Oxygen Photolysis in Solid Molecular Hydrogen: Details Associated with the Production of Water

Aaron I. Strom

Undergraduate Research Day, April 29th 2017

Mentor: Professor David T. Anderson
Department of Chemistry, University of Wyoming
Laramie, WY 82071

Outline

I. Introduction to cold chemistry and its significance

II. A walk through the lab and the basics of spectroscopy and theory

III. Discuss implications and interpretation of experimental results and our conclusions thus far

I want to teach you something about chemistry!

Freezing an explosion - Impulse

Endeavor shuttle
STS-134 mission, May, 2011

Consider the reaction:

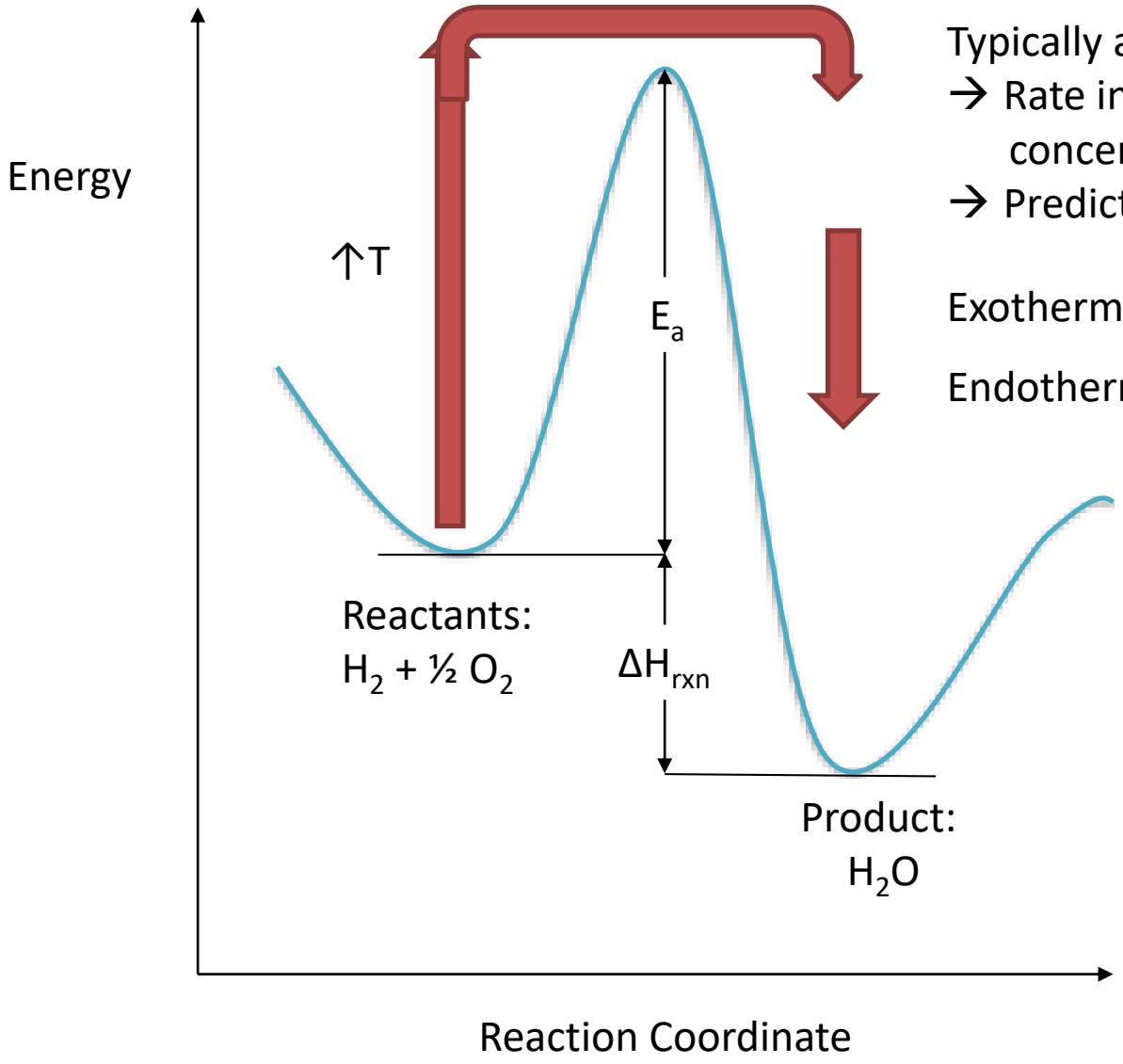
$$2\ H_2 + O_2 \rightarrow 2\ H_2O + \textit{LOTS}\ \text{of heat!}$$

