HD gas purification for polarized HDice target production at Jefferson Lab

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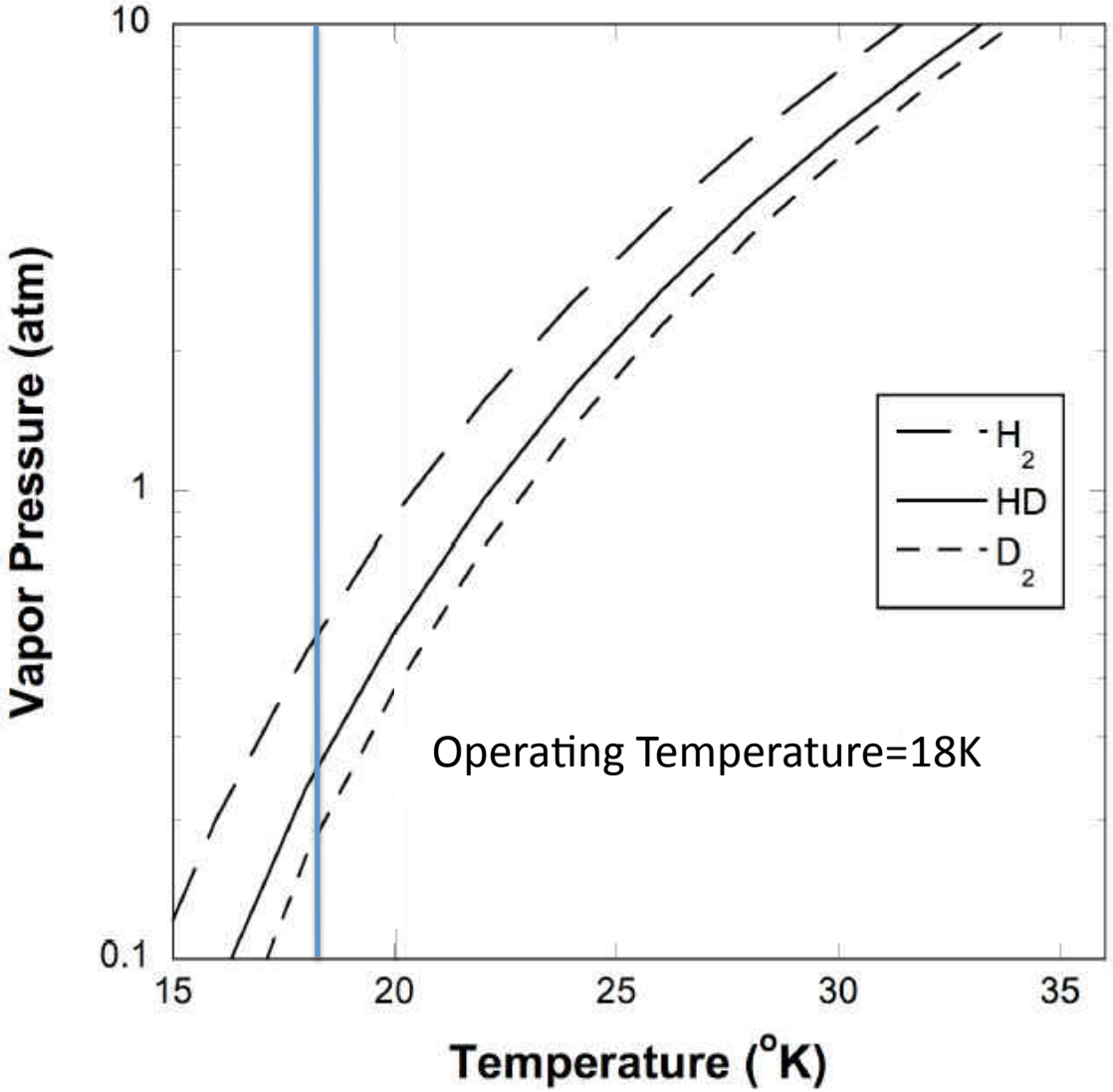
Overview

- Commercial HD Gas contains 0.5-2.0% H_2 and D_2
- To produce targets, the H_2 and D_2 must be reduced
  - Require small, carefully controlled concentrations
- Isotopic separation is done using distillation
  - Operate at low temperature to liquefy and obtain good boiling point (partial pressure) differences
  - Apply heat to boil the liquid
  - Use a packed column for good efficiency
- Gas monitoring
  - Residual Gas Analyzer
  - Gas chromatography
  - Raman Scattering

