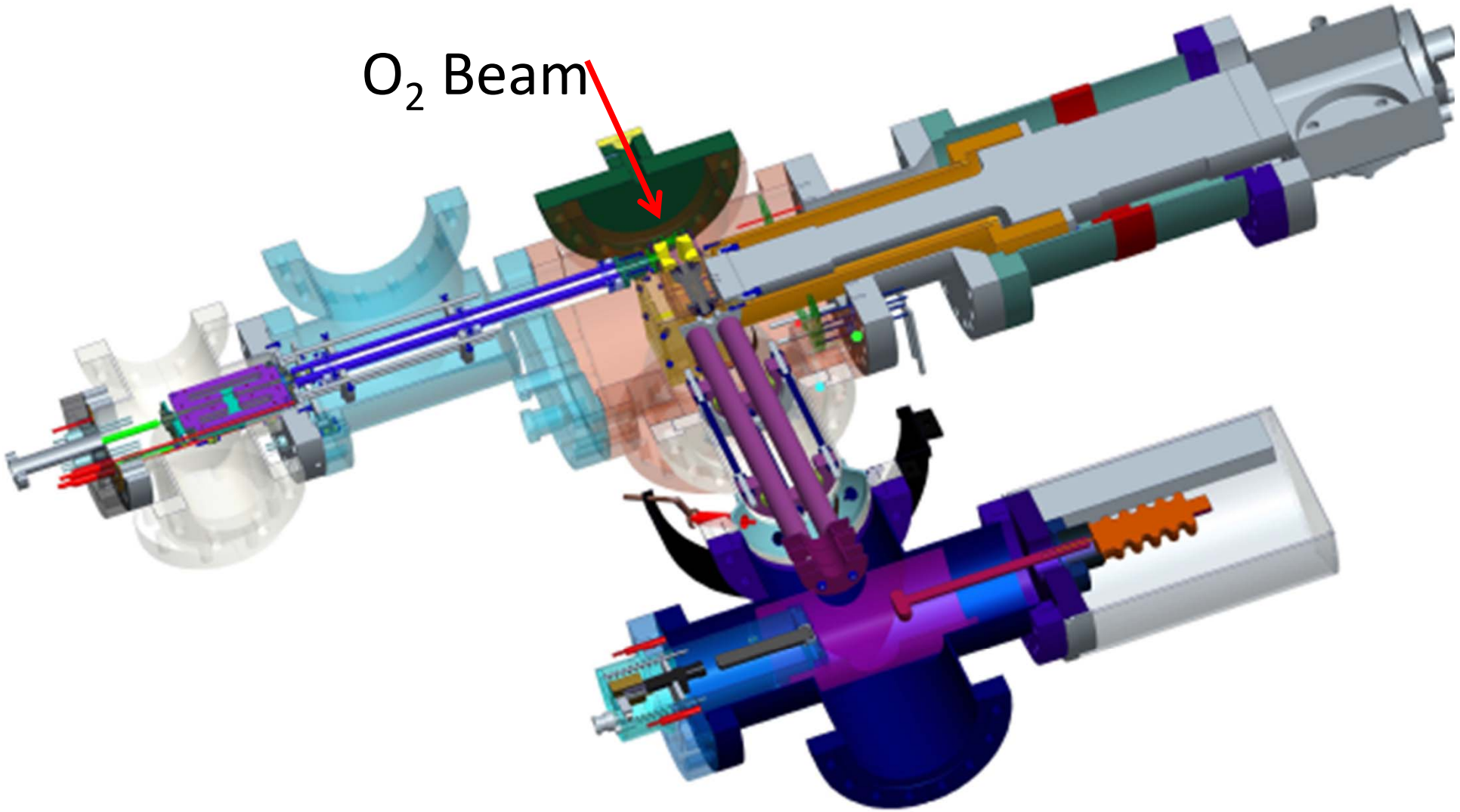
Light Induced Reactions



# Towards State Preparation: Collaboration with Dieter Gerlich