- **Potential application: High energy density matter**

  Ideal ratio: 1:1 O:H_2

Photo credit: NASA - https://apod.nasa.gov/apod/ap110518.html

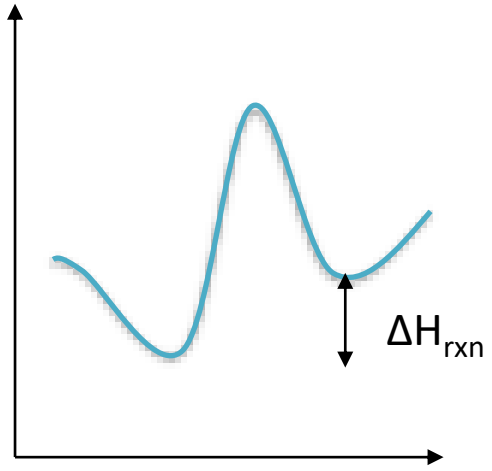
Classical vs. Quantum Chemistry



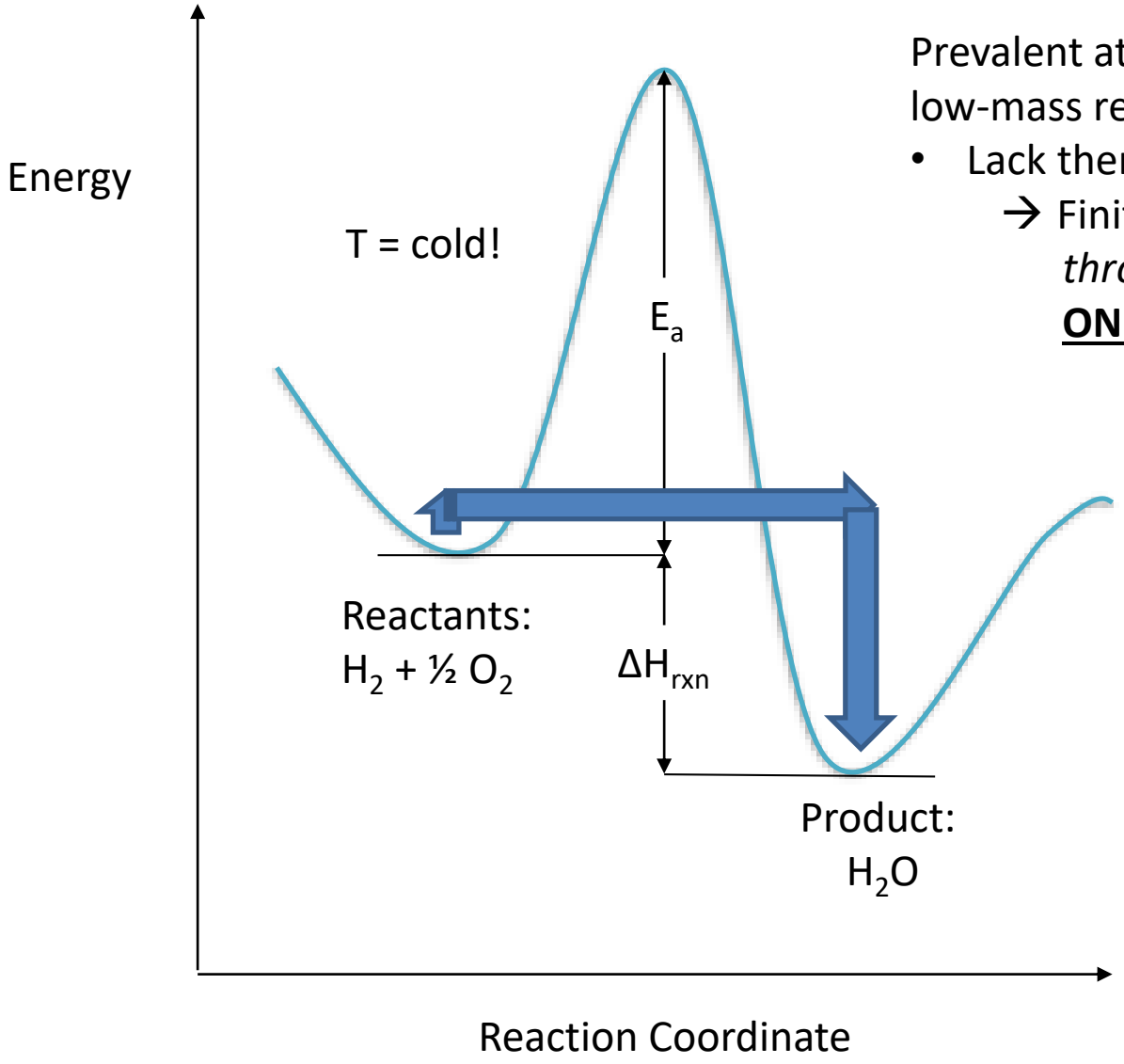
Typically add heat until reaction occurs
→ Rate increases with temperature or concentration
→ Predictable & well understood

Exothermic: $0 > \Delta H_{rxn}$ (release energy)

Endothermic: $0 < \Delta H_{rxn}$ (absorb energy)



Classical vs. **Quantum** Chemistry



Prevalent at low temperatures and with low-mass reagents

- Lack thermal energy to surmount barrier
  → Finite probability to tunnel *through* barrier…
  ONLY IF reaction is exothermic!

Interstellar Chemistry

Photo credit: Peter Lik, “Stargazer”

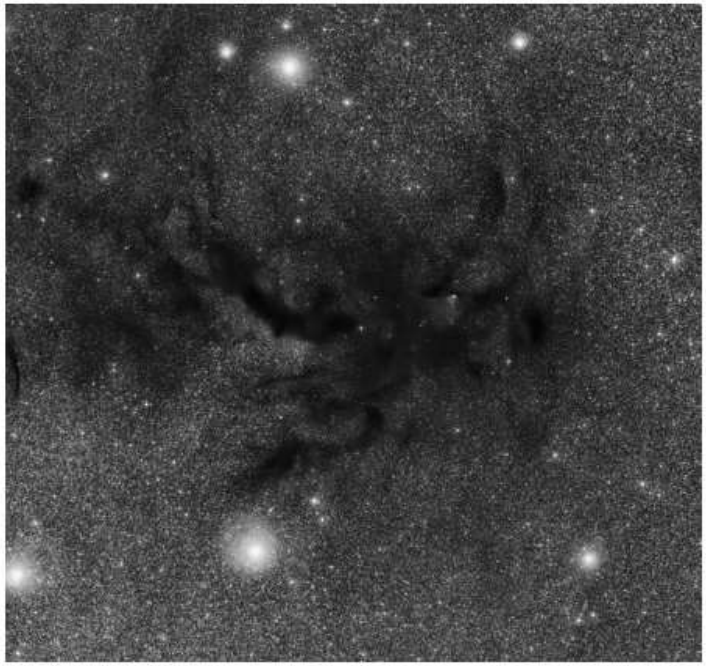
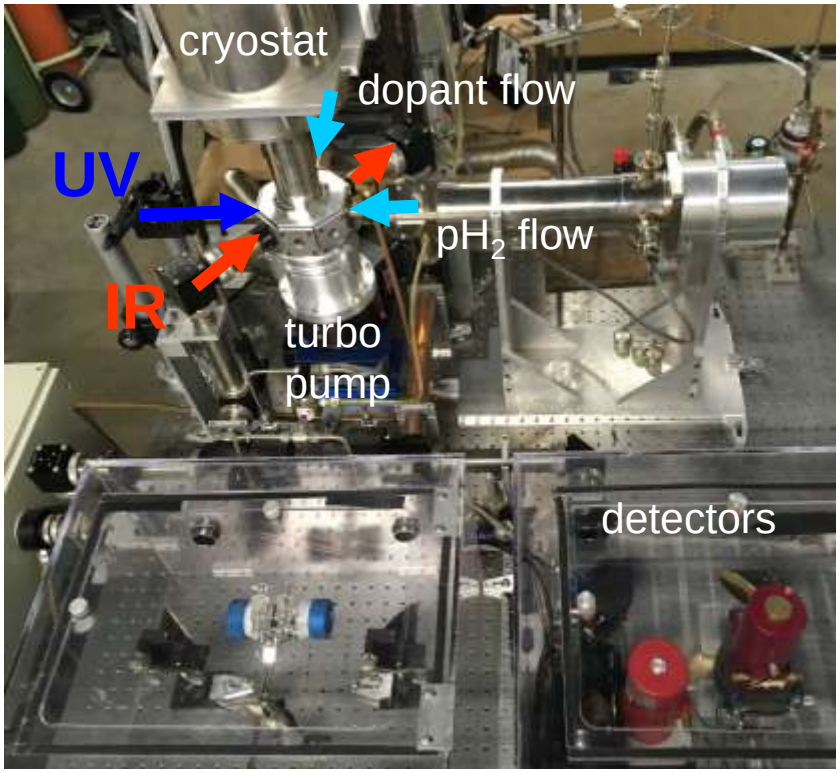