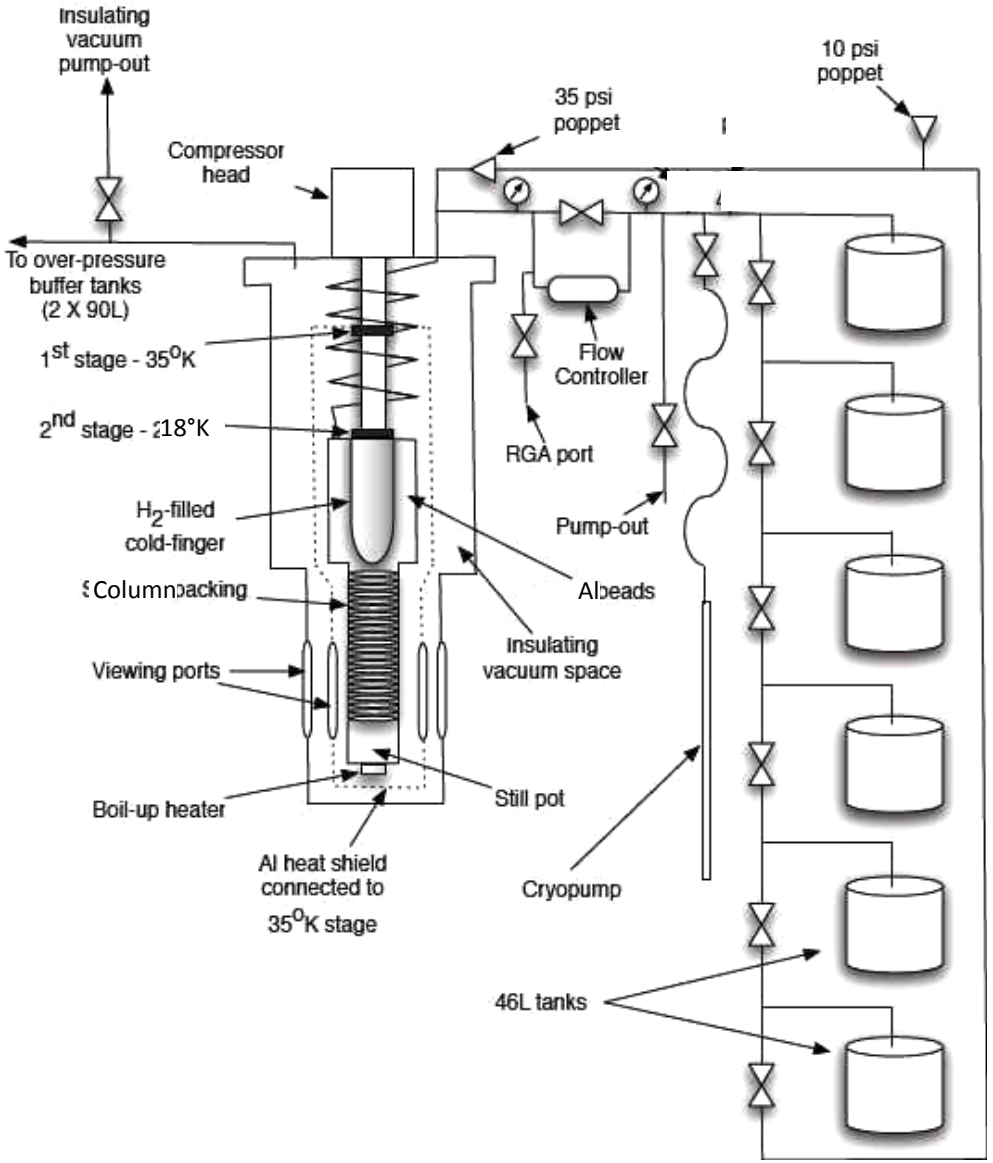
Isotopic Separation

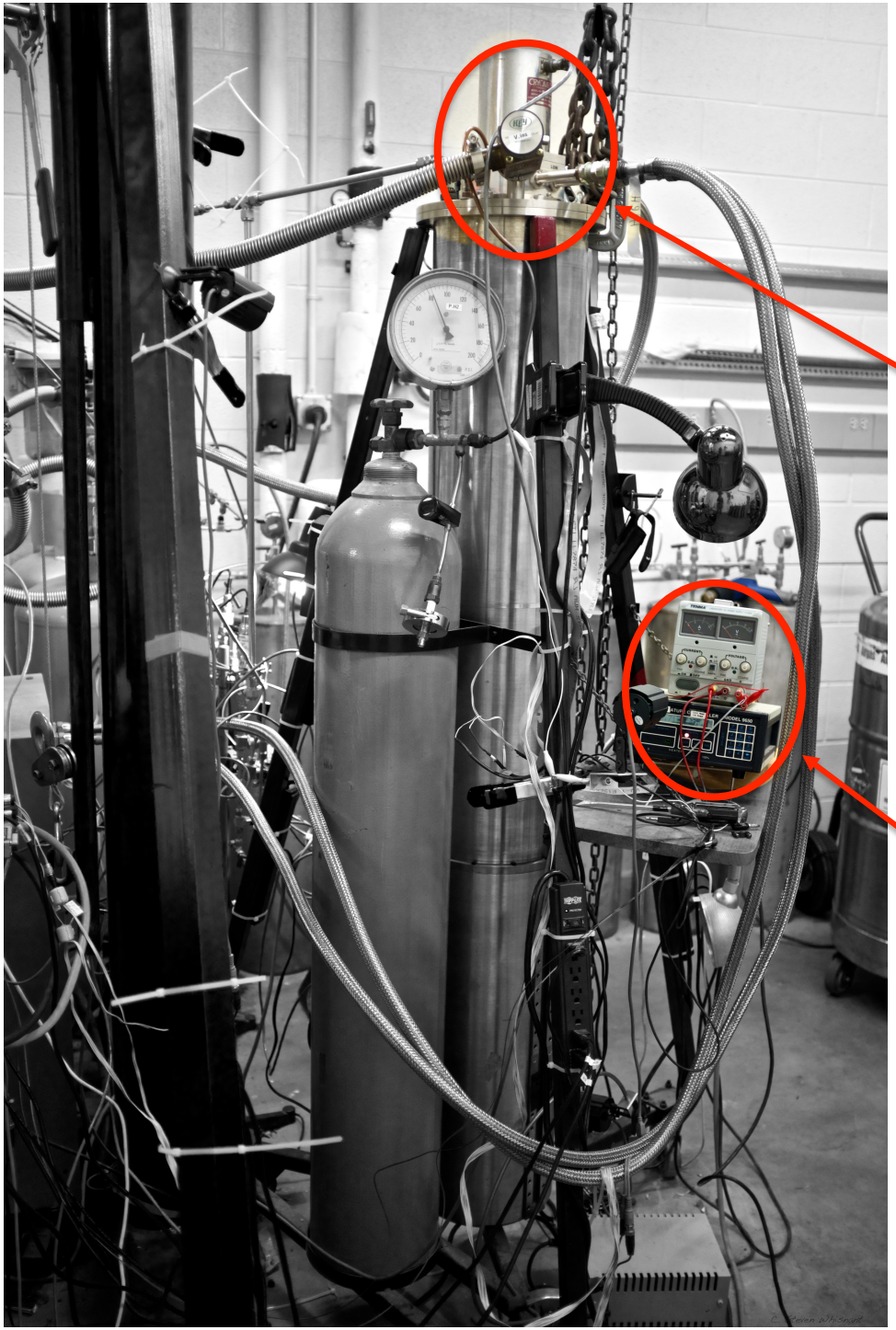


H_2, HD, and D_2 have significantly different vapor pressures at low temperature.

This allows separation using distillation techniques.

Low Temperature Distillery





- Mechanical refrigerator
  - Two-stage system
    - 1st stage: ~35 K
    - 2nd stage
      - » T_{min}=11K
      - » T_{oper}=18K
- Temperature control & boil-up power supply
  - Typical boil-up power ~ 2.3W
- 18K ➔ P ~ 260 mbar
- Extraction rate = 1 mole/day

Packed Distillation Column

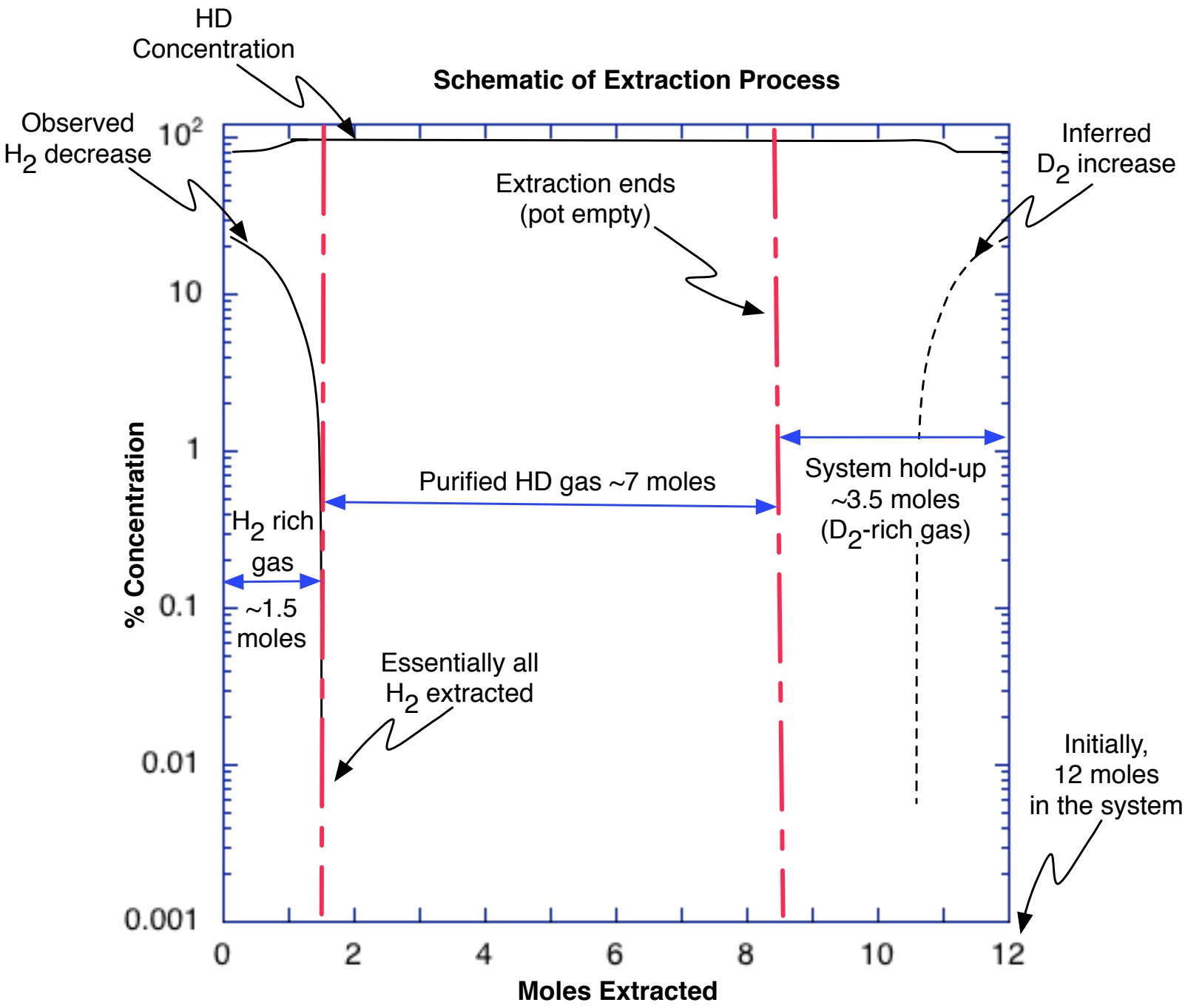
- Heli-pak
- Improves efficiency
  - Nucl. Inst. Meth. 664 (2012) 347
  - http://www.wilmad-labglass.com/Products/LG-6730-104/

