Compact (L)H_2 Storage with Extended Dormancy in Cryogenic Pressure Vessels

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Project ID # ST003

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: **October 2004**
- End date: **Sept. 2011**
- Percent complete: **80%**

Barriers

- **A. Volume and weight**
- **B. Cost**
- **O. Hydrogen boil-off**

Targets

- **Ultimate volume target**
- **Ultimate weight target**

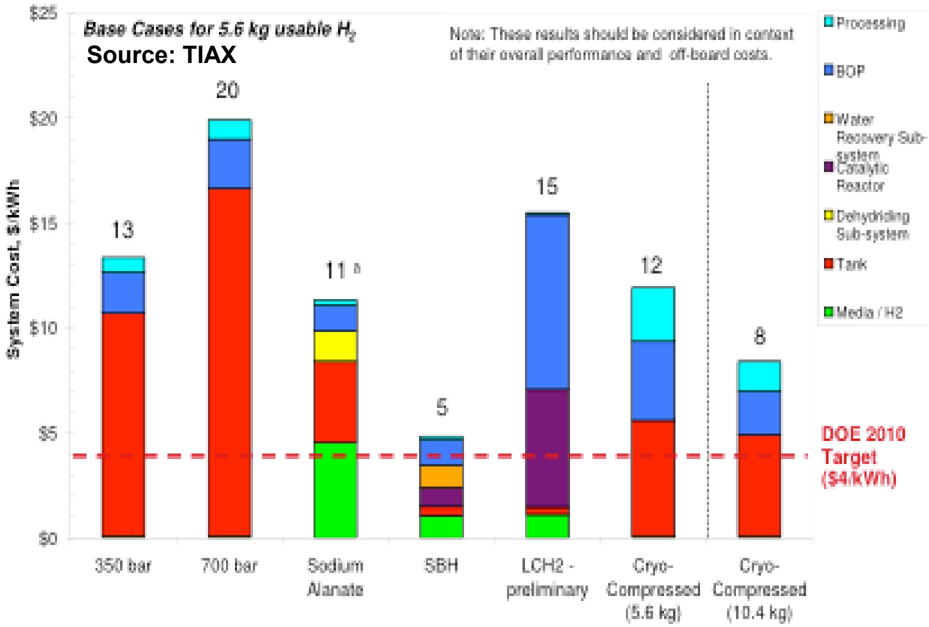
Budget

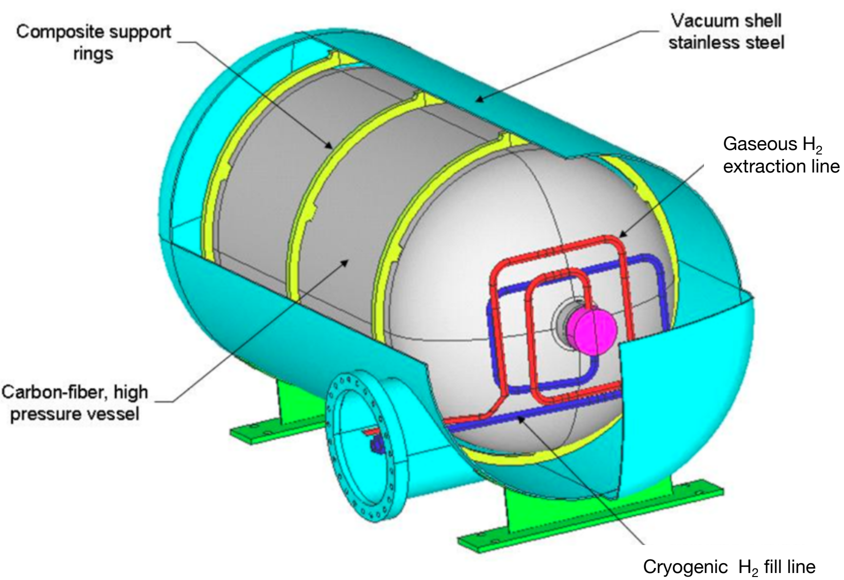
- Total project funding
  - DOE: **$4.5M**
- Funding for FY09:
  - **$2.25M**
- Funding for FY10:
  - **$440k**

Partners

- **CRADA** with BMW
- **CRADA** with Structural Composites Industries (SCI)

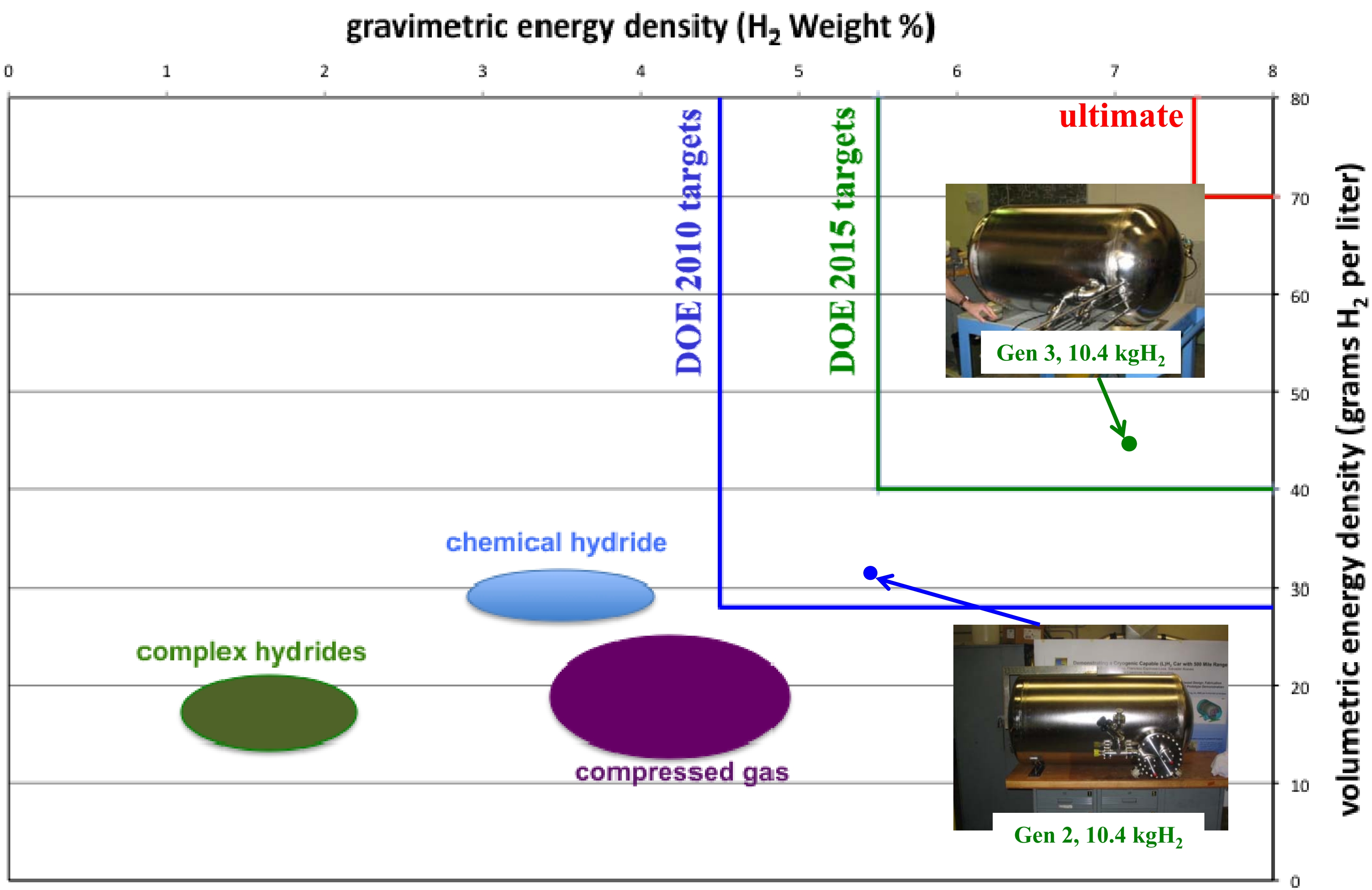
Relevance: High density cryogenic hydrogen enables compact, lightweight, and cost effective storage



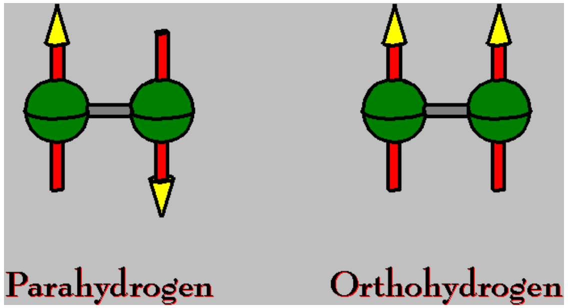


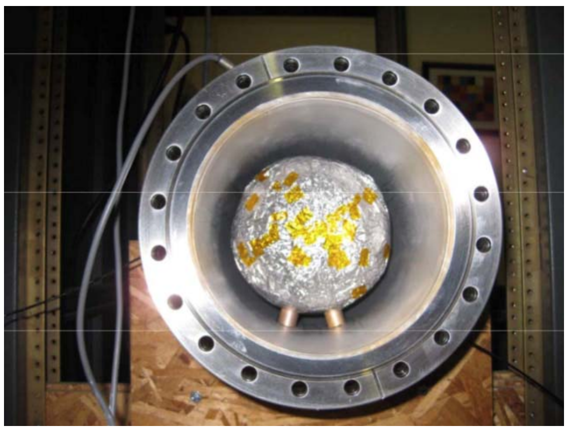
- ***Cost effective:*** **Cryogenic vessels use 2-4x less carbon fiber, reducing costs sharply at higher capacity**
- ***Compact:*** **235 L system holds 151 L fuel (10.3-10.7 kg H_2)**

Relevance: Cryogenic pressure vessels can *exceed* 2015 H_2 storage targets and approach *ultimate*