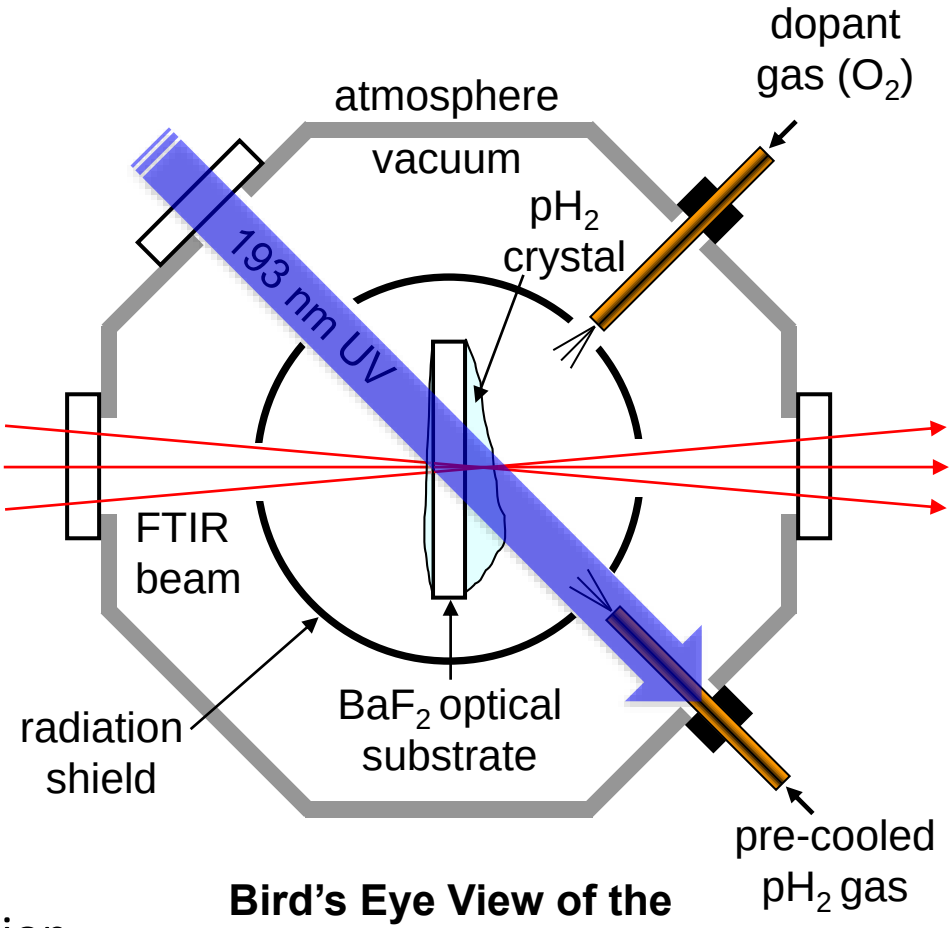
Fig. (3). This picture shows Barnard 59, part of a vast dark cloud of interstellar dust called the Pipe Nebula. The image was captured by the Wide Field Imager on the MPG/ESO 2.2-metre telescope at ESO's La Silla Observatory. Credit: ESO.

How does chemistry occur in interstellar space?

“Quantum Tunneling to the Origin and Evolution of Life,” F. Trixler, *Cur. Org. Chem.* **17**, 1758-1770 (2013).

Experimental Procedure (welcome to the lab!)