Windows in vacuum container
and thermal shield permit viewing
the boiling liquid hydrogen

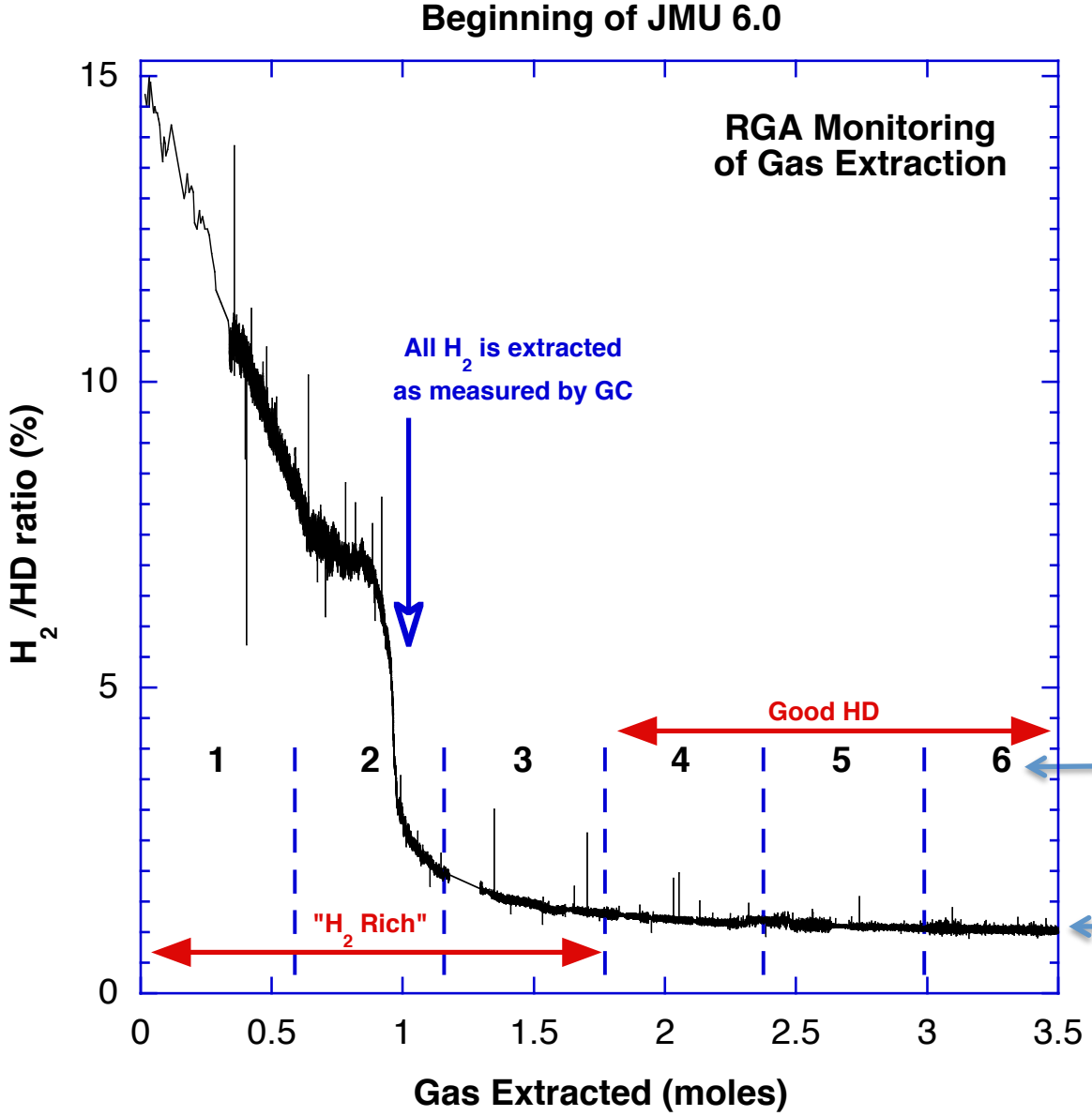
…has often enabled system debugging

Gas Handling

- Manifold with 2-mole stainless tanks
- Gas moved between tanks using LHe and a cold trap
- Long term storage at low pressure in Al tanks


Schematic of Extraction Process
HD Concentration
Observed H_2 decrease
Inferred D_2 increase
Extraction ends (pot empty)
Purified HD gas ~7 moles
H_2 rich gas ~1.5 moles
Essentially all H_2 extracted
System hold-up ~3.5 moles (D_2-rich gas)
Initially, 12 moles in the system
% Concentration
10^2
10
1
0.1
0.01
0.001
0
2
4
6
8
10
12
Moles Extracted

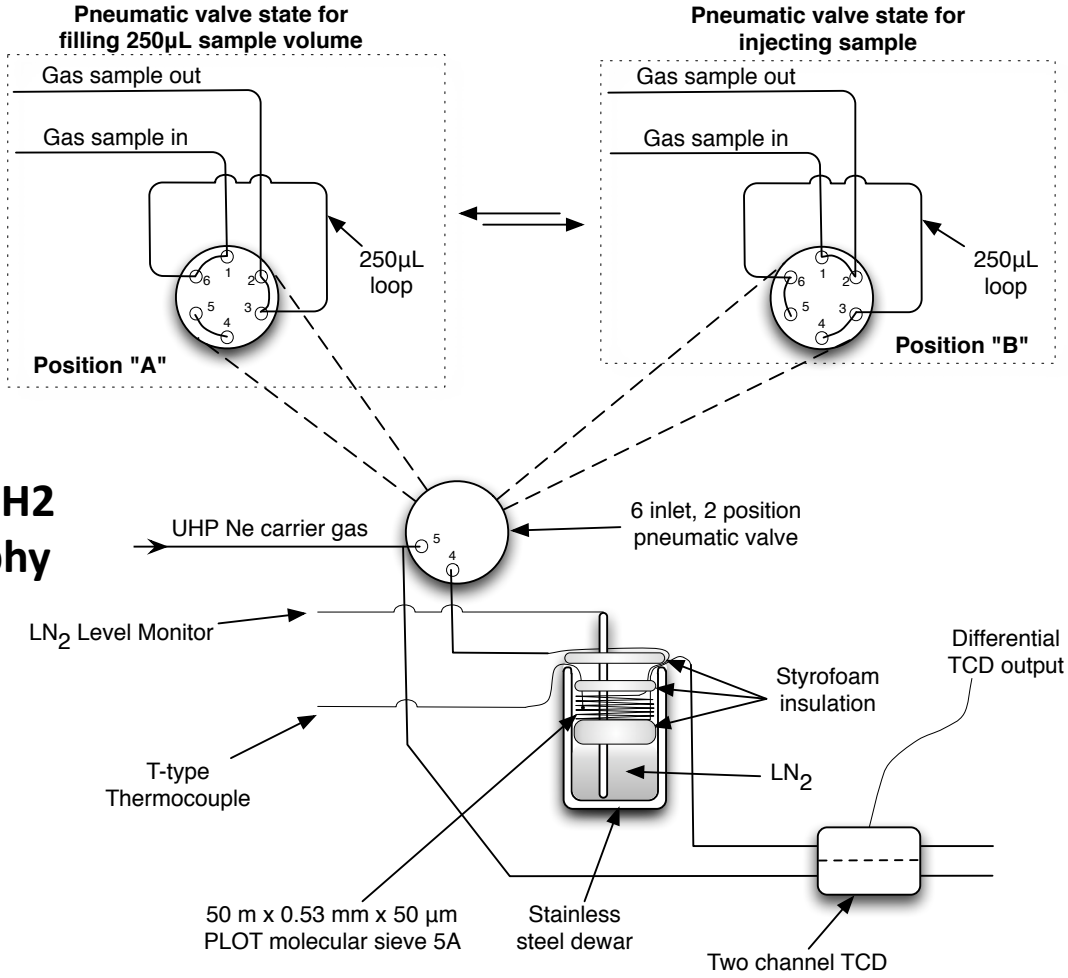
Distillery Operation



2-mole tanks filled to ~260 mbar each

Limit of RGA sensitivity

Low Temperature Gas Chromatography



Measuring the relative concentration of H2 and D2 in HD gas with gas chromatography