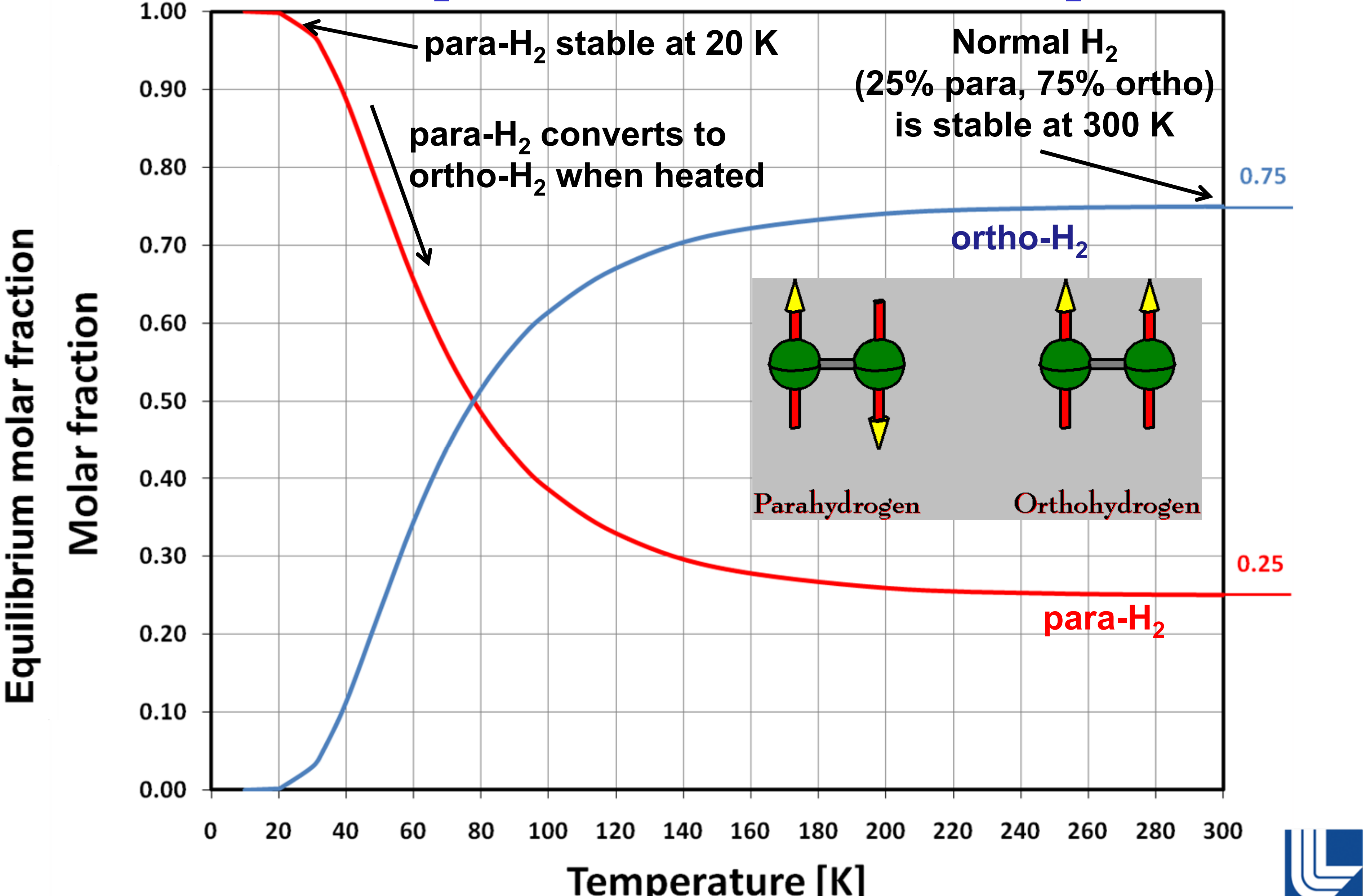
Approach: reduce/eliminate H_2 venting losses by researching vacuum stability, insulation, and para-ortho conversion



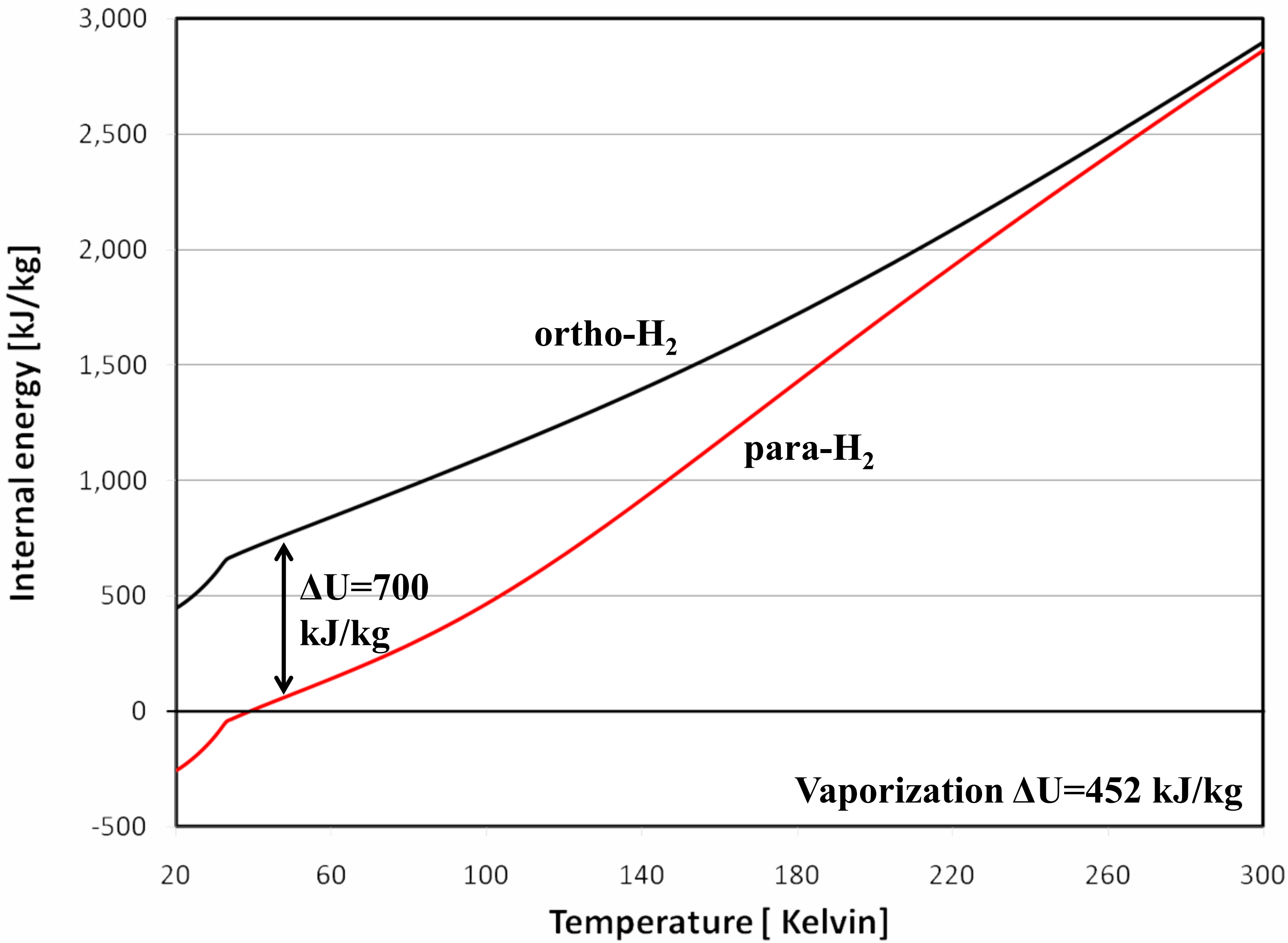


- ***Determine para-ortho effect on pressurization and venting losses***
- ***Directly measure para-ortho populations***
- ***Determine vessel heat transfer mechanism (radiation vs. conduction)***
- ***Evaluate vacuum stability by measuring pressure vessel outgassing***
- ***Test ultra thin insulation for improved vessel volume performance***
- ***Improve vessel design based on experimental results***

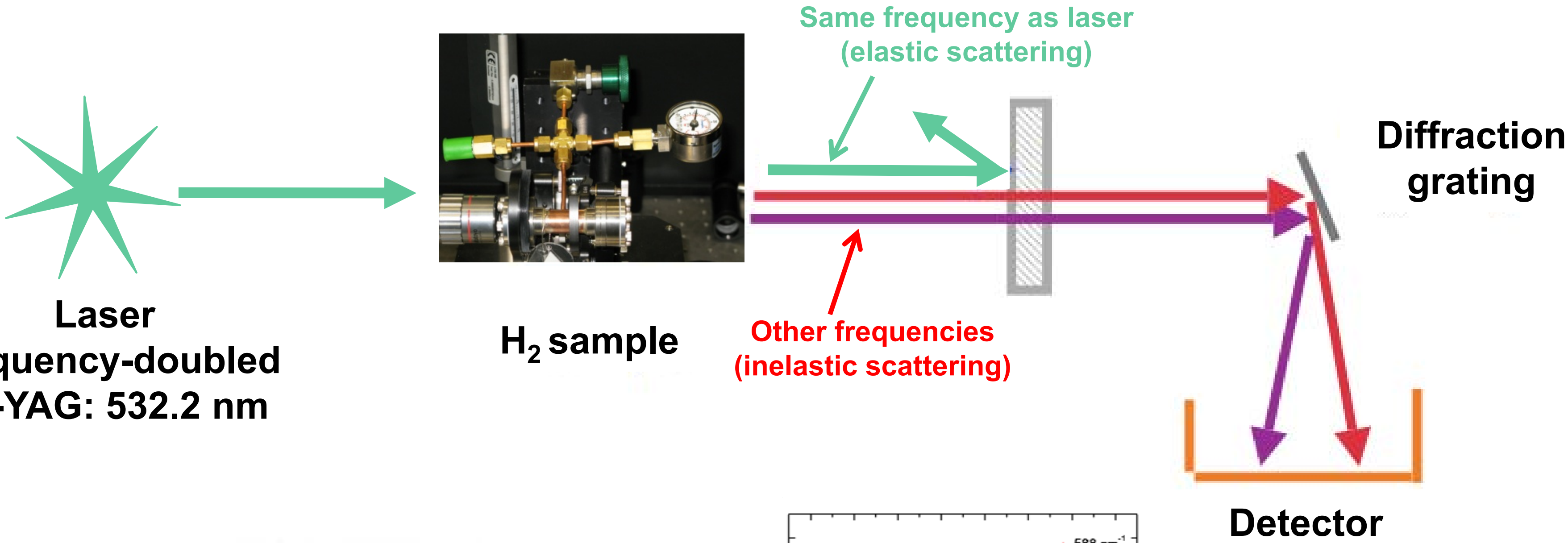
Hydrogen has two nuclear spin states: para-H_2 (stable at 20 K) and ortho-H_2