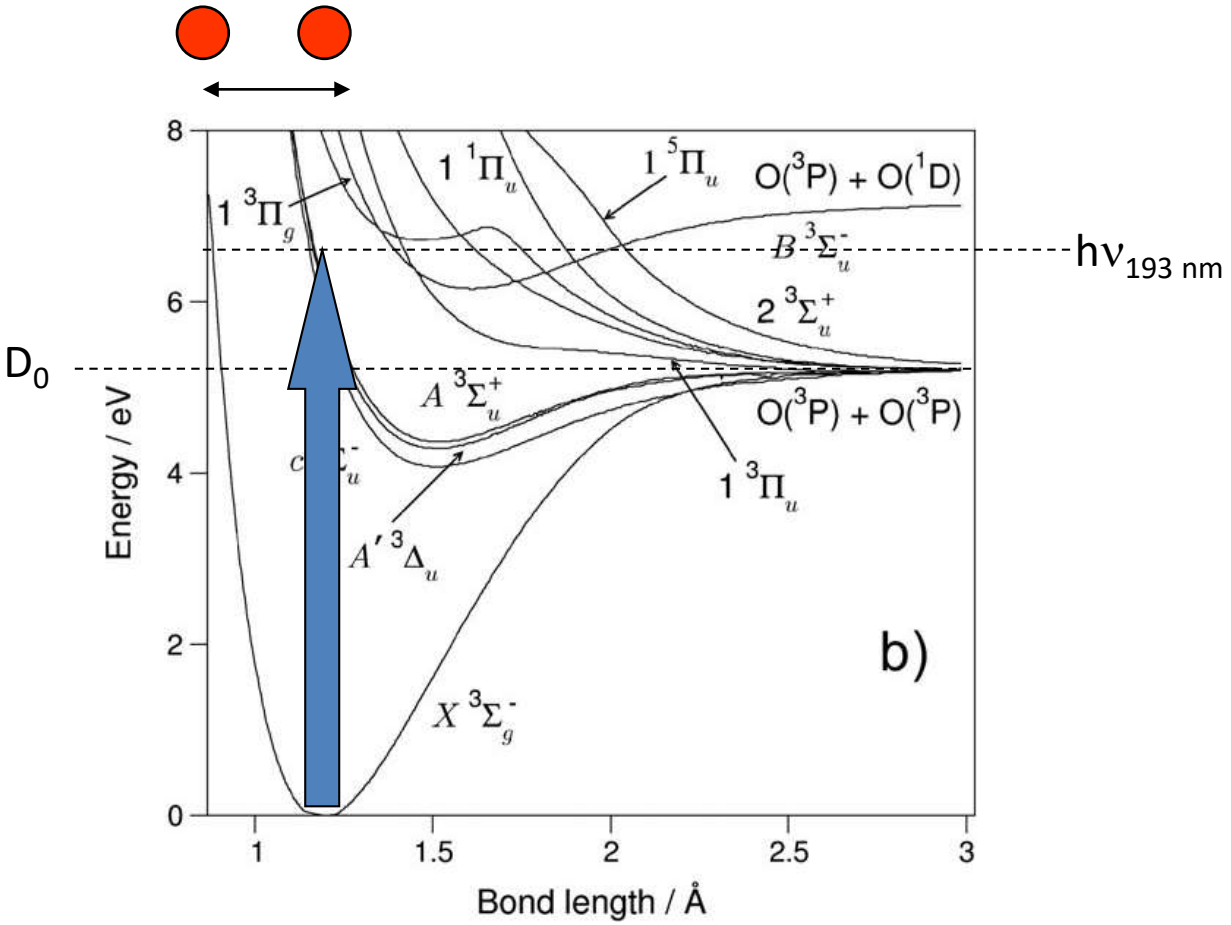


Bird's Eye View of the Liquid Helium Bath Cryostat
(1.6 – 5 K; aka near -450 °F)

– Monitor chemical identity & concentration based on spectral frequency & intensity

[1] M. Fajardo & S. Tam, *J. Chem. Phys.* **108**, 4237- 4241 (1998).

Photochemistry of O_2 inside solid hydrogen



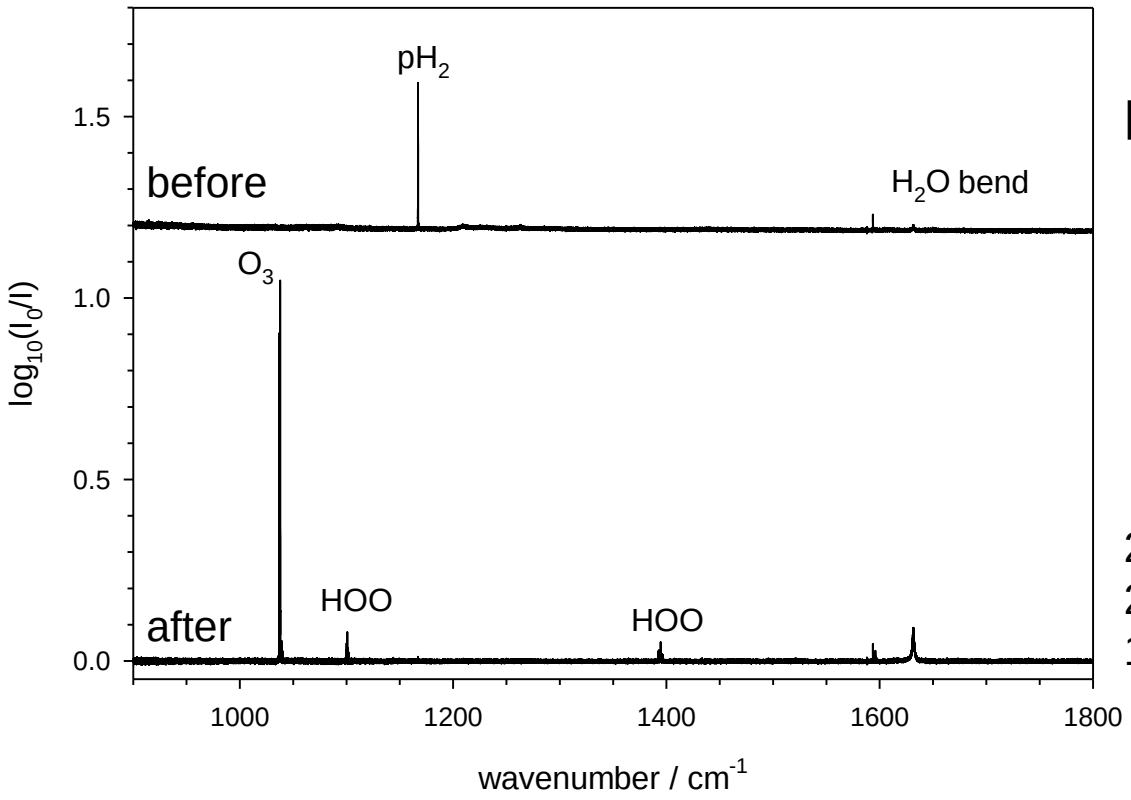
$h\nu_{193\ nm} \approx 51{,}800\ cm^{-1}$