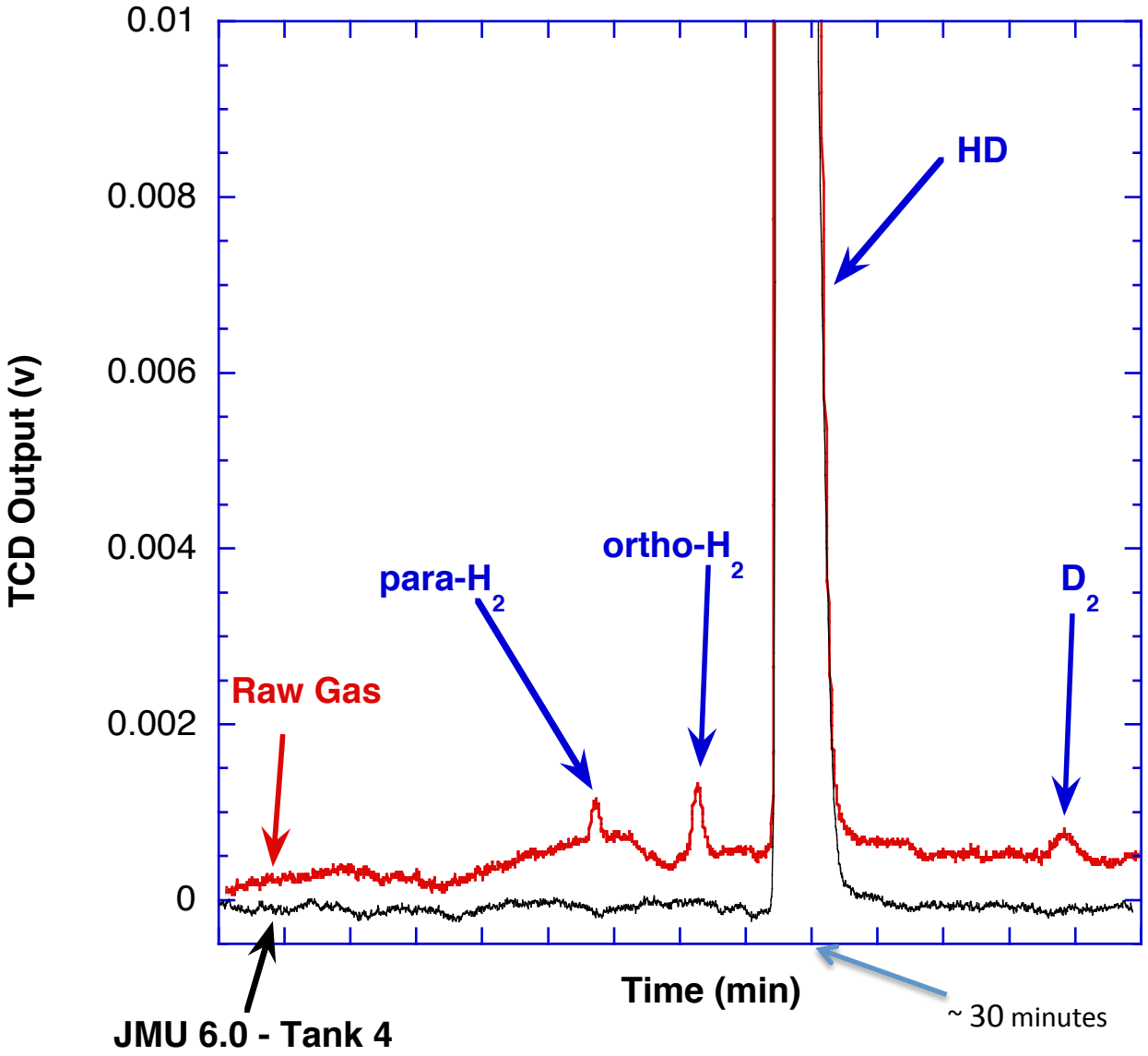
Whisnant, Hansen, and Kelley

Rev. Sci. Inst. **82**, 024101 (2011)

Chromatography Column

- Off-the-shelf PLOT 5A capillary column
  - ValcoPLOT® VP-Molesieve GC Capillary Column
  - Length=30 m, ID=0.53 mm, Film Thickness=50µm
  - http://www.sisweb.com/gc/vici/vpmol.htm (CFS-X-03053-500)
- Column operated between T≈115K - 130K
  - Immersed in a roughly equal mixture of LN_2 and iso-pentane
  - ΔT during a run is 1-2K
  - Run-to-run variation is larger as LN_2 boils away
  - As T increases: separation and retention time decreases

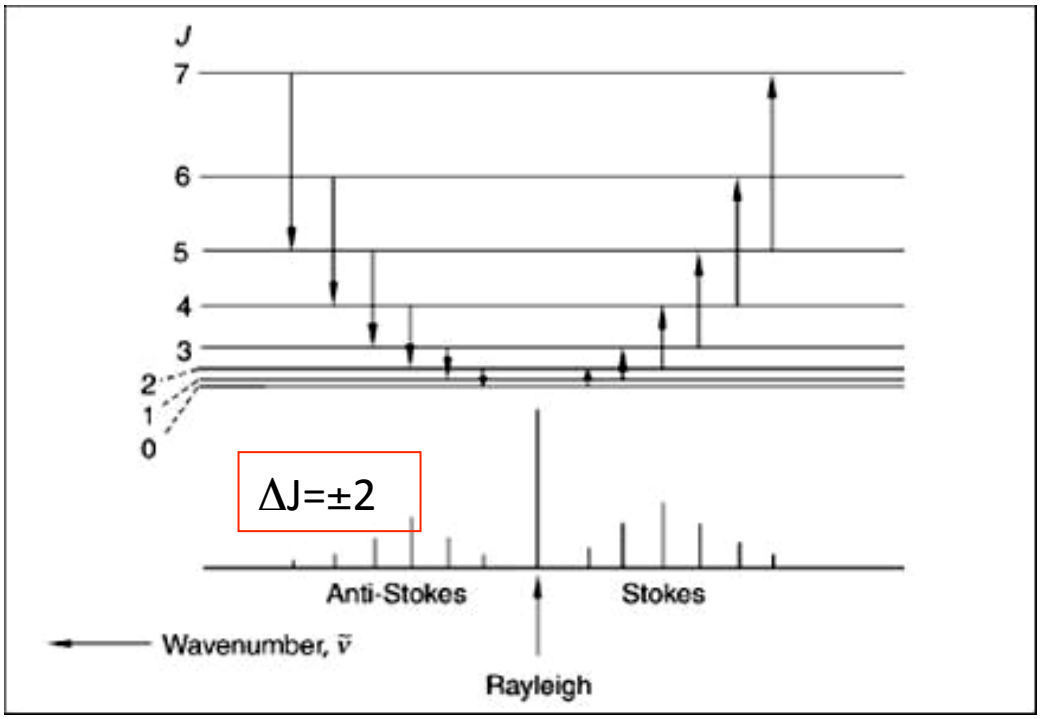
Monitoring with Gas Chromatography



- For accurate results, sample must be run several times and averaged
- Gas sample collected in 75 ml bottle at 2 ATM
  - Yields ~ 3-4 injections
- TCD gives a H_2 and D_2 detection threshold of a few X 10^{-3}
  - Limited by noise
  - Noise is primarily microphonics
- Precision is improved by averaging the results of several runs

Raman spectroscopy: laser scattering from rotational states

Raman spectroscopy does not dissociate HD molecules and it is used to provide measurements of H_2 and D_2 relative concentrations in HD gas at the 10-5 level.



Molecular rotational energy levels are given by:

$$E_R = \hbar^2 \frac{J^2}{2I} = hcb_0 J(J+1)$$

where:

$$b_0 = \frac{h}{8\pi^2 I}$$

and I is the molecule moment of inertia.

Distance among levels is higher for lighter molecules.