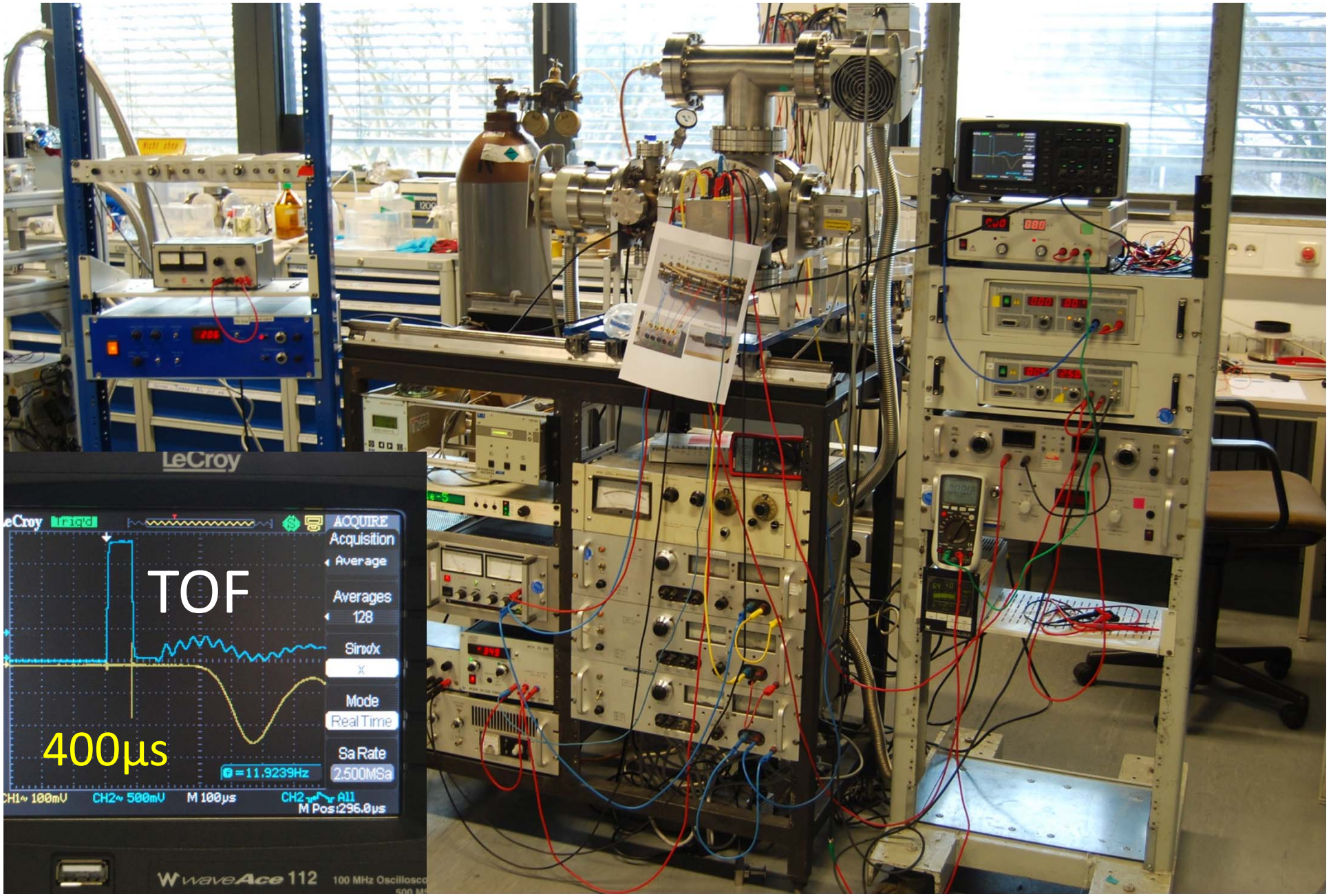


# COLTRAP: Combined Molecular Beam & Trap

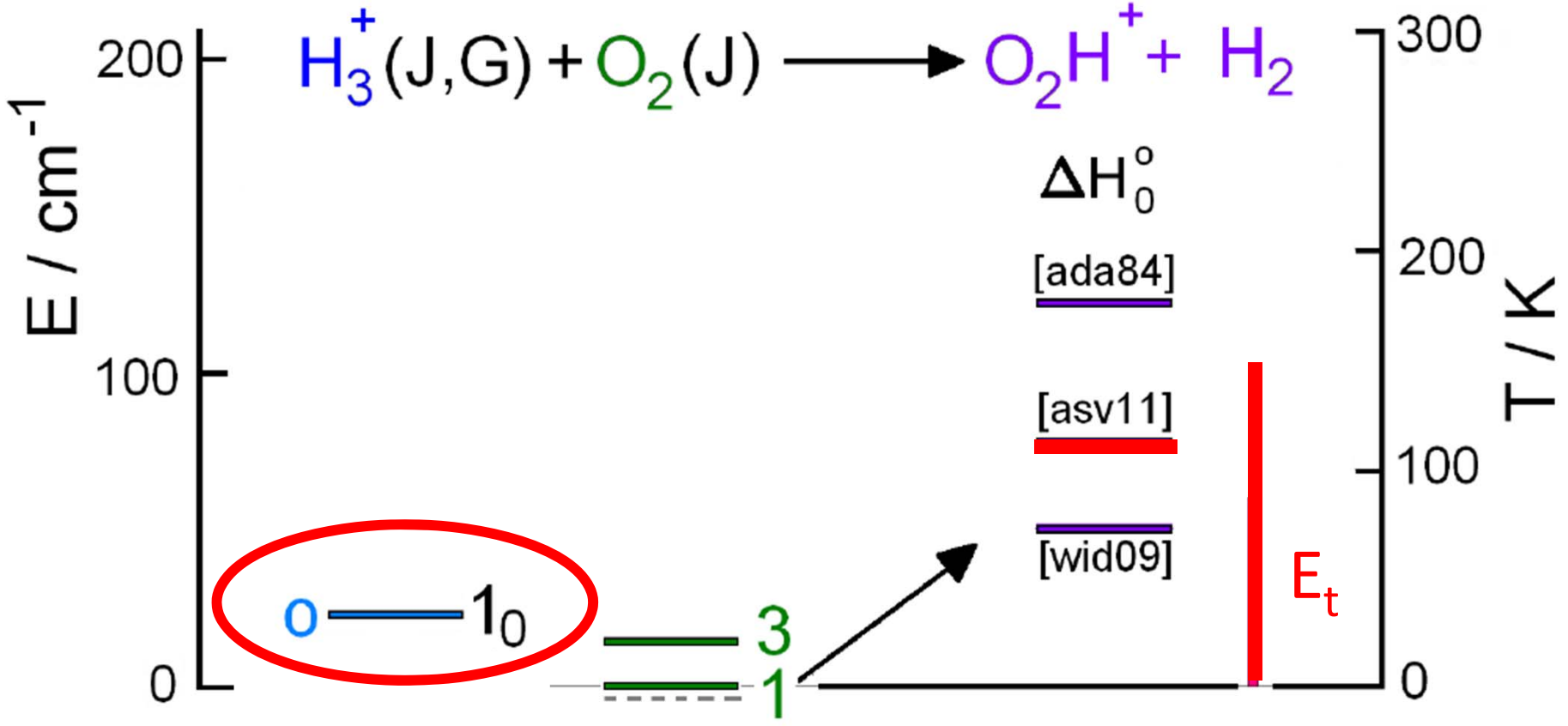



Towards State Preparation: Collaboration with Dieter Gerlich

# Molecular Beam Testing

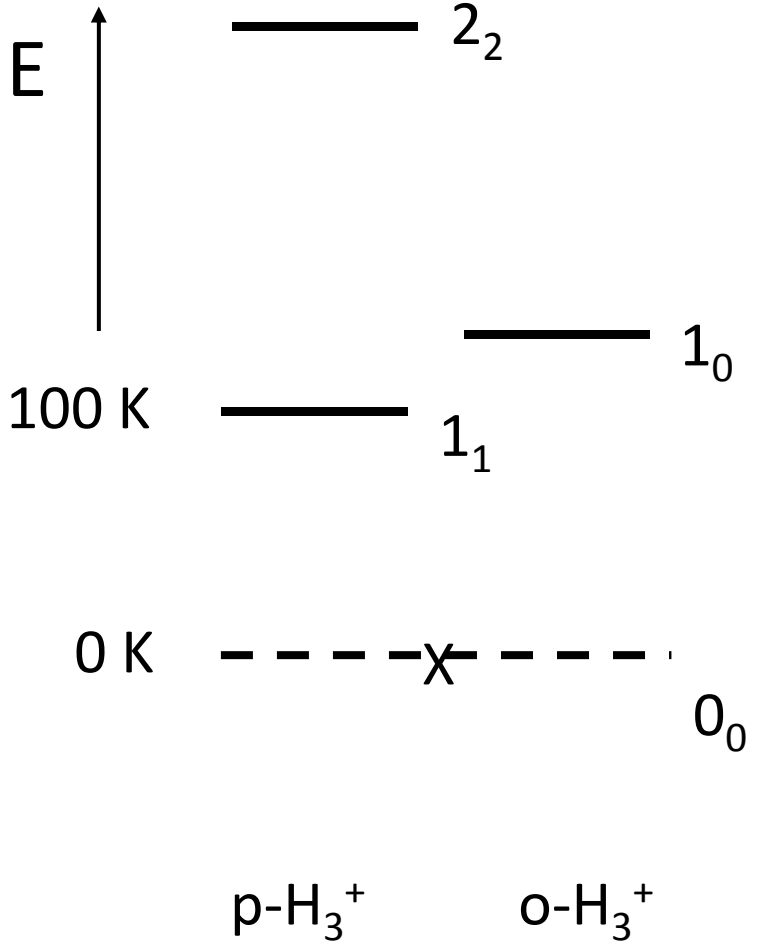


# Towards State Preparation: Collaboration