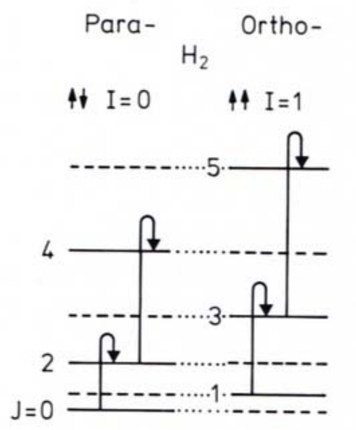


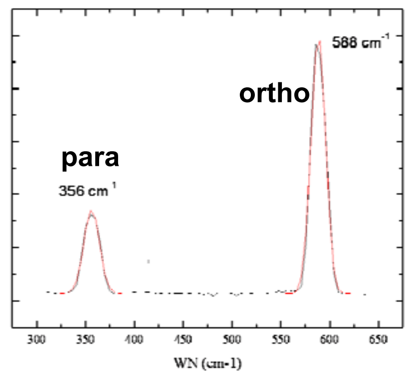
Para-ortho conversion absorbs energy & increases dormancy (equivalent to a second evaporation)



Rotational Raman spectroscopy quantifies the population of para-H_2 and ortho-H_2 energy levels







$J=0 \longrightarrow J=2$ $J=1 \longrightarrow J=3$

Rotational transition lines for normal H_2 (75% ortho)

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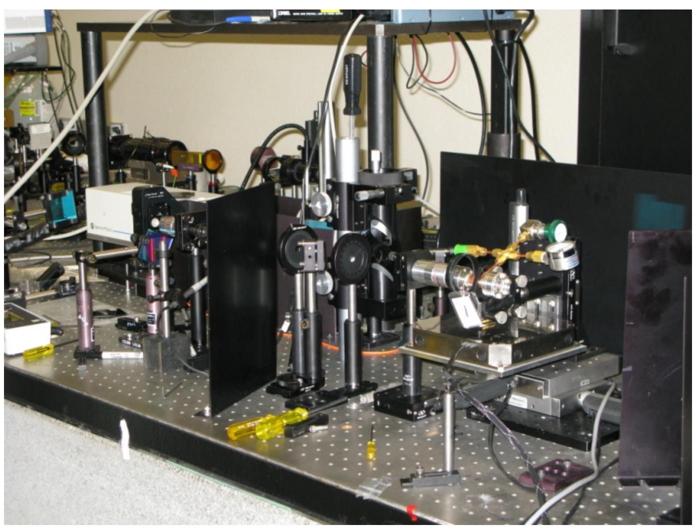
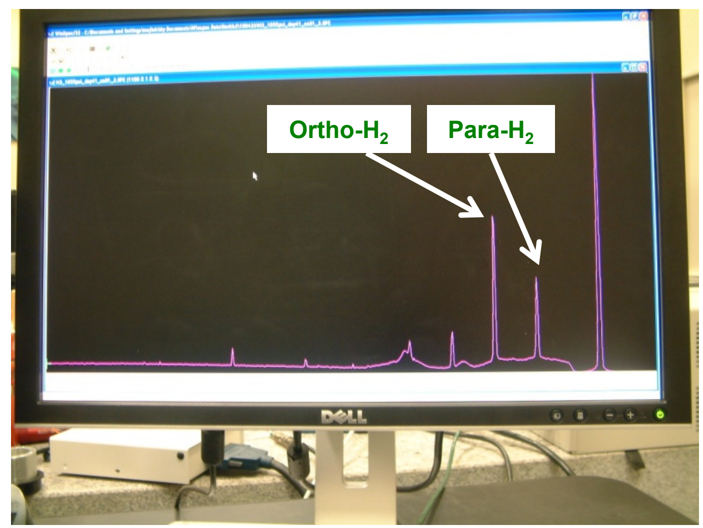
Gas samples from full-scale vessel were analyzed for para-H_2 concentration within 10 minutes of collection