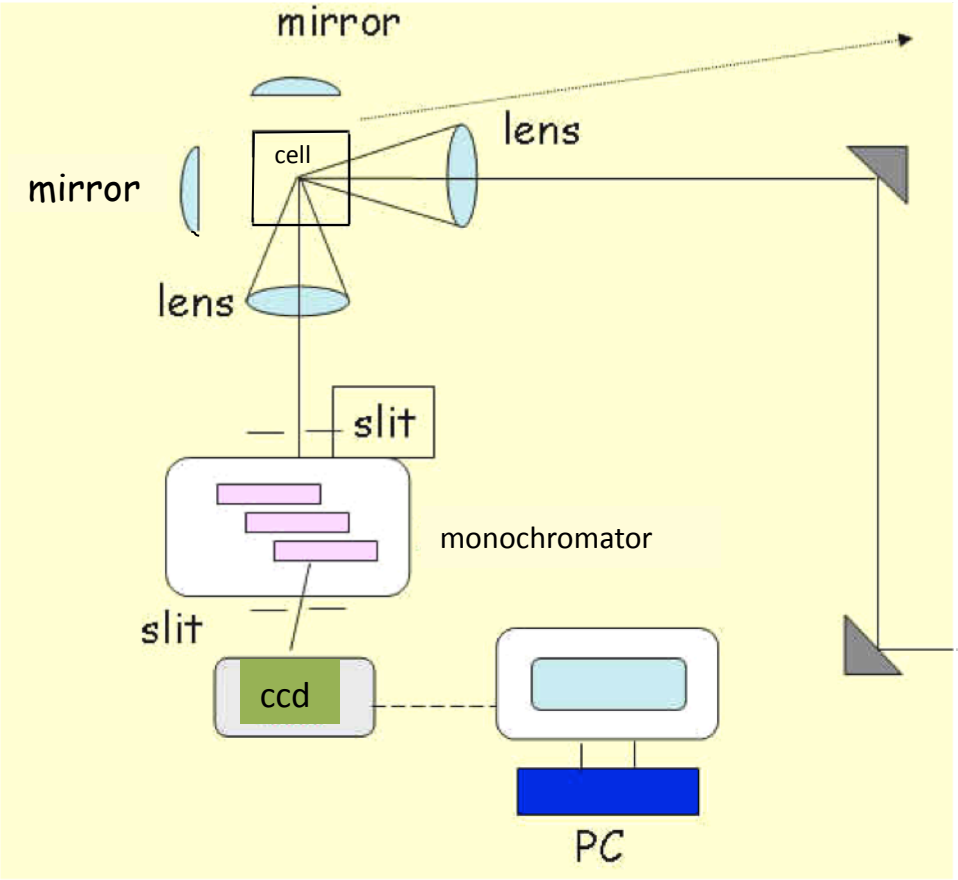
Raman scattering occurs when Laser light is absorbed and re-emitted by a molecule while the rotational state changes: the scattered light is shifted from the Laser energy by:

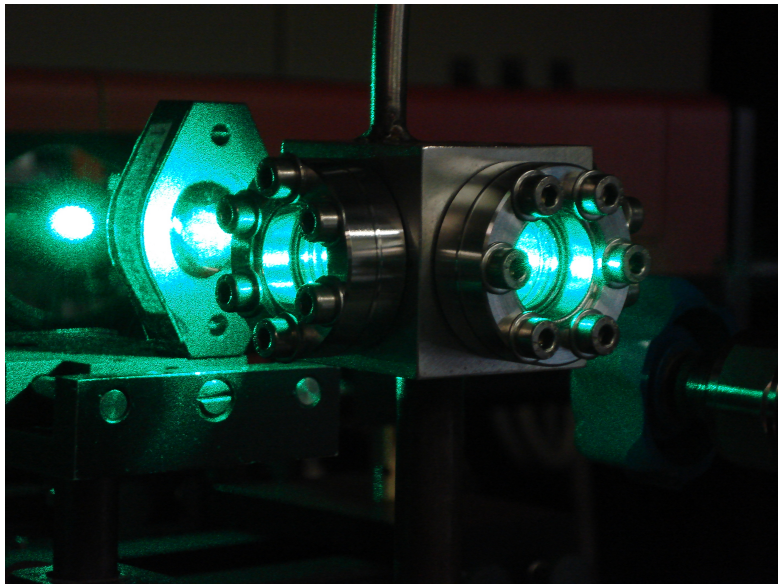
$$\Delta E = hcb_0(J+2)(J+3) - hcb_0 J(J+1) = hcb_0(4J+6)$$

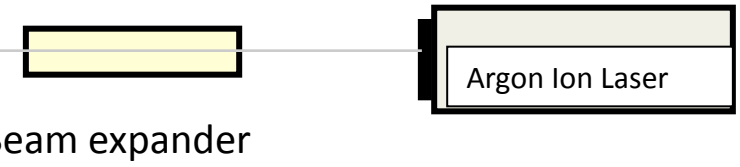
Selection rules $\Delta J=\pm 2$ connect ortho- to ortho- and para- to para- molecular states.

Raman set-up

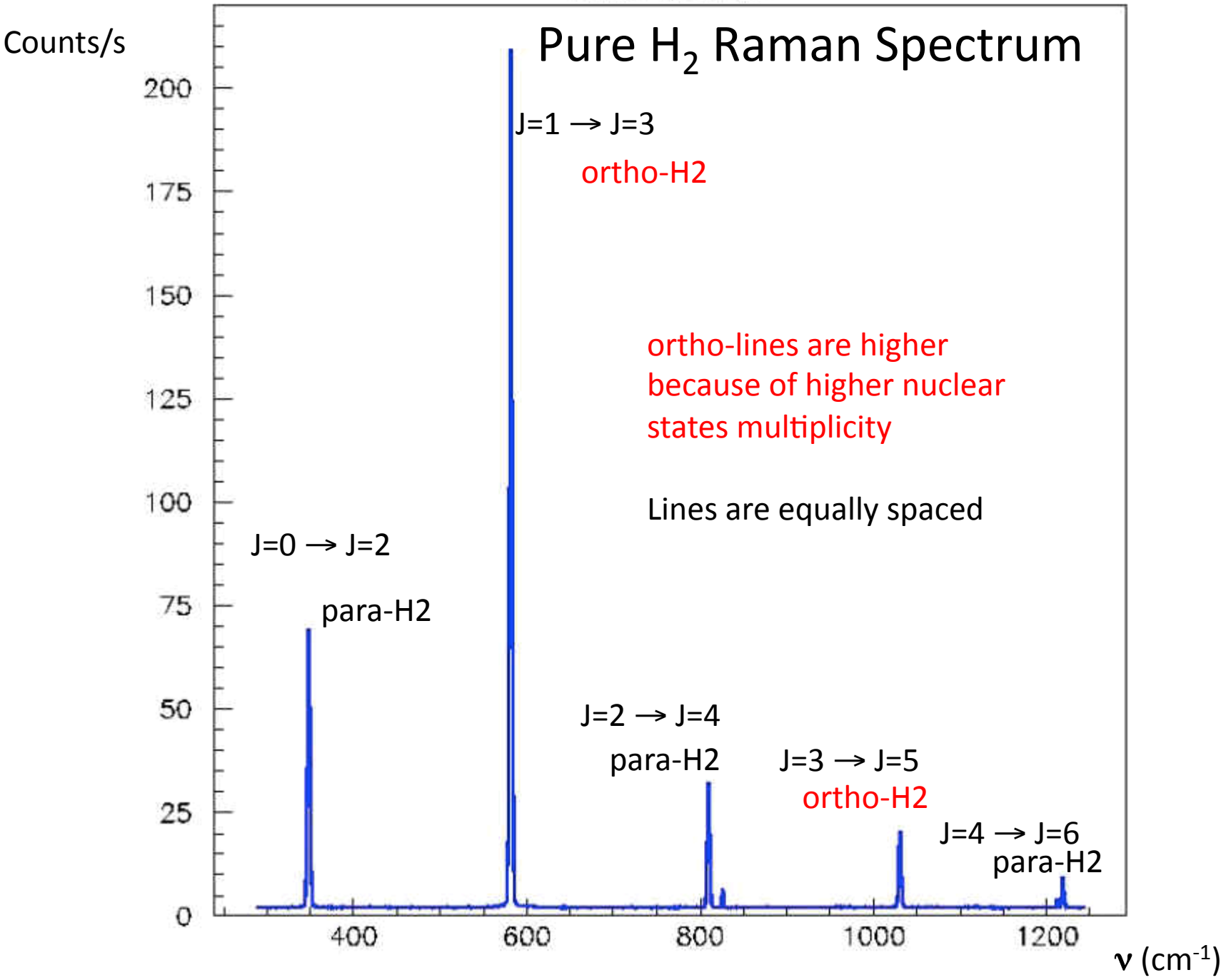
- The gas to be analyzed is used to fill the cell.
- The Laser light is focused at the center of the cell and reflected back by a mirror to increase the useful incoming power.
- The scattered light is reflected by a mirror and expanded in a parallel beam to enter the monochromator slit.