$D_0 = 5.12\ eV = 41{,}300\ cm^{-1}$

M. Brouard, R. Cireasa, A.P. Clark, F. Quadrini and C. Vallance, *PCCP* **8**, 5549-5563 (2006).

Photochemistry of O_2 inside solid hydrogen

$$O_2 + h\nu_{193\ nm} \rightarrow 2\ O(^3P) \rightarrow\rightarrow O_3 + H_2O$$



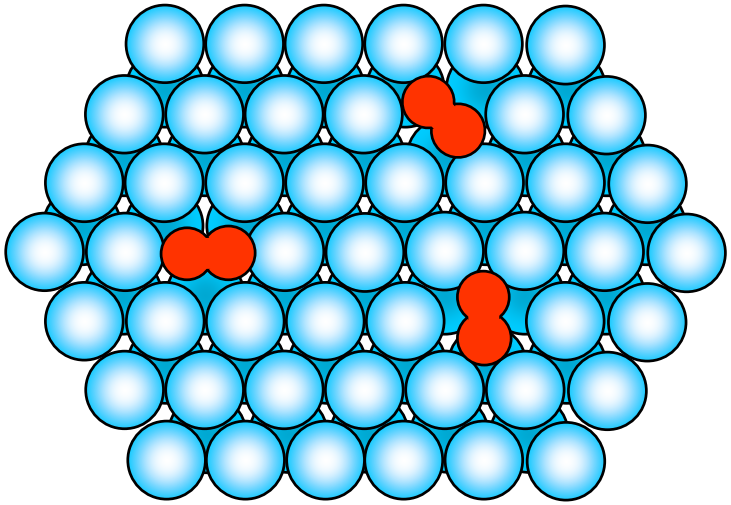
[O_2] = 10 ppm

20 min
20 Hz, 0.5 mJ pulse^{-1}
193 nm

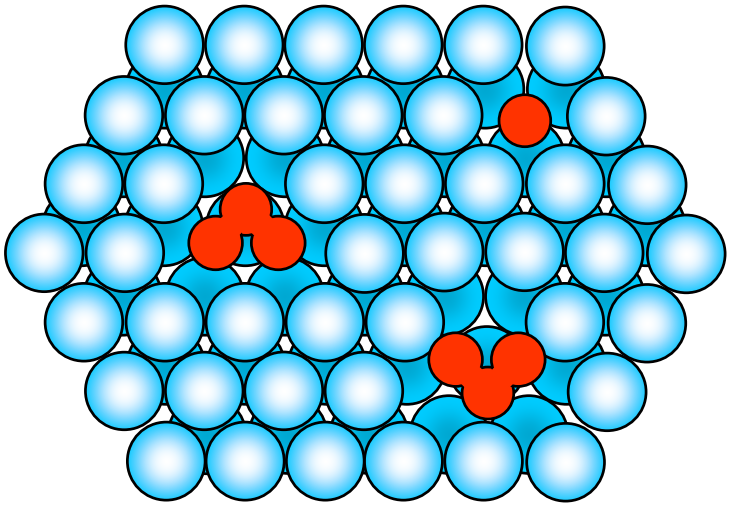
Assignments from O_3/Ar studies:* ν_1 = 1105 cm^{-1}, ν_3 = 1040 cm^{-1}

[*] L. Andrews and R.C. Spiker, Jr., *JPC* **76**, 3208 (1972).

Oxygen recombination dynamics in solid H_2



193 nm



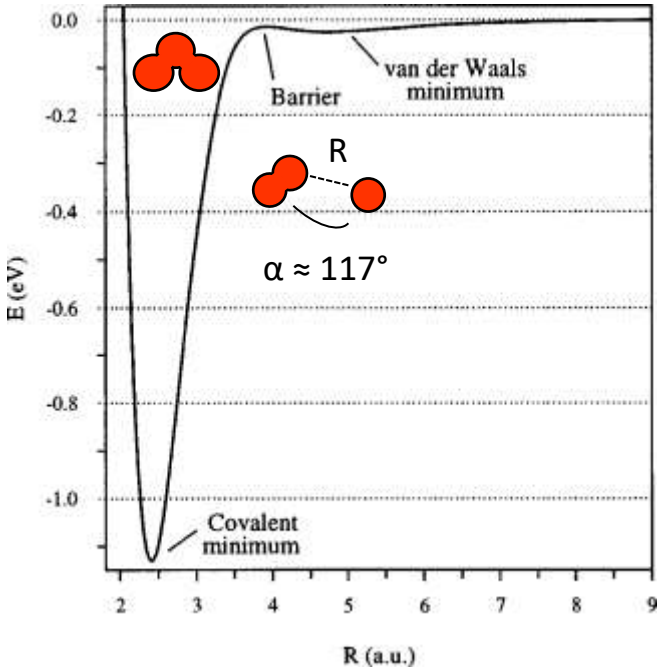
before

after

$O_2 + h\nu_{193\ nm} \rightarrow 2\ O(^3P)$

$O_2 + O(^3P) \rightarrow O_3^*$

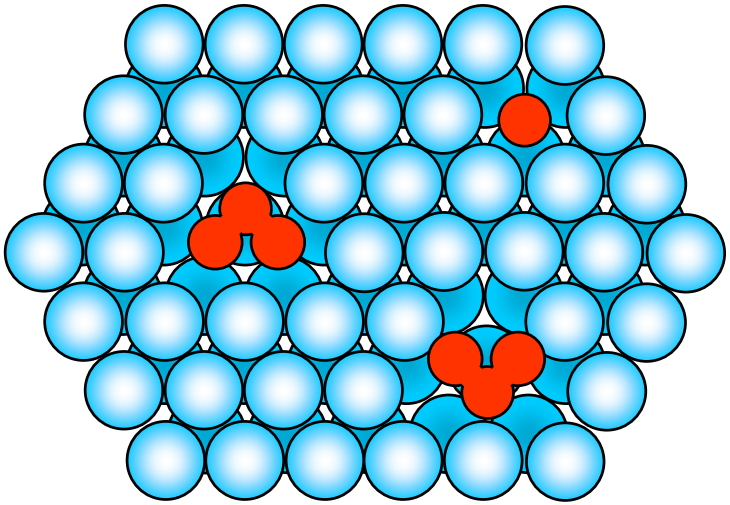
$O_3^* + H_2 \rightarrow O_3 + H_2$



- Ozone formation provides indirect proof of O-atoms in solid pH_2

D. Babikov, *JCP* **119**, 6554 (2003).

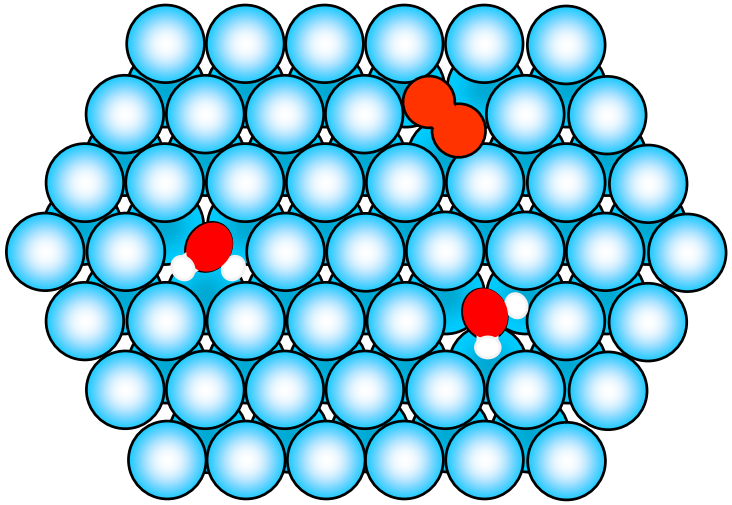
Formation of water in solid H_2



before

193 nm

(again*)