Full-scale vessel

Sample delivery (~10 min) to laser lab

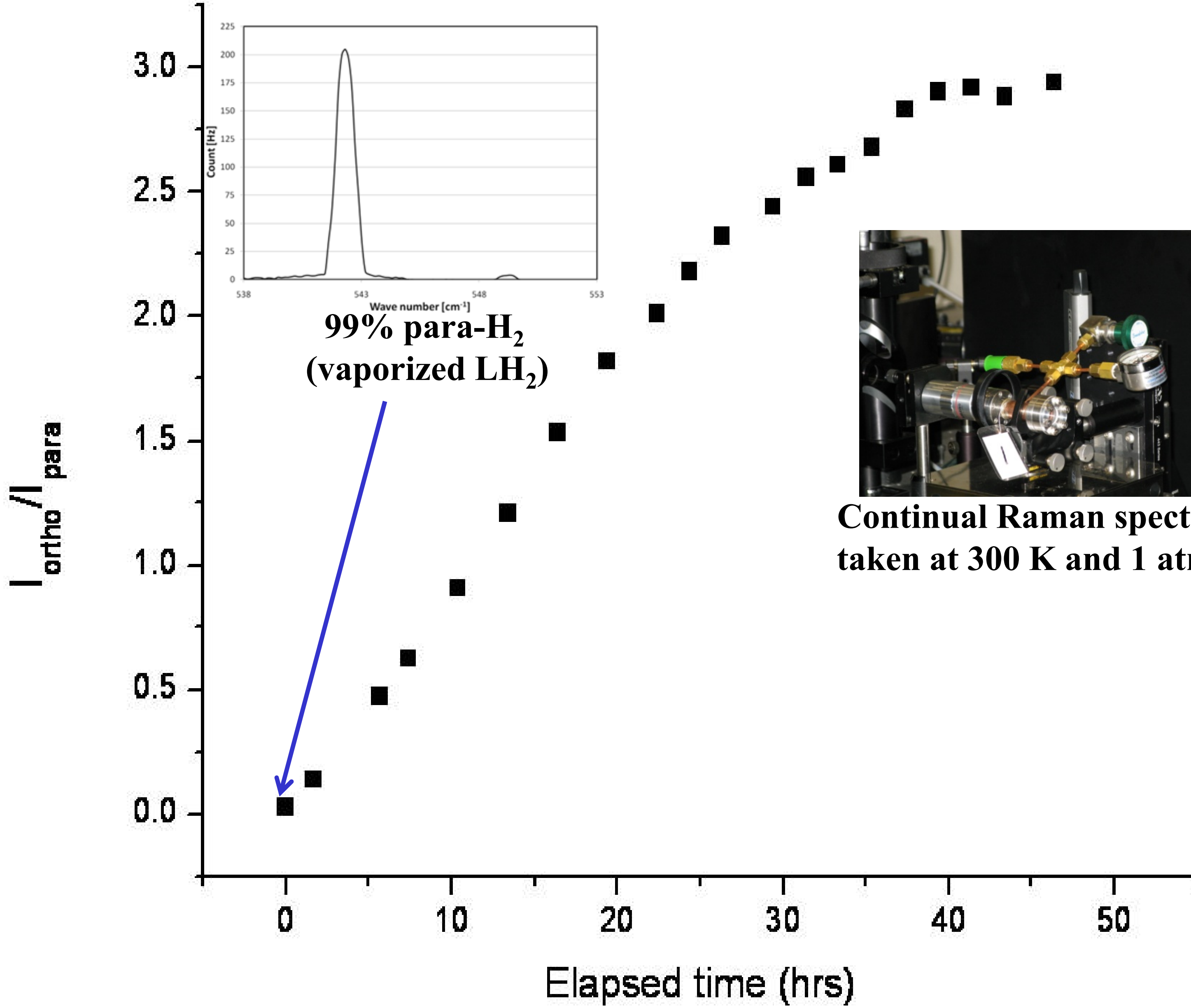


Confocal laser Raman system



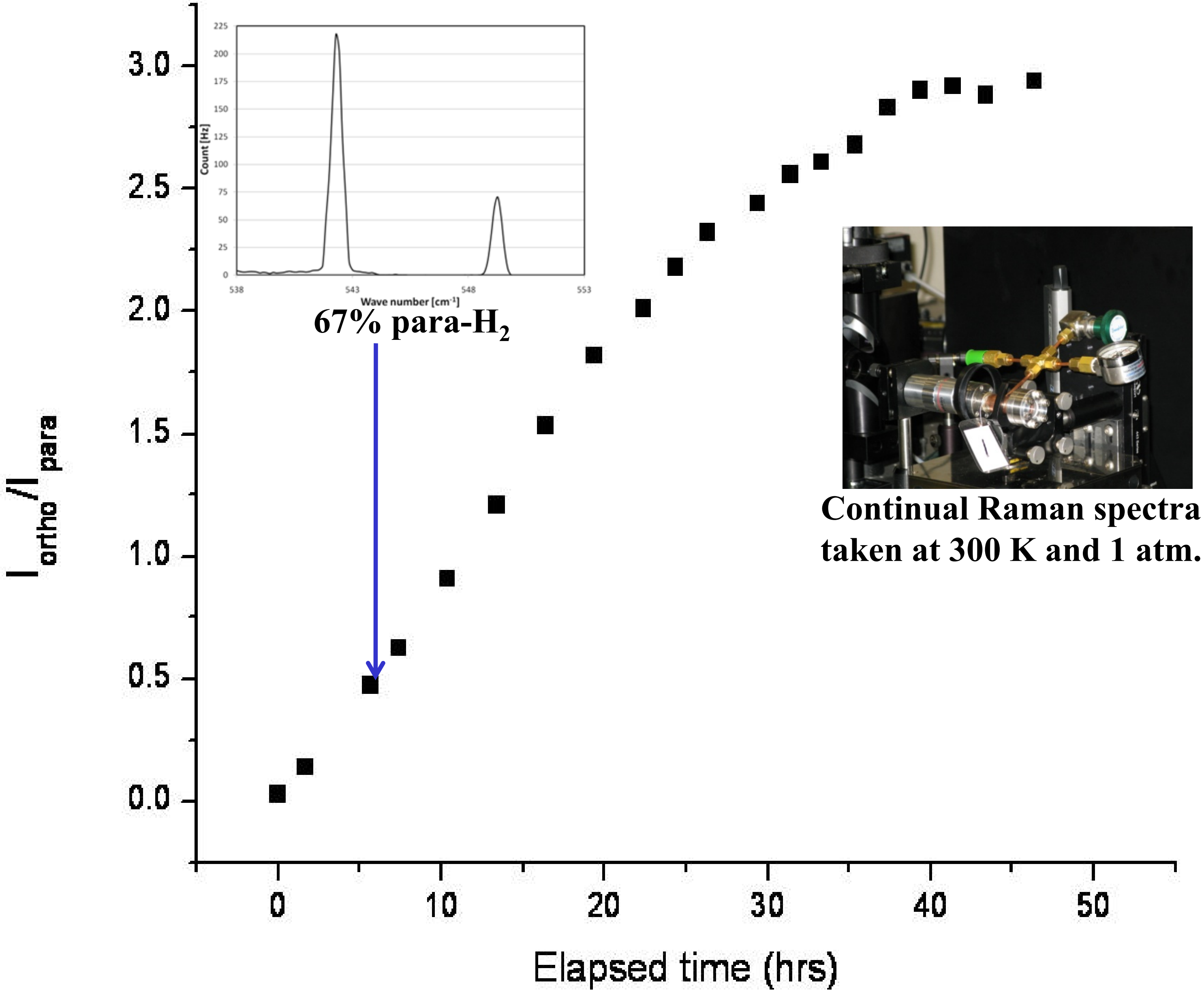
Spectral results

Continual monitoring of para-ortho H_2 conversion In sample vessel validated experimental procedures



Continual Raman spectra taken at 300 K and 1 atm.

Continual monitoring of para-ortho H_2 conversion In sample vessel validated experimental procedures



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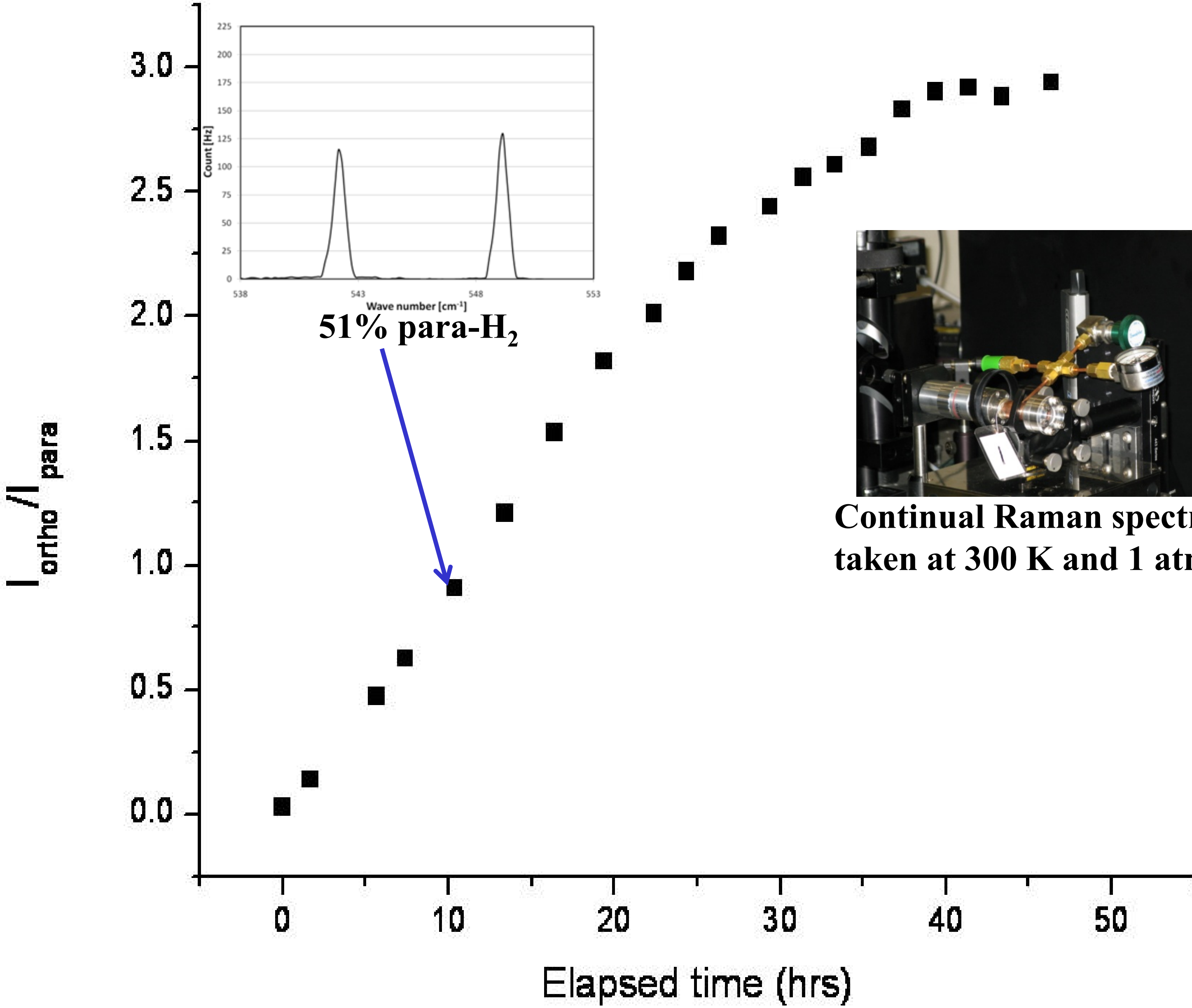

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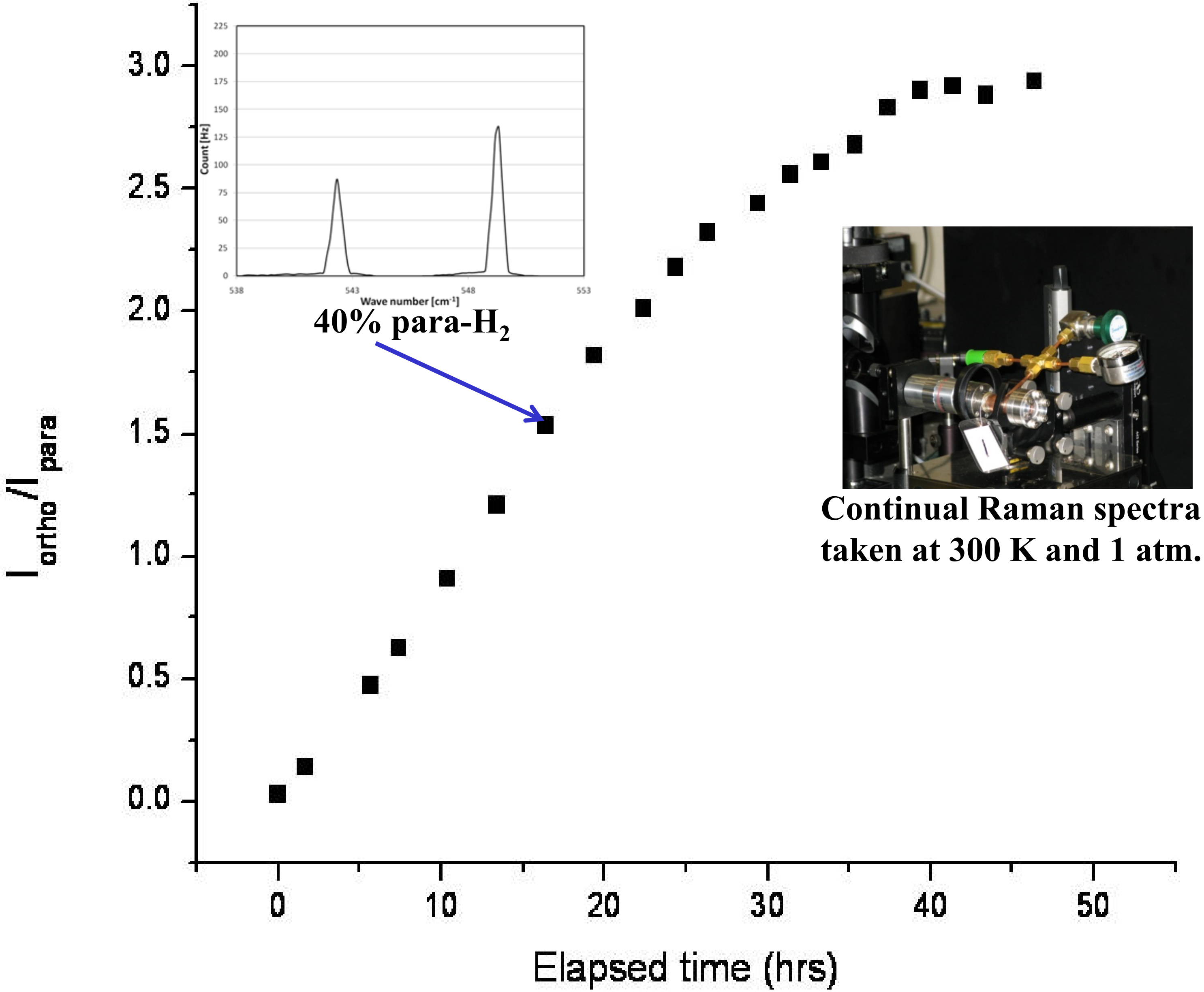