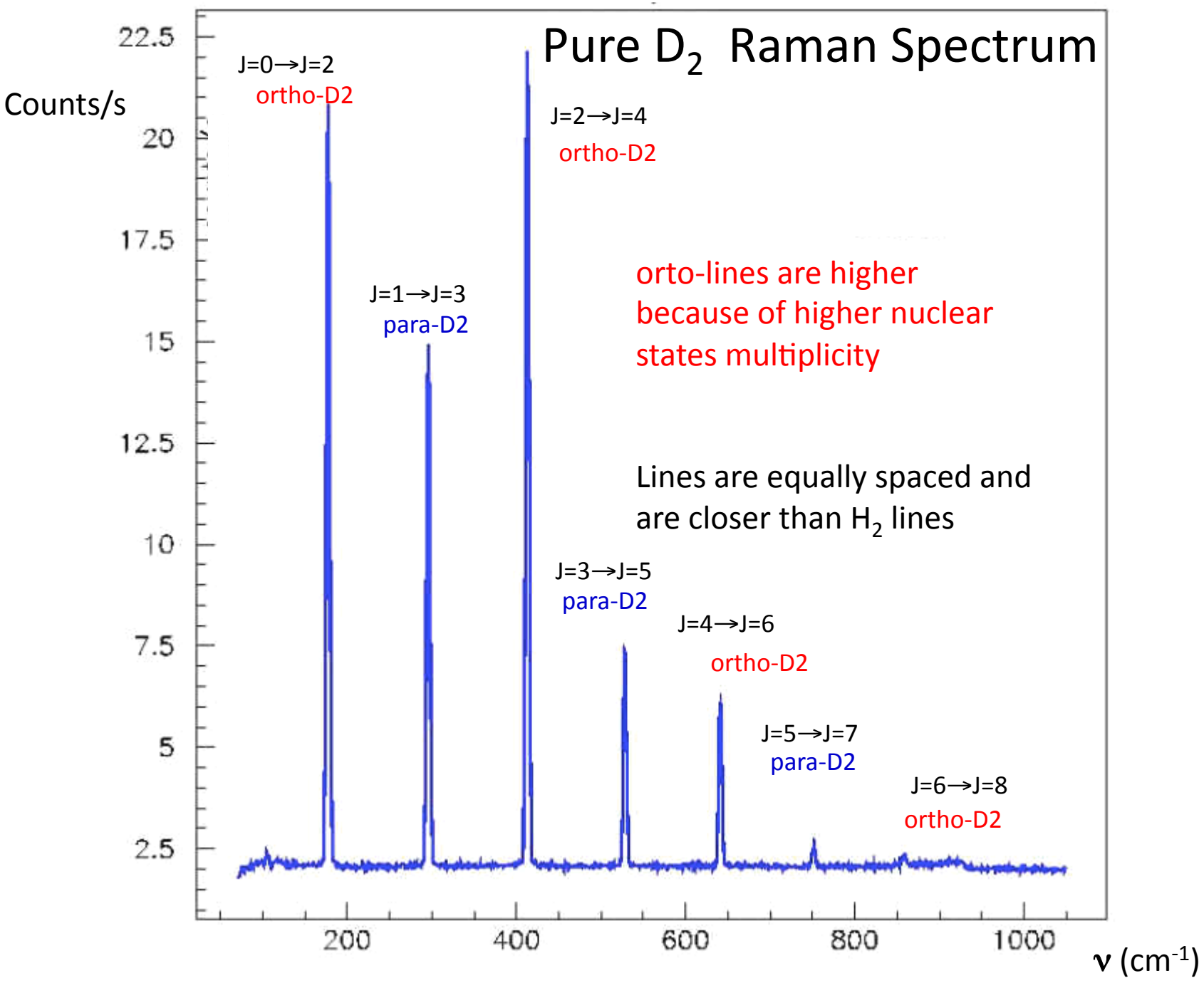


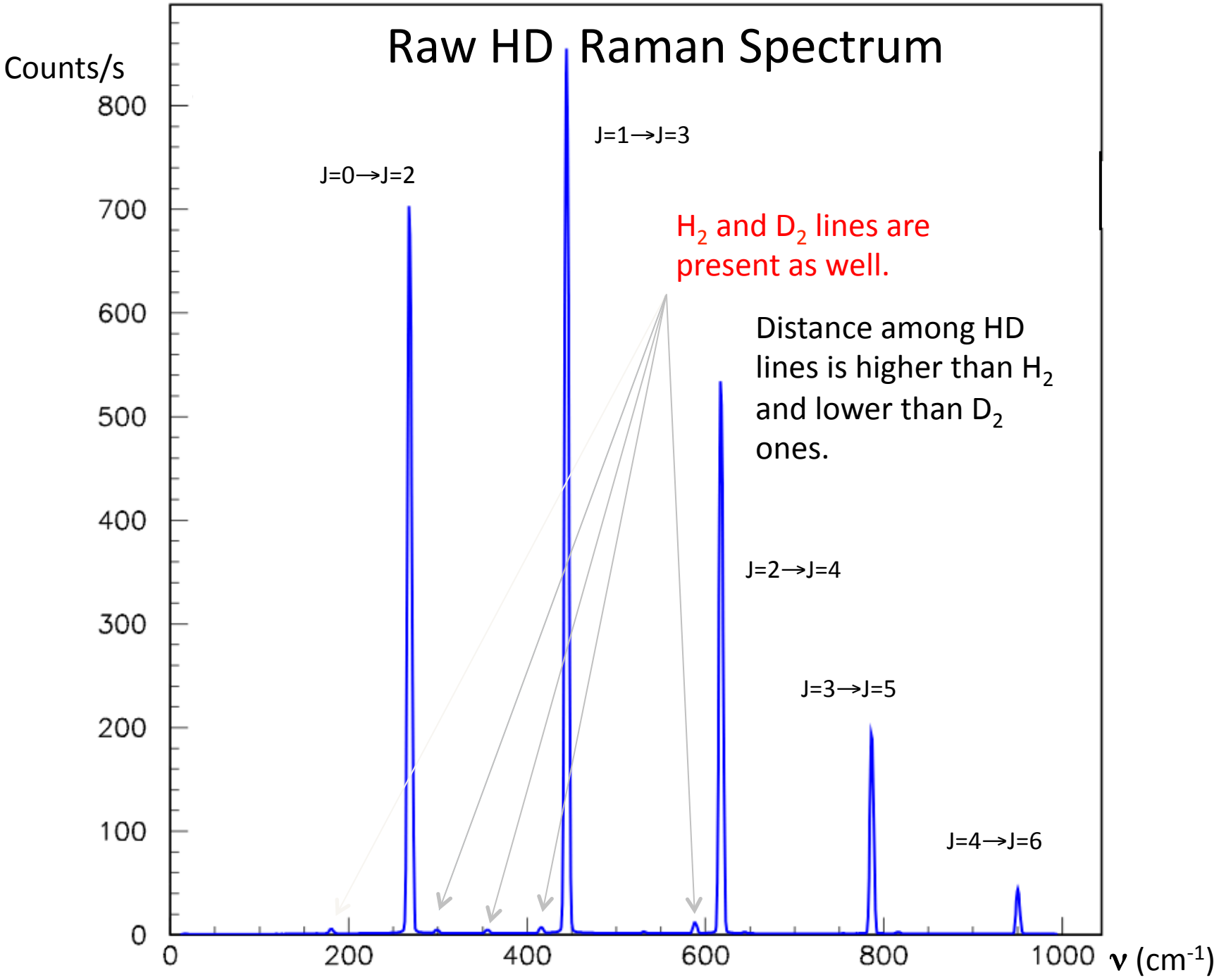




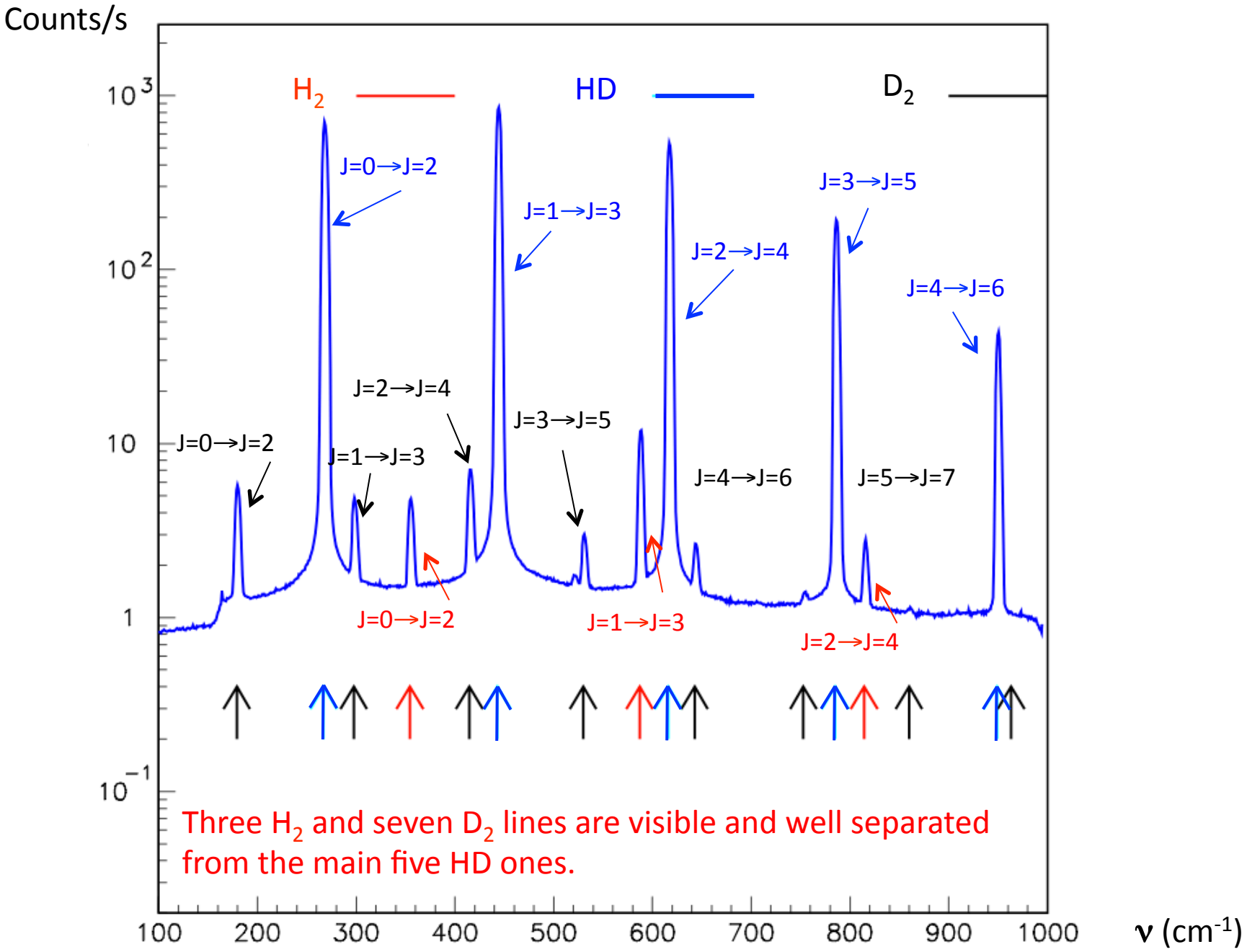
The scattered light spectrum is detected by a cooled CCD and recorded by a PC.


Counts/s
Pure H_2 Raman Spectrum
200
175
150
125
100
75
50
25
0
400
600
800
1000
1200
ν (cm-1)
J=1 → J=3
ortho-H2
ortho-lines are higher because of higher nuclear states multiplicity
Lines are equally spaced
J=0 → J=2
para-H2
J=2 → J=4
para-H2
J=3 → J=5
ortho-H2
J=4 → J=6
para-H2


Pure D_2 Raman Spectrum
Counts/s
22.5
20
17.5
15
12.5
10
7.5
5
2.5
200
400
600
800
1000
ν (cm^{-1})
J=0→J=2
ortho-D2
J=1→J=3
para-D2
J=2→J=4
ortho-D2
J=3→J=5
para-D2
J=4→J=6
ortho-D2
J=5→J=7
para-D2
J=6→J=8
ortho-D2
orto-lines are higher because of higher nuclear states multiplicity
Lines are equally spaced and are closer than H_2 lines


Raw HD Raman Spectrum
Counts/s
800
700
600
500
400
300
200
100
0
0
200
400
600
800
1000
ν (cm-1)
J=0→J=2
J=1→J=3
J=2→J=4
J=3→J=5
J=4→J=6
H2 and D2 lines are present as well.
Distance among HD lines is higher than H2 and lower than D2 ones.