after

$O_2 + h\nu_{193\ nm} \rightarrow 2\ O(^3P)$

$O_2 + O(^3P) \rightarrow O_3^*$

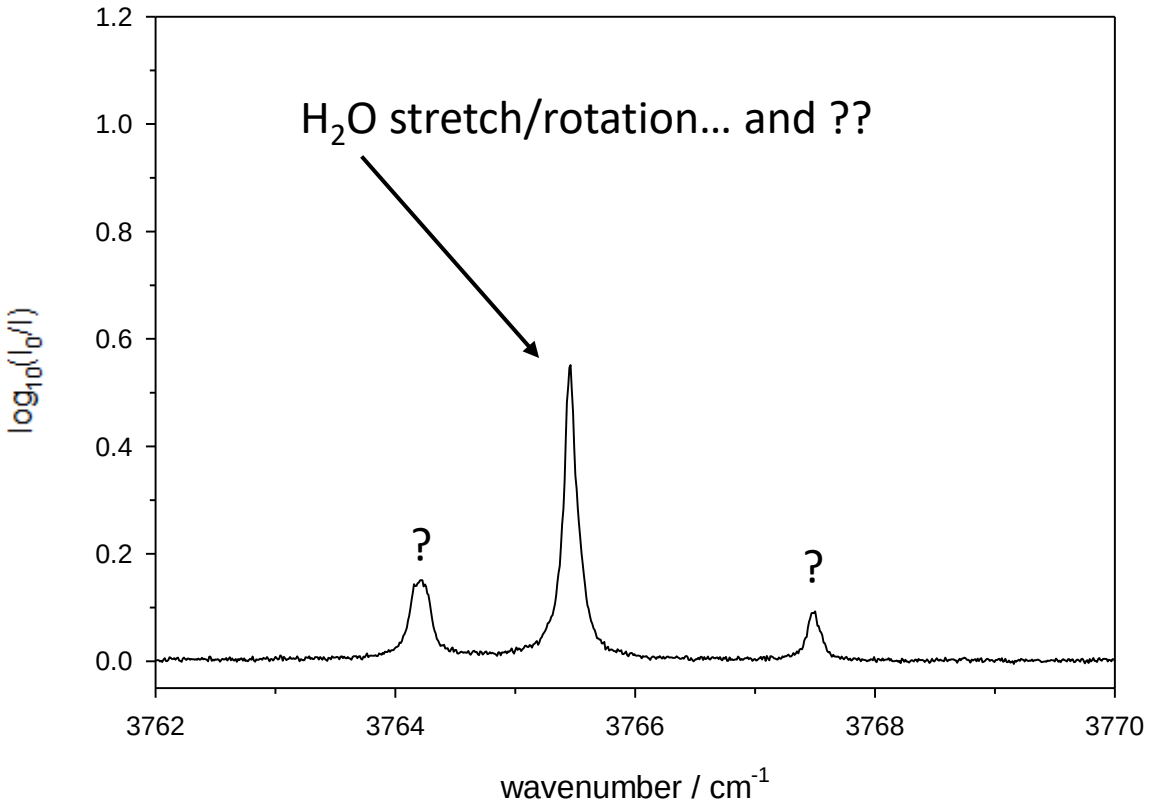
$O_3^* + H_2 \rightarrow O_3 + H_2$

$O_3 + h\nu_{193\ nm} \rightarrow O_2 + O(^1D)$

$O(^1D) + H_2 \rightarrow OH + H$

$OH + H_2 \rightarrow H_2O + H$

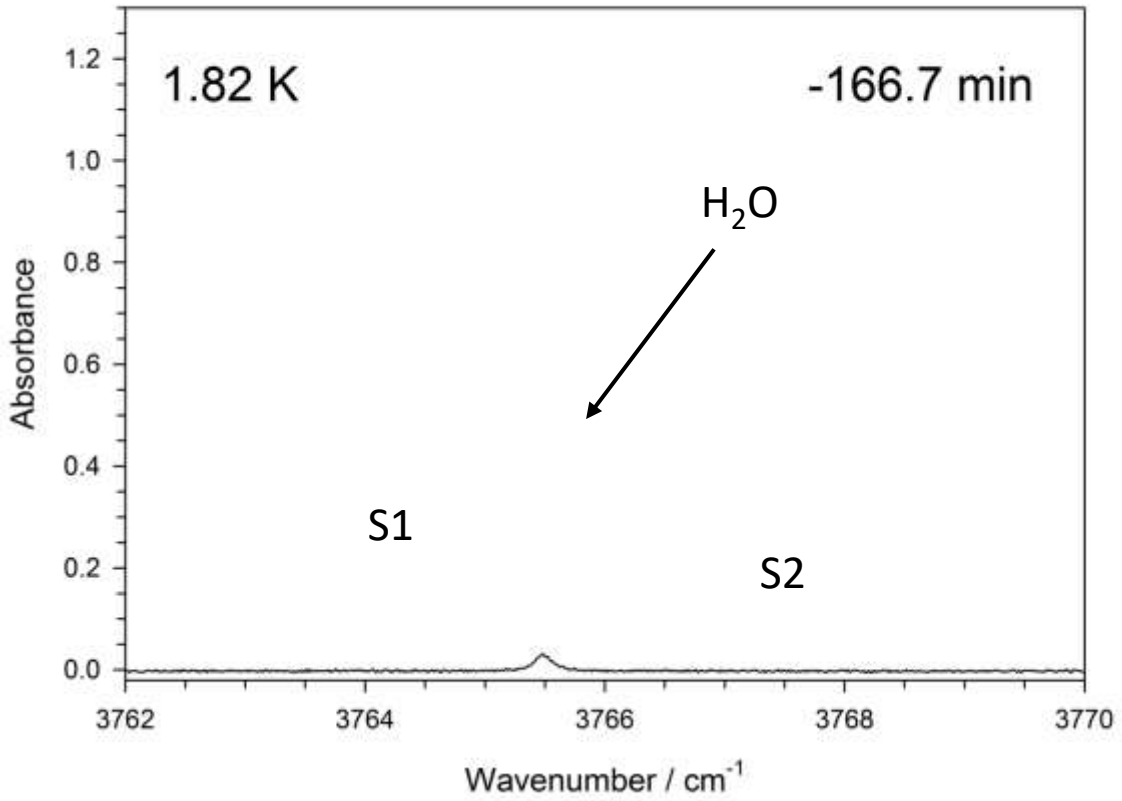
Infrared satellite features of the water molecule