with Dieter Gerlich




o-$H_3^+$ + o/p $H_2$ ⟶ **?**

# A Chairman‘s Dream Experiment



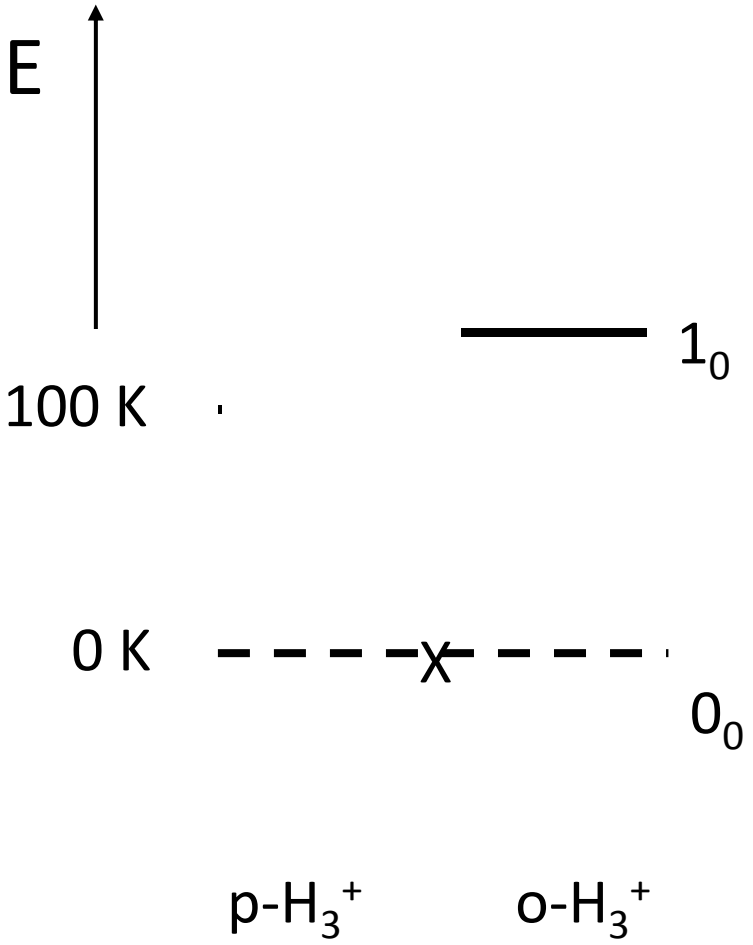

Step 1:

Prepare $1_0$ Level

by chemical quenching

$H_3^+ + O_2$

# A Chairman‘s Dream Experiment



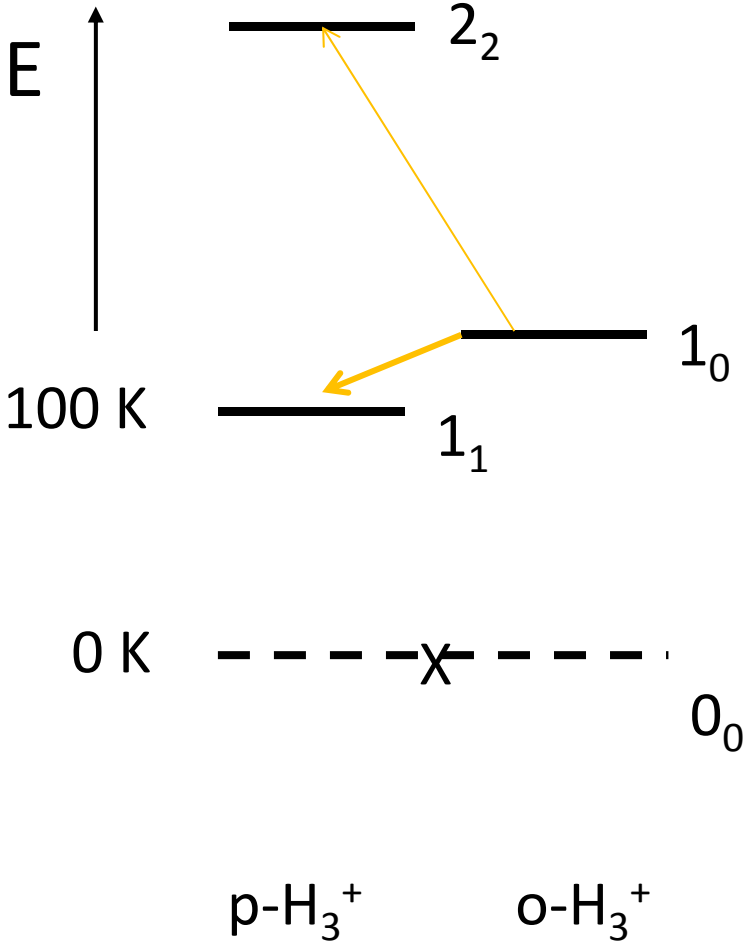

Step 1:

Prepare $1_0$ Level

by chemical quenching

$H_3^+ + O_2$

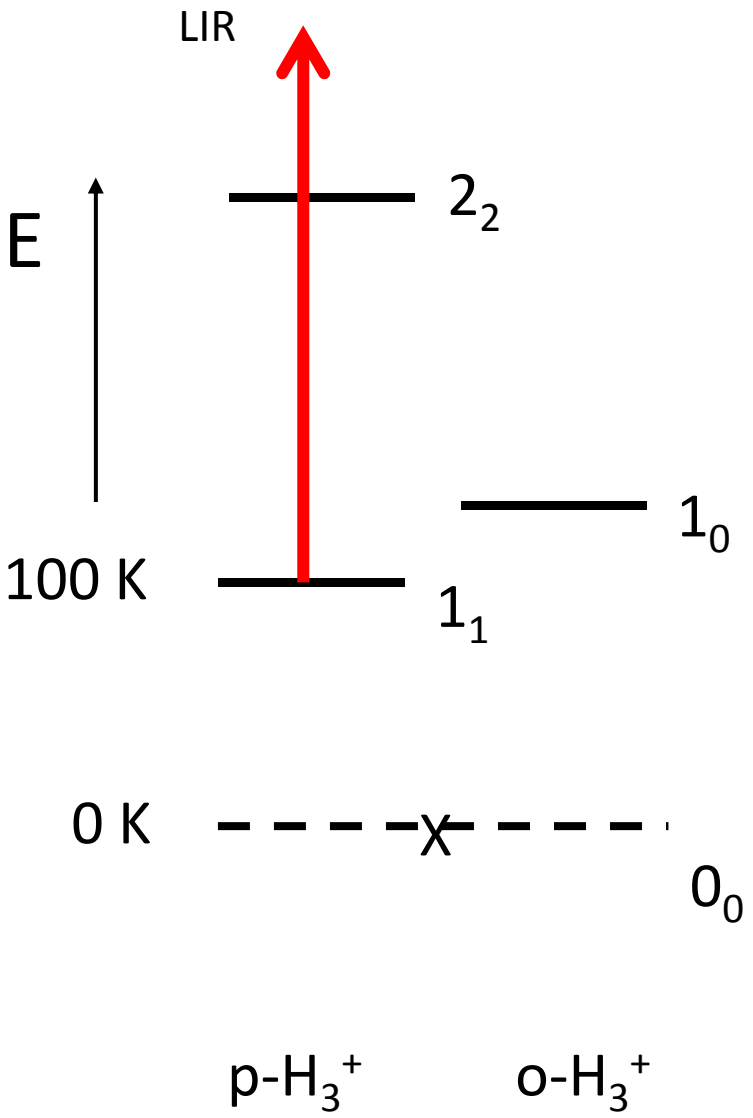
# $H_3^+$ Dream Experiment




Step 2:

Inelastic Collisions
e.g. with $H_2$

# $H_3^+$ Dream Experiment

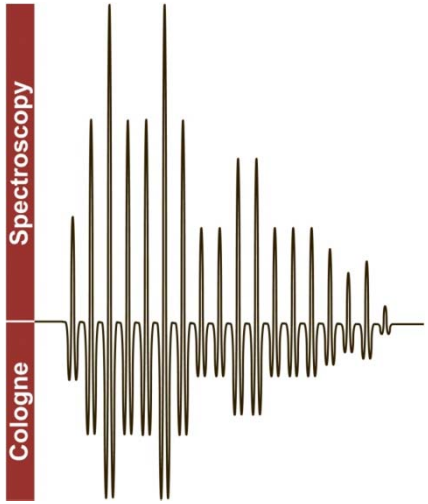



Step 3:

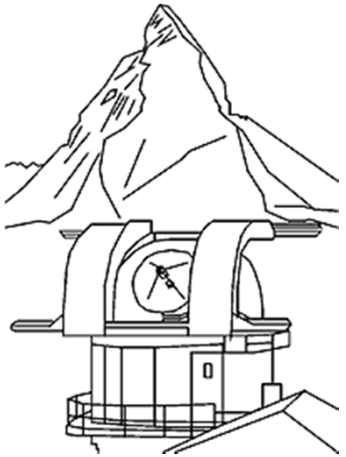
Probe Level Population with LIR

$$H_3^+ + O_2 \longrightarrow H_2 + O_2H^+$$

*Chicheley Hall, February 9, 2012*




# Cold trap experiments on $H_3^+ + O_2$ proton transfer



Stephan Schlemmer

Universität zu Köln

- The THz view into the Sky: Astrophysical Picture
- $H_2D^+$ / $H_3^+$ in Space and Laboratory
- $H_3^+ + O_2$ Proton Transfer
- Preparing a single rotational state of $H_3^+$