Raw HD Raman Spectrum - log scale



Raman spectrum analysis

- The relative content of H_2 and D_2 contaminants in HD gas is determined fitting all the peaks in the frequency range between 100 and 1000 cm-1 higher than the original Laser frequency (stokes lines).

- Peaks intensities are determined from the Gaussian fit parameters

- By studying the dependence upon the temperature and upon the index J of each rotational level it is possible to determine the relative number of molecules in the sample for the different chemical species.

- The minimum relative amount that may be detected is lowered by increasing the Laser power and by reducing the background fluctuations

we use a 15 Watts Laser and we integrate the spectrum over 1 hour to average over noise fluctuations

Comparing Raman and GC

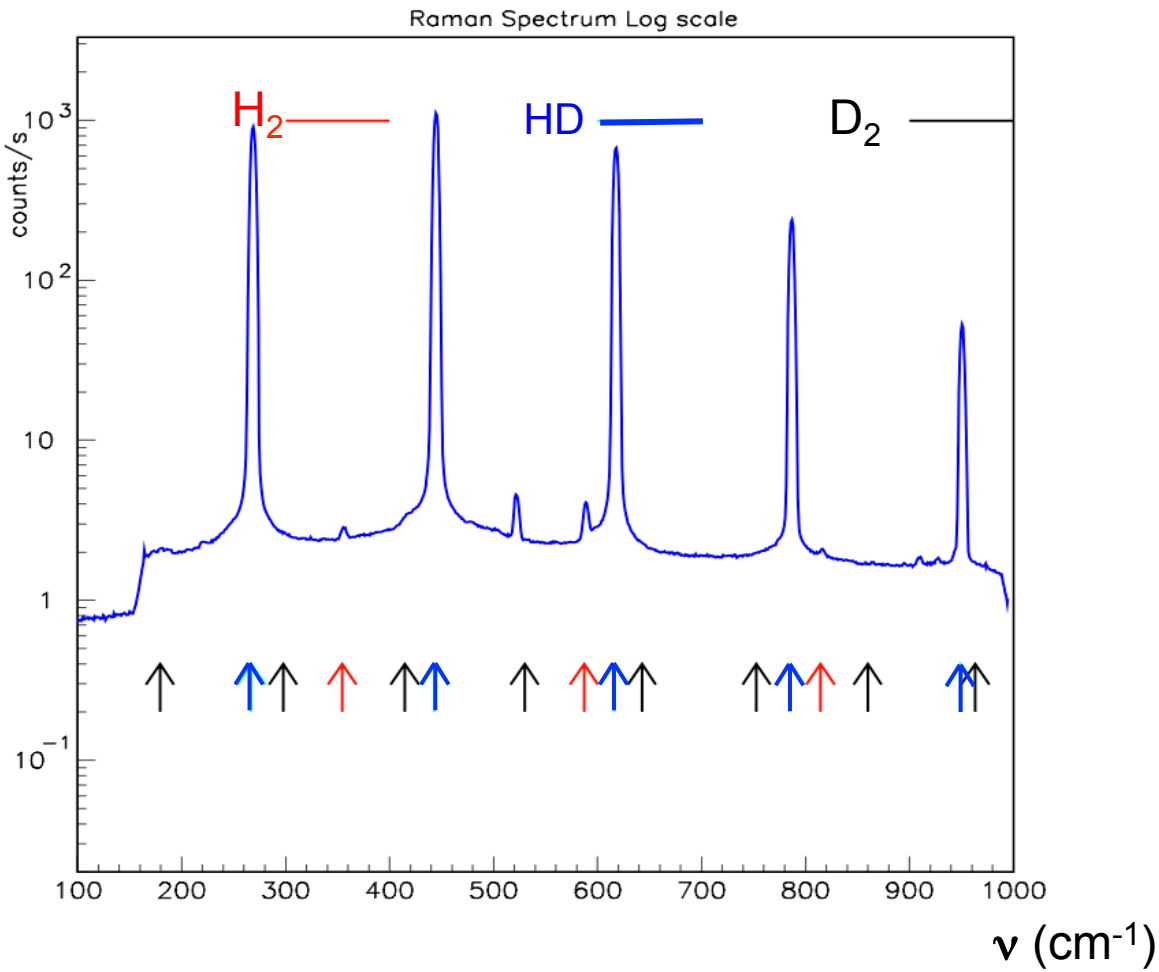
- Raw HD before purification:
  - Raman
    - $H2/HD = (7.0 \pm 0.6) \times 10^{-3}$
    - $D2/HD = (8.0 \pm 0.07) \times 10^{-3}$
  - GC
    - $H2: (7.0 \pm 0.14) \times 10^{-3}$
    - $D2: (11.0 \pm 0.22) \times 10^{-3}$