- not due to water/H_2 isomeric complexes

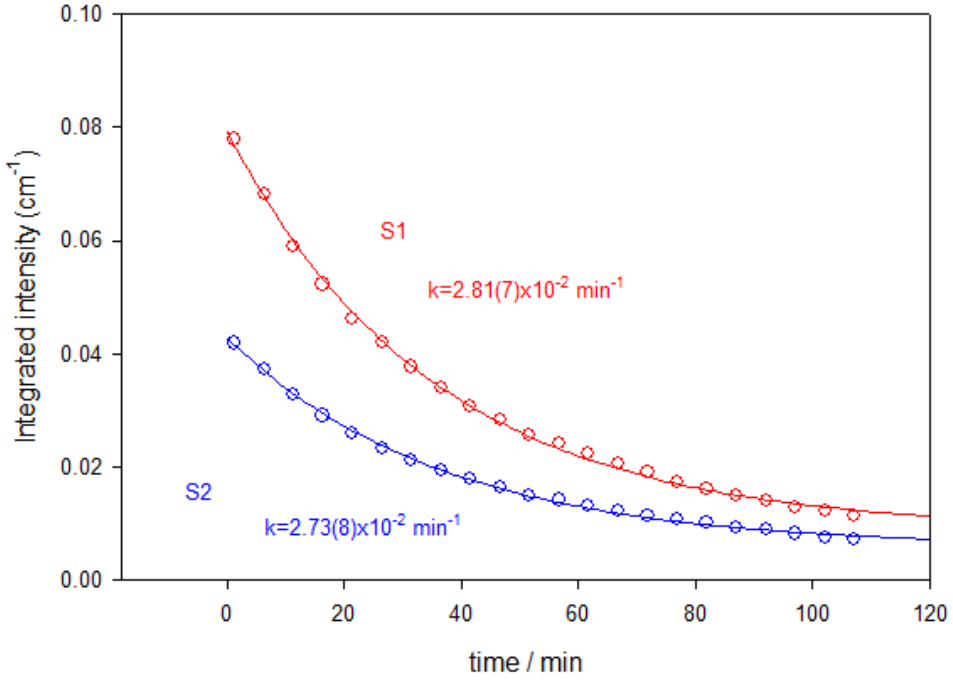
[1] M. E. Fajardo, S. Tam, and M. E. DeRose, *J. Mol. Struct.* **695-696**, 111 (2004).

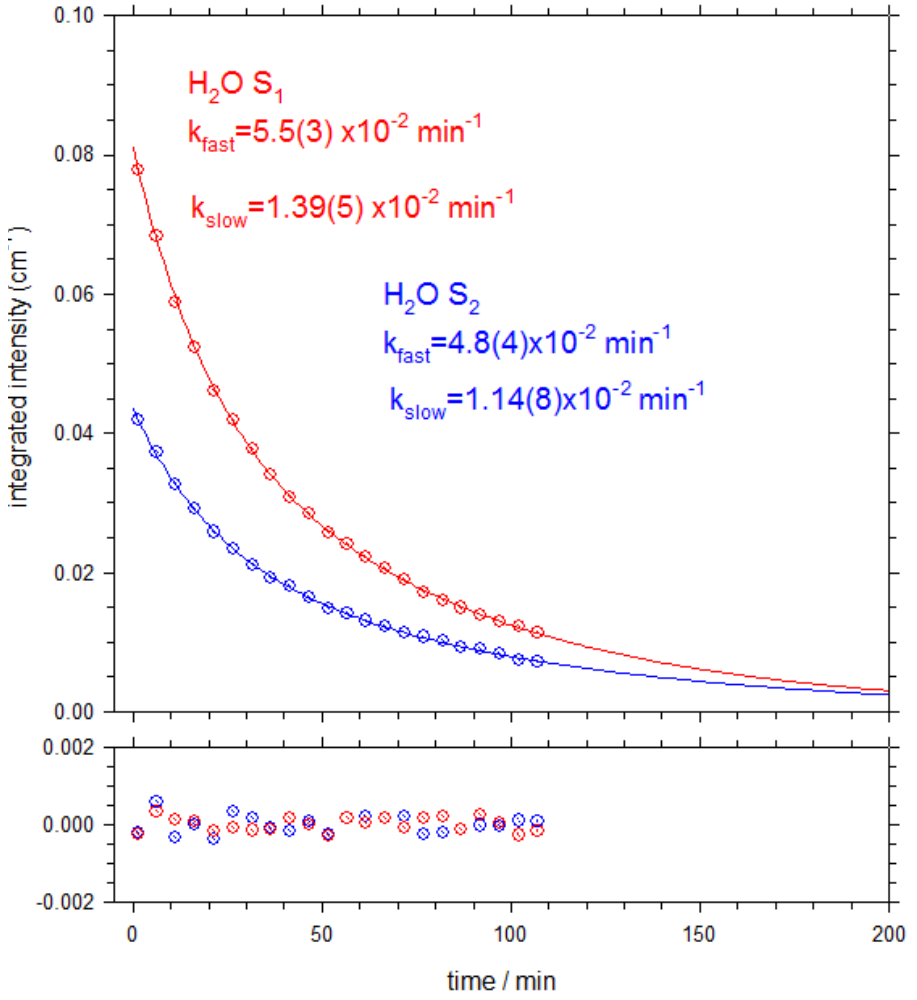
Time-dependent changes after 193 nm UV photolysis



D.T. Anderson *et. al.*, *JPC Lett.* **3**, 342-347 (2012).

Tracking the decay of water satellite features





Formation of water next to vacancies in solid H_2

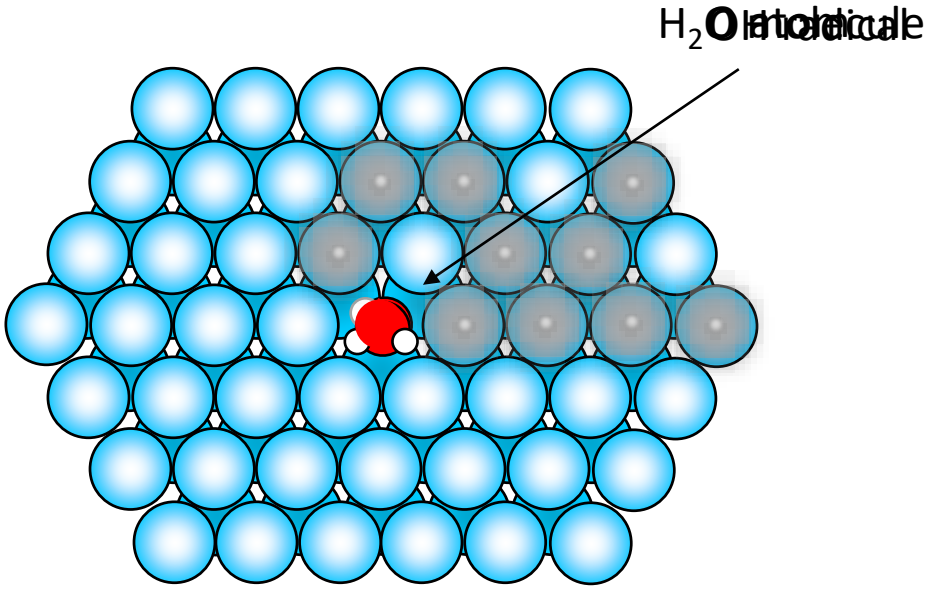
Find qualitative lifetime result:

$\tau_{water} \approx 30\text{-}40$ min

Decay lasts longer in other systems:[1]

$\tau_{FA} = 115.2 \pm 6.7$ min

Potential for unique chemical phenomena in various dopant-H_2-host environments that produce water! [2]



Toy/PowerPoint model of the transformation

[1] D.T. Anderson *et. al.*, *JPC Lett.* **3**, 342-347 (2012).

[2] W.R. Wonderly and D.T. Anderson, *Low Temp. Phys.* **38**, 673-678 (2012).

Conclusions

I. Form O_3 from O_2 photolysis - signaling production of O-atoms - and H_2O production follows photolysis of O_3
   - Achieving a 1:1 O:H_2 concentration for use as rocket fuel is not feasible due to mobility & reactivity of O-atoms in cryogenic H_2

II. Recognize spectroscopic signatures of nascent H_2O within chemical environments that differ from equilibrium signals

III. The time-dependent response of these water satellites could be anomalous when compared to previous findings – but, there is certainly evidence of low-temperature quantum-chemistry occurring within the hydrogen crystal

Acknowledgements

The Anderson Group - Fundamental Studies Near the Low Temperature Limit:

Left - Right: Myself, Morgan Balabanoff and Dr. Fred Mutunga

Dr. David Anderson

Financial support:

WYOMING
NASA Space Grant Consortium

WYOMING RESEARCH SCHOLARS PROGRAM
UNIVERSITY OF WYOMING

Questions or Comments?

Reaching Liquid Helium Temperatures

Liquid Helium Bath Cryostat

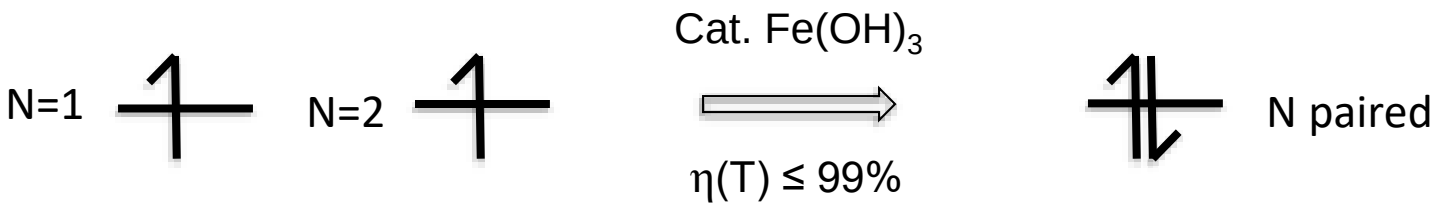
<u>Cool down procedure:</u>

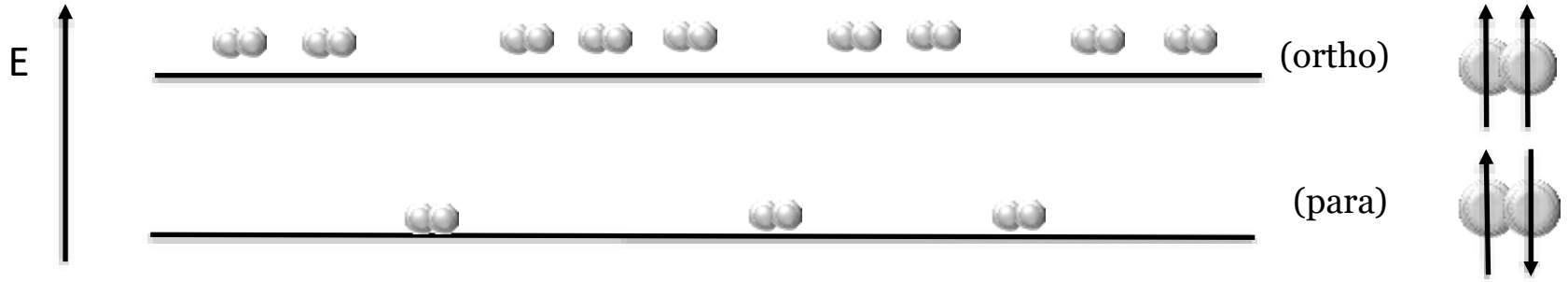
1. Precool with liquid N_2 to 77 K
2. Sap heat in cryostat with liquid He
   - He boiling point = 4.2 K (1 atm)
3. Fill bath and regulate pressure

Experimental range of 1.5 – 5.0 K.

Ortho→Para Hydrogen Conversion

- "Normal" hydrogen consists of 3:1 ortho-para H_2
- Consider the two nuclei (N) of H_2
  - Multiplicity, M = 2I+1; I = ±1/2 (Nuc. Spin Quantum #)
  - Fermions are antisymmetric w.r.t. exchange



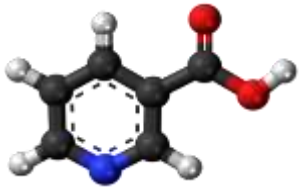


Future Plans

Vitamin B_3 production in solid hydrogen

- An essential water soluble vitamin

  Potential prebiotic seed/catalyst



Vitamin B_3
(a.k.a. niacin or nicotinic acid)

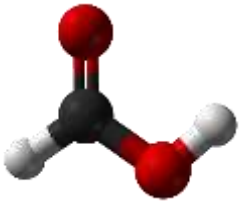
- 193 nm photolysis of pyridine (C_5H_5N) in pH_2

  MeOH or FA / pyridine multi-dopant experiments

  e.g., FA + 193 nm → HCO, HOCO, H_2O, etc.

  HOCO + py. + 193 nm → Vit. B_3 (via *meta*-substitution)?

  Also extend to CO and O_2 non-polar ice mixtures



Formic
Acid (FA)

- Could this vitamin be formed via quantum tunneling reactions?