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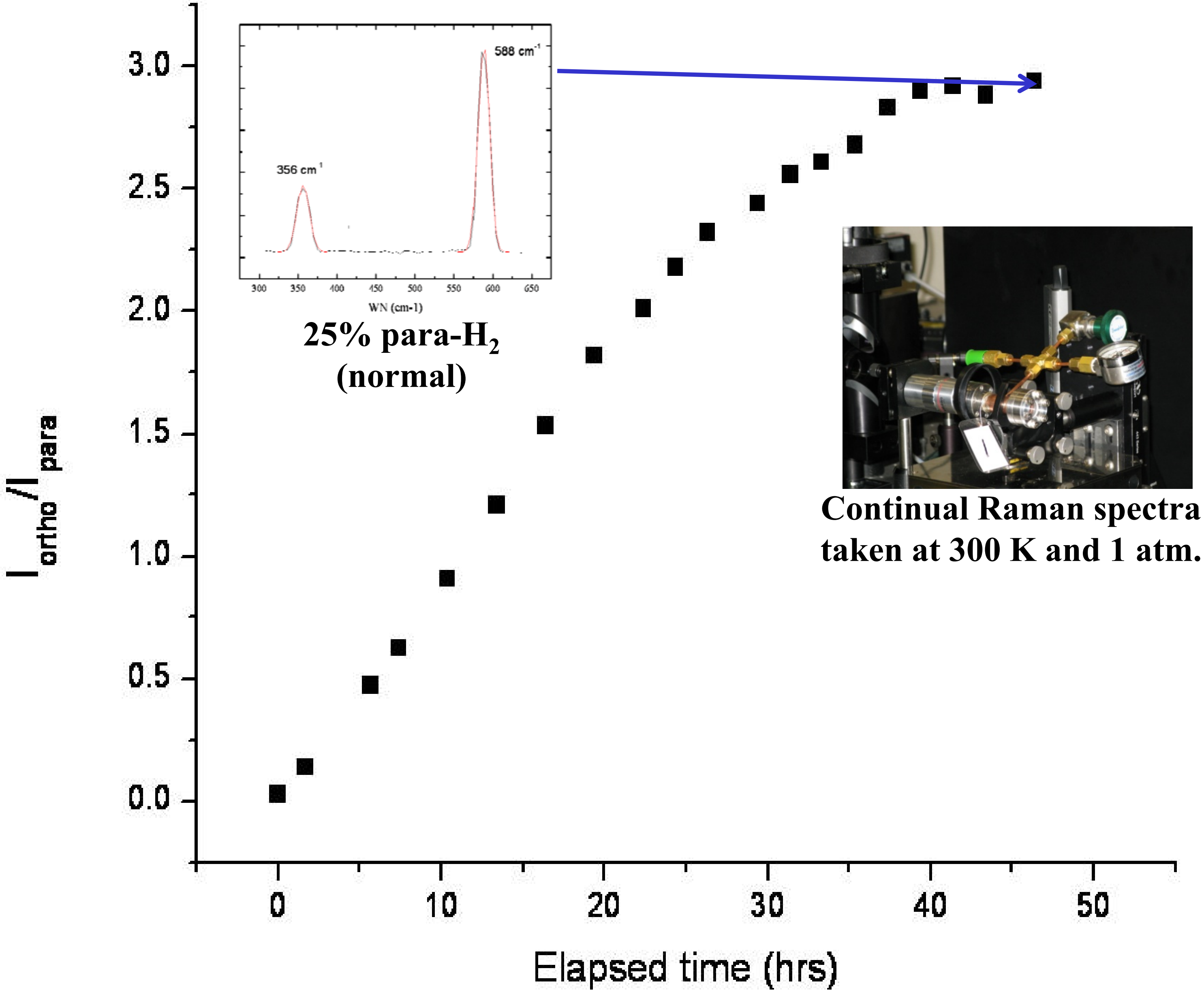
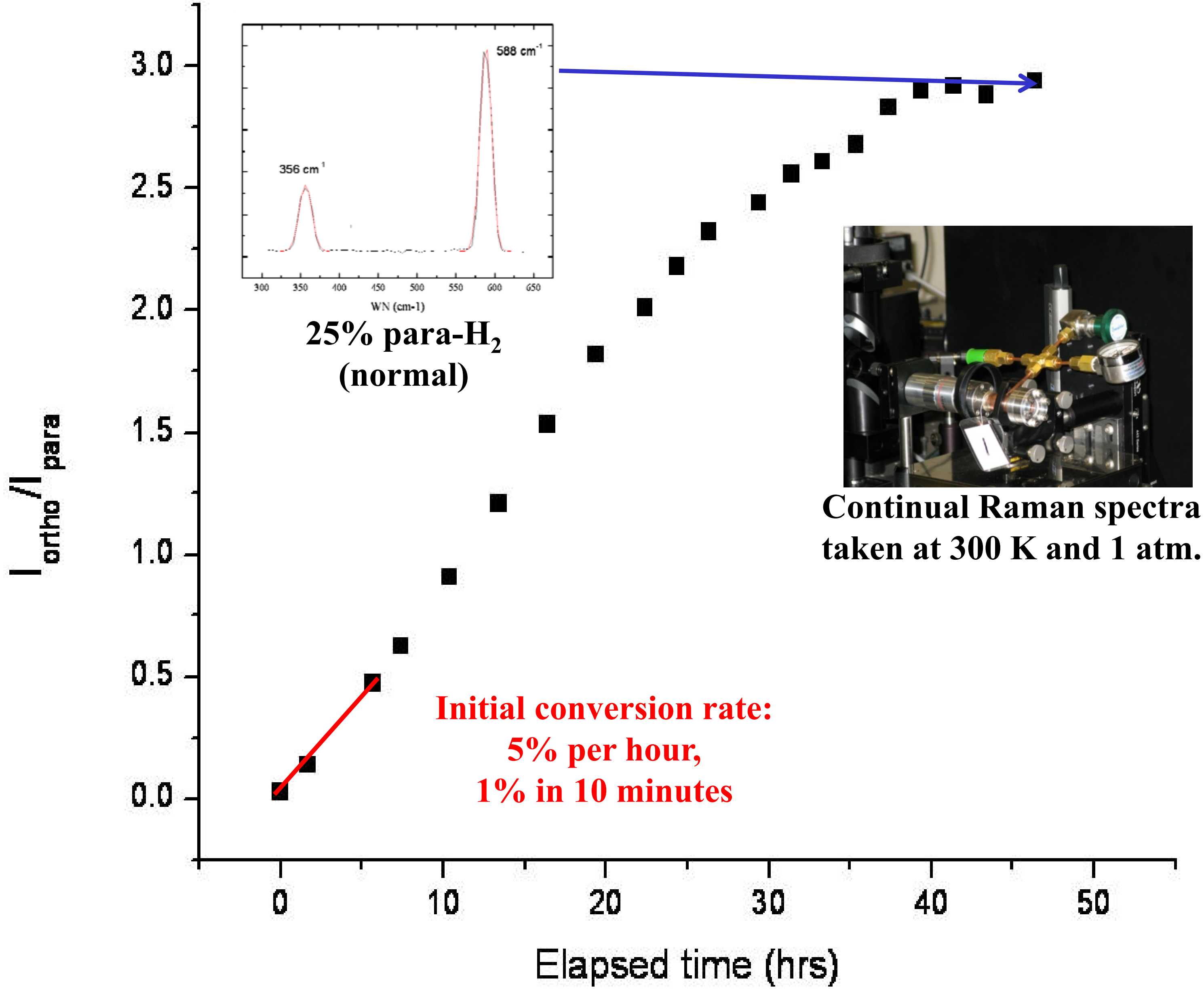
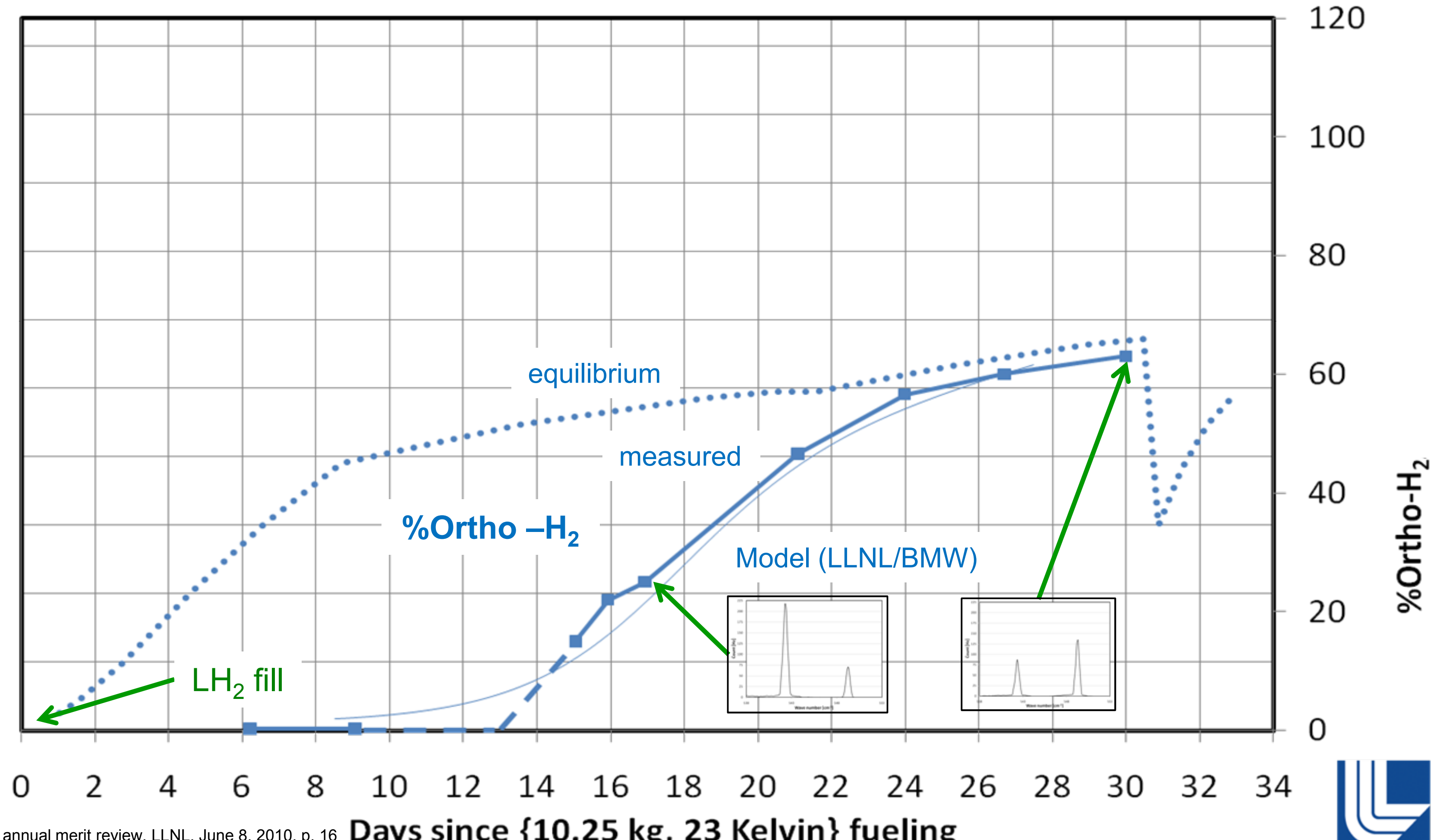


Continual Raman spectra taken at 300 K and 1 atm.

Continual monitoring of para-ortho H_2 conversion In sample vessel validated experimental procedures



Raman measurements of samples from Prius show a 12 day lag of ortho conversion then S-curve approach to equilibrium



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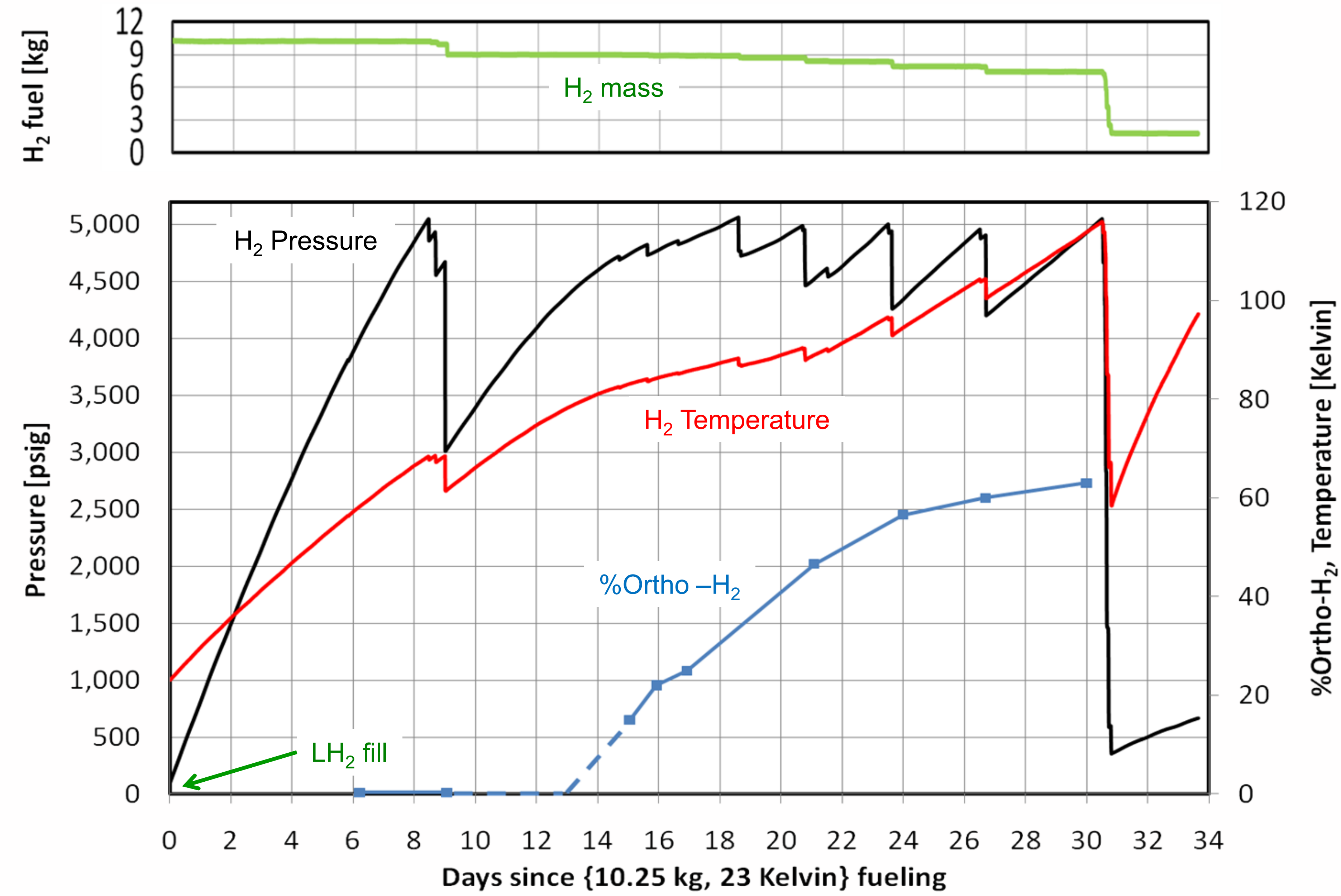
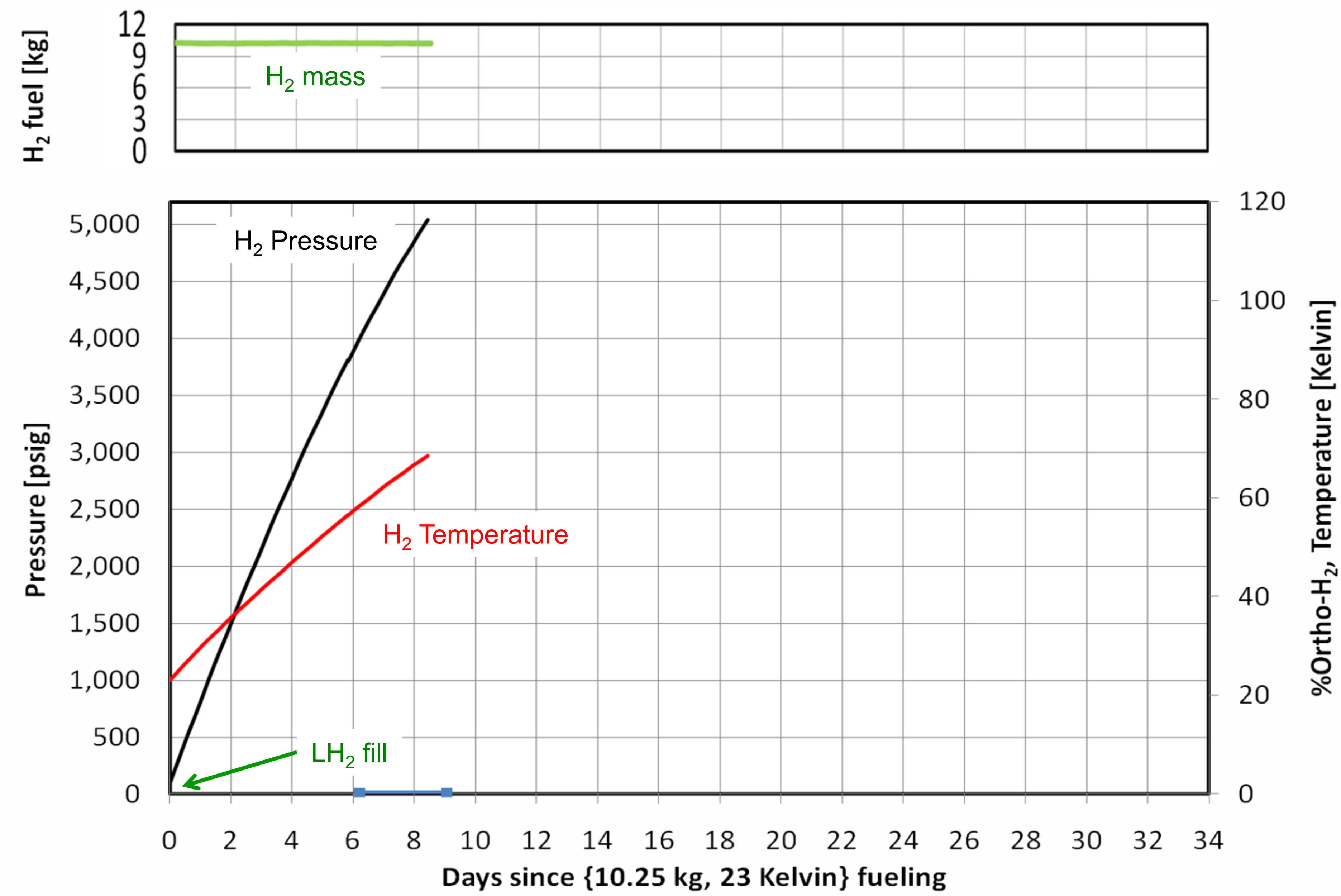
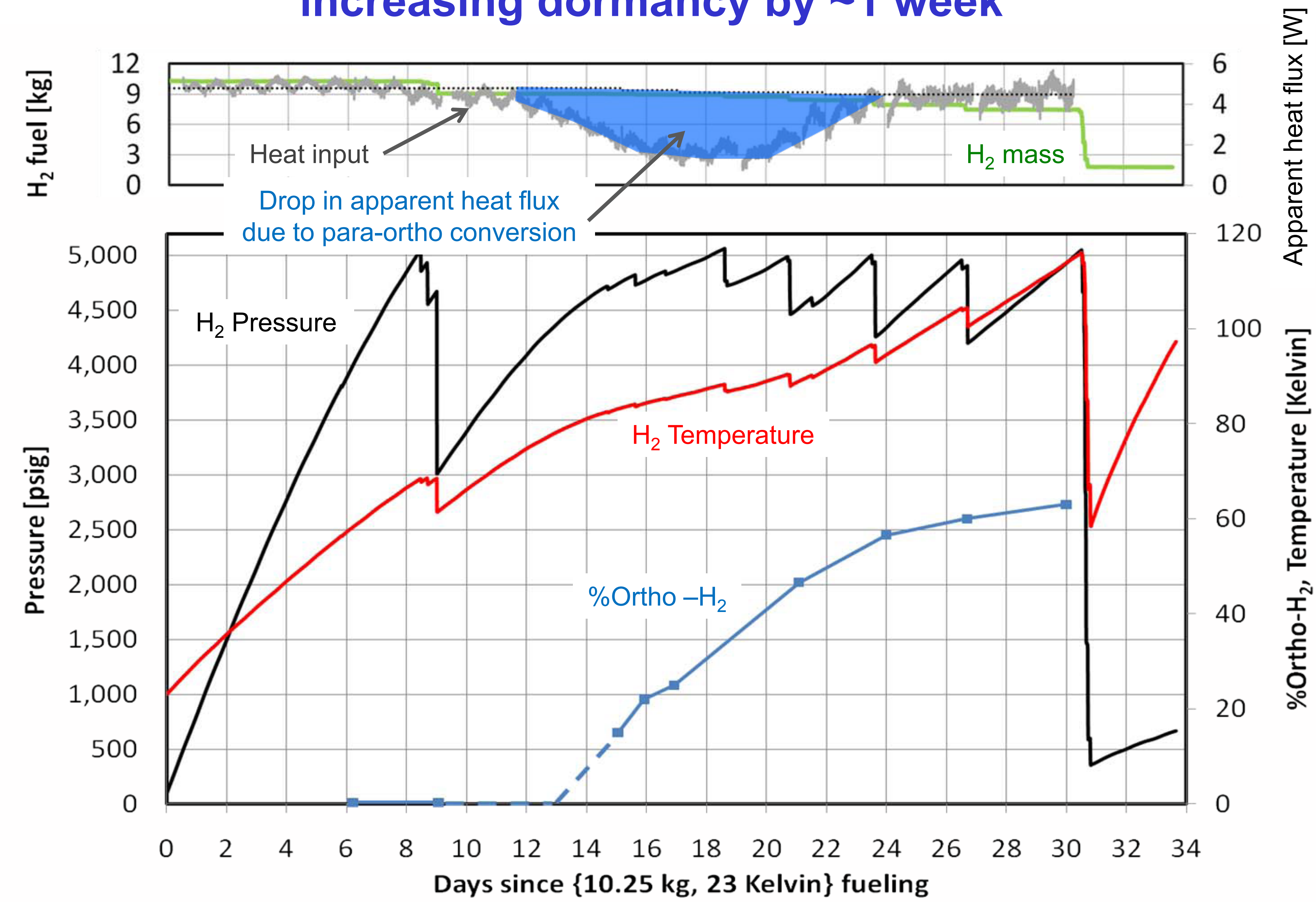
LLNL's 5,000 psi cryogenic pressure vessel fueled with LH_2 retained 75% of its fuel after a 1 month experiment



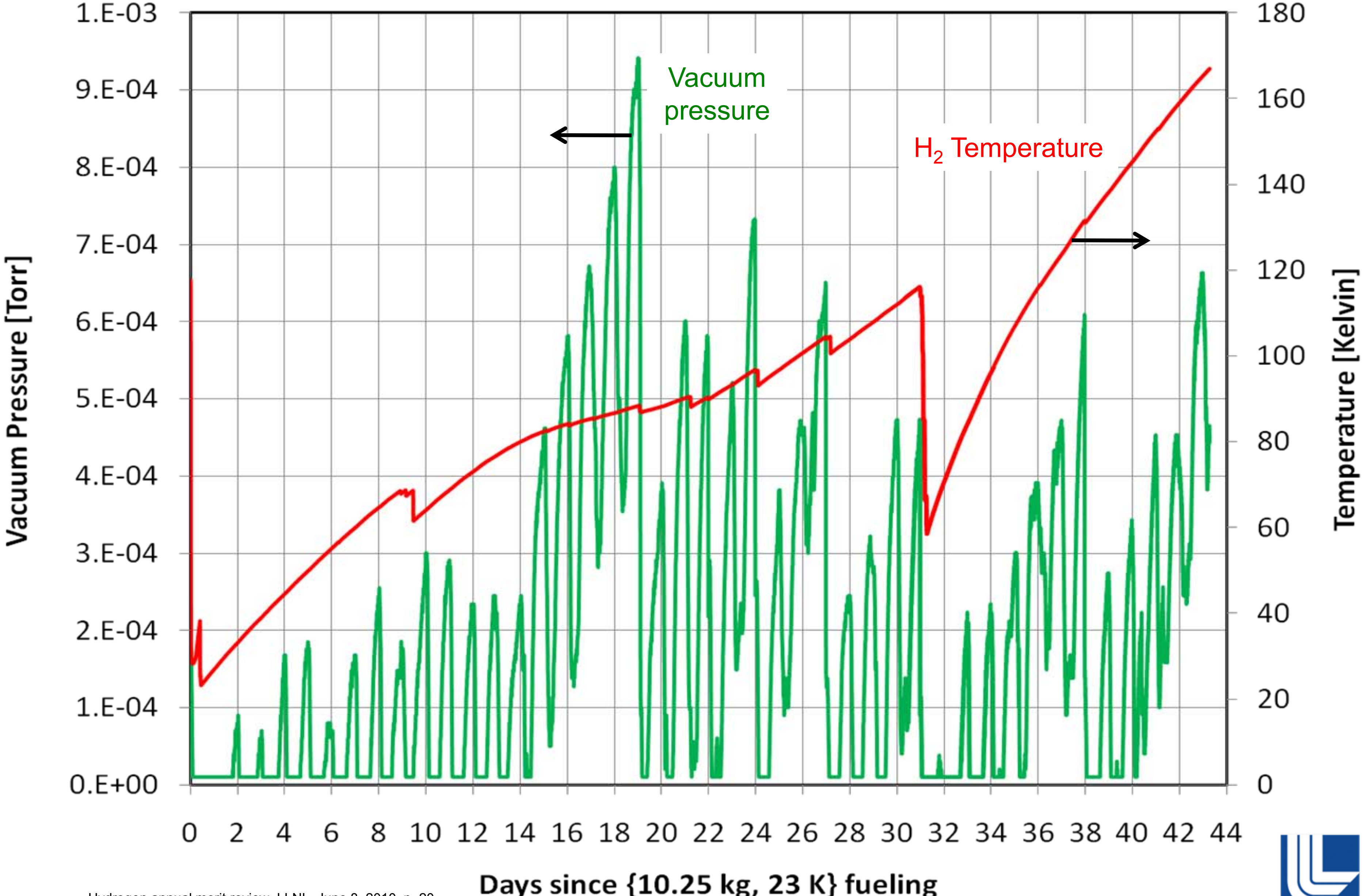
A 95% full vessel warms from 23 K to 69 K in 8.3 days, pressurizing to 5,000 psi with no evaporative loss



Conversion to ortho-H_2 was observed between 75 and 110 K increasing dormancy by ~1 week



Without a getter, vacuum quality degraded measurably after two weeks, at temperatures above 80 K



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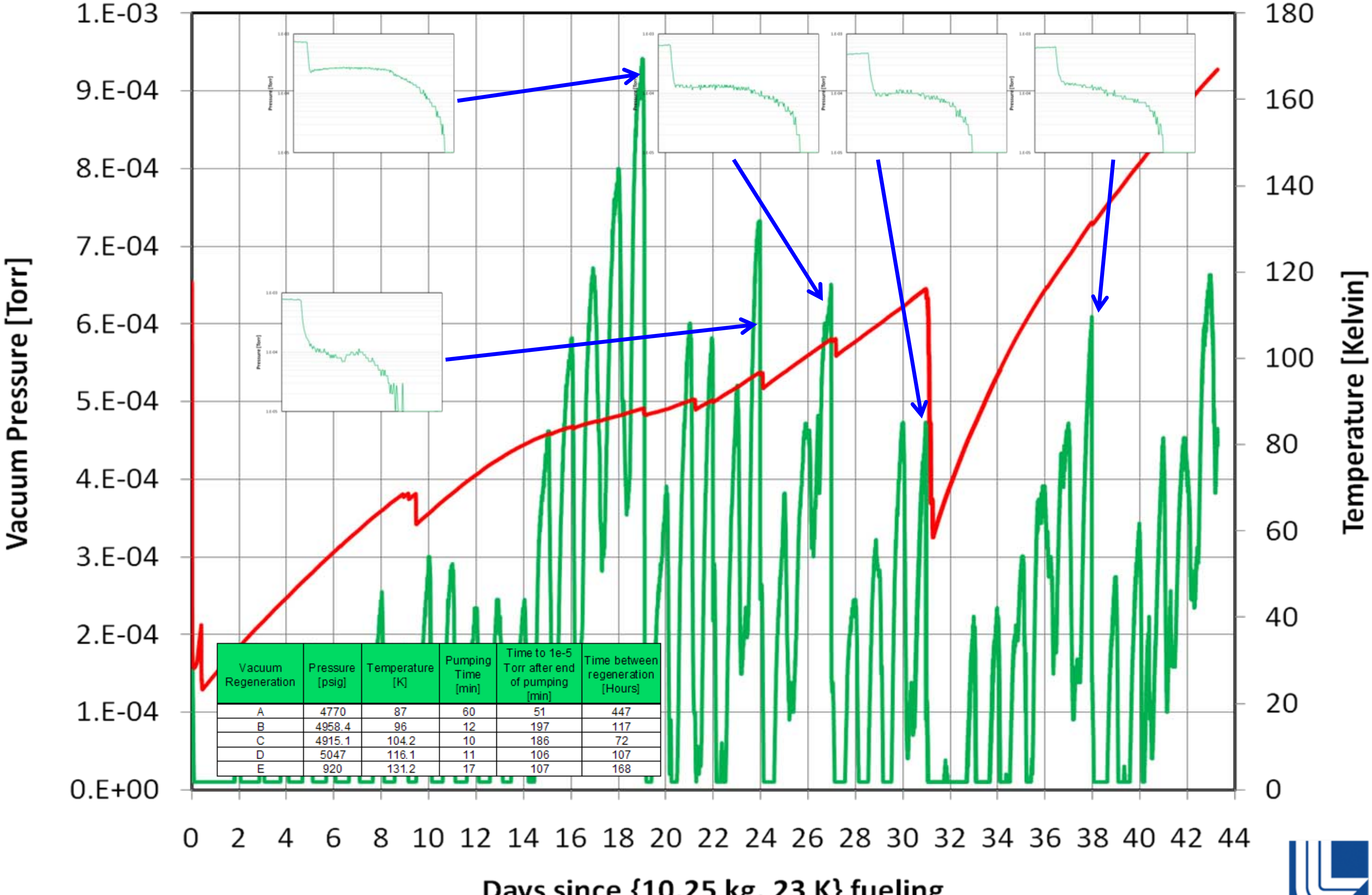
Limited vacuum pumping (~ 10 minutes every 4 days) restored vacuum quality even at higher temperatures



Vacuum Regeneration	Pressure [psig]	Temperature [K]	Pumping Time [min]	Time to 1e-5 Torr after end of pumping [min]	Time between regeneration [Hours]
A	4770	87	60	51	447
B	4958.4	96	12	197	117
C	4915.1	104.2	10	186	72
D	5047	116.1	11	106	107
E	920	131.2	17	107	168

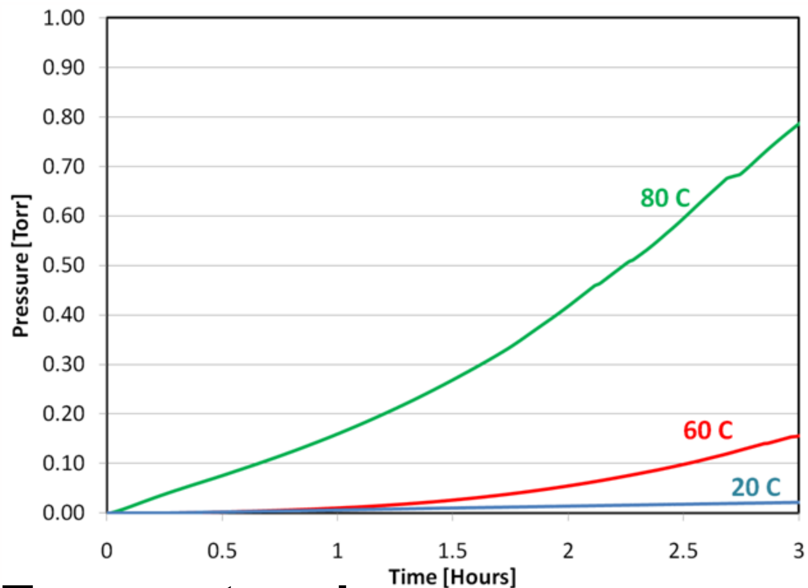
Composite outgassing research necessary for establishing suitable getters for long-term vacuum stability

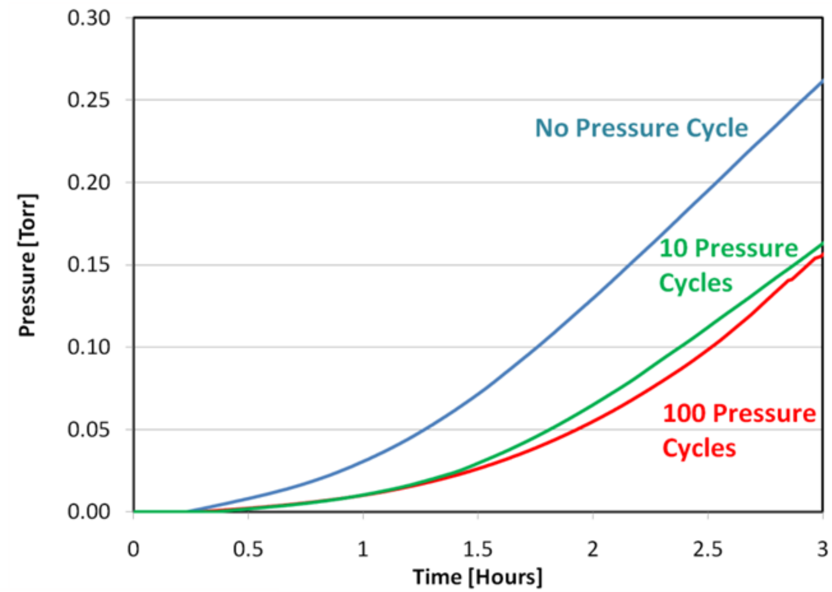
Oven in pressure cell

1 liter vessel under vacuum in oven

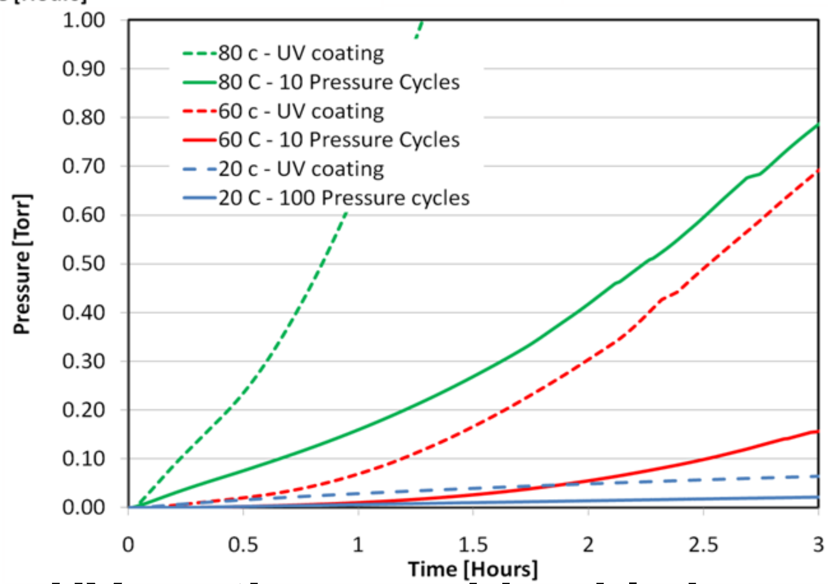
- ***Pre-bake vessels to 80°C:*** **Determine if H_2O can be essentially eliminated**
- ***Run outgassing tests at 20, 60 and 80°C:*** **Establish effect of temperature on outgassing rate and composition**
- ***Cycle vessels 10 & 100 times with cooled gas:*** **separate mechanical and thermal effects by cycling vessels without compression heating**
- ***Outgassing from vacuum cured vessels with/without UV coating:*** **Investigate processing effects on outgassing, and potential cycling effects on coatings**

We have quantified composite vessel outgassing as a function of temperature, pressure cycling, and surface treatment





Temperature is most important factor in determining outgassing



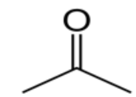
Number of pressure cycles at fixed temperature plays a relatively minor role

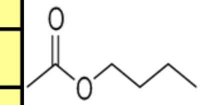
Significant increase in residual gas pressure is mainly due to small vacuum volume and not representative of automotive-sized vessels

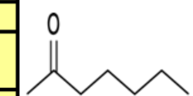
UV coating considerably increases vessel outgassing

Water is eliminated by baking but hydrocarbons are not. Detailed outgassing composition necessary for finding appropriate getters for long-term vacuum stability

	Experiment 1, no cycling			**Experiment 2: 10 cycles**			**Experiment 3: 100 cycles**			**Experiment 4: 100 cycles**	
Compound (and boiling point)	**20C**	**60C**	**80C**	**Cycle test**	**60C**	**80C**	**Cycle test**	**20C**	**60C**	**20C**	**60C**
Water (100ºC)	0	0	0	0	0	0	0	0	0	0	0
Acetaldehyde (20.2ºC)					56	140	12	<1	14	<1	36
Acetone, (56.5ºC)	<1	180	760	140	140	580	170	11	150	<1	390
Ethanol, (78.4ºC)			96			97			20		98
Isopropyl alcohol (83.6ºC)	<1	60	80	48	110	220	38	<1	80	<1	160
Acetic acid butyl ester (126ºC)	<1	690	1700	270	260	1200	370	10	380	55	740
Ethyl benzene (136ºC)	<1	20	50	9	10	36	16	<1	18	1.1	46
Xylenes, total (140ºC)	<1	76	240	33	39	160	53	3	72	4.1	160
Styrene (145ºC)	<1	21	64	9.2	11	47	14	<1	18	1.1	37
2-heptanone (151ºC)	<1	1300	3000	350	570	2400	460	23	770	23	1300
1, 3, 5 trimethylbenzene (164ºC)	<1	2	<1	1.2	1.7	4.4	1.6	<1	2.2	<1	<1
1, 2, 4 trimethylbenzene (169ºC)	<1	2.8	10	1.6	2.1	7.1	2	<1	3.6	<1	5.4
Carbon disulfide	<1						39	48	10	<1	16
Total hydrocarbons	**0**	**2351.8**	**6000**	**862**	**1199.8**	**4891.5**	**1175.6**	**95**	**1537.8**	**84.3**	**2988.4**







We are acquiring a pressurized cryogenic H_2 fueling capability

BMW cryogenic high-pressure pump

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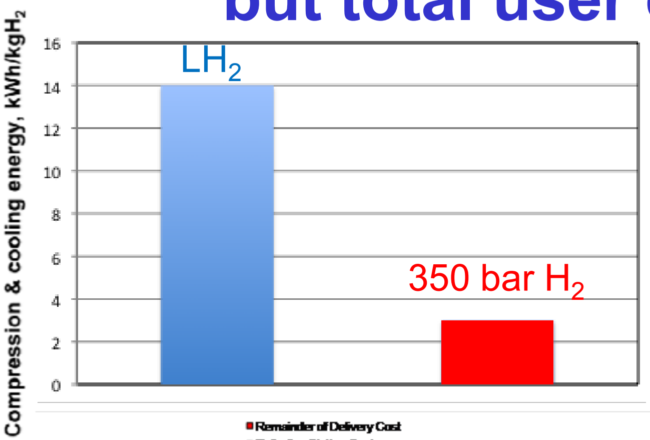
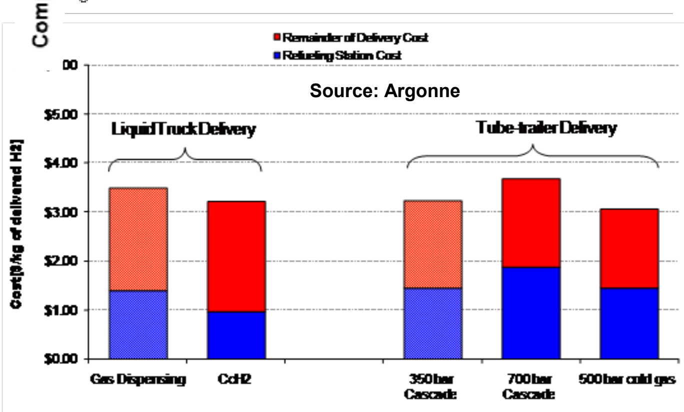