JMU 5 – tank 2

Ion-Ar Laser: 12 W power

$H_2/HD = (61 \pm 2)\ 10^{-5}$

$D_2/HD = (5 \pm 3)\ 10^{-5}$



H_2 and D_2 peaks were not visible in the chromatogram

Summary

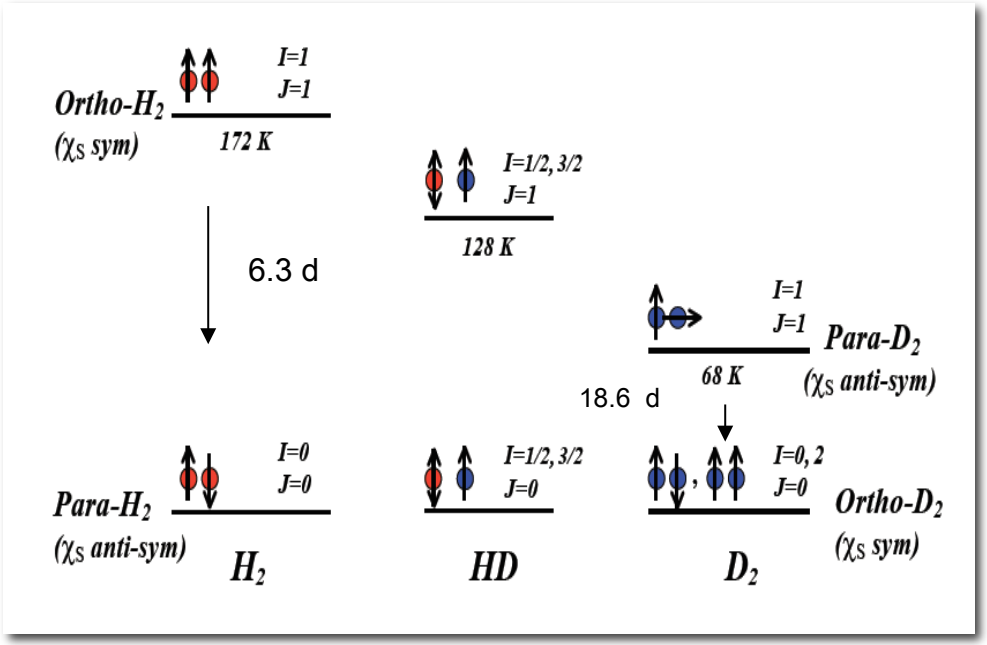
- Low-temperature distillation permits separation of H_2, HD, and D_2 to a few parts in 10^{-4} or better
- Measurement techniques available for monitoring purity (in increasing sensitivity and complexity)
  - Residual gas analysis
  - Gas chromatography
  - Raman scattering
- Gas production underway

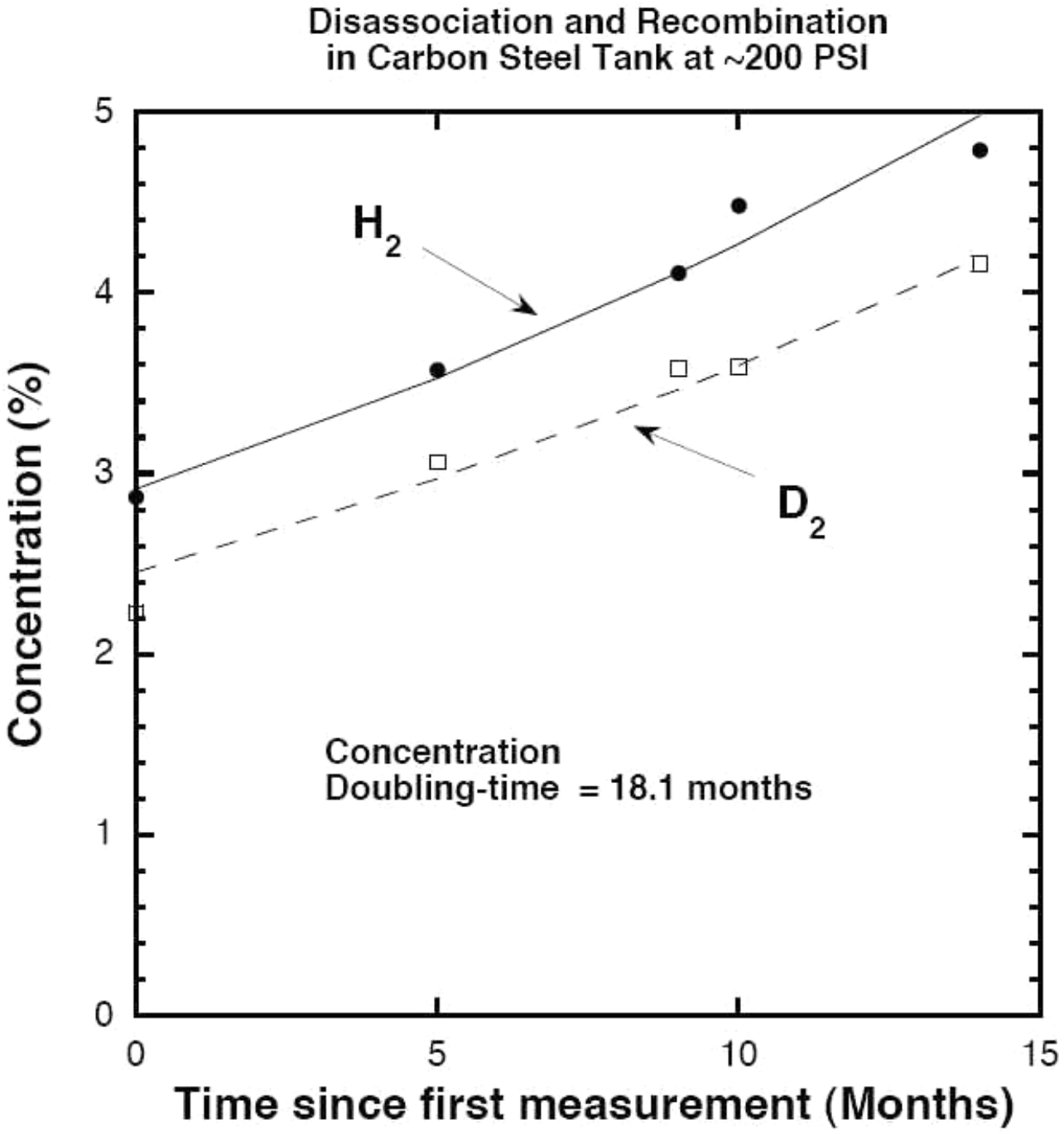
The Need for Purity

Creating a frozen spin target with significant relaxation time requires that H_2 and D_2 concentrations be small and carefully controlled.

Longitudinal relaxation time T_1H

$$\frac{1}{T_1^H} \propto \left(c_1^H\right)^{2.1}\left(c_1^D\right)^{1.6}$$





Gas is stored at < 2 ATM in specially treated Al cylinders to minimize this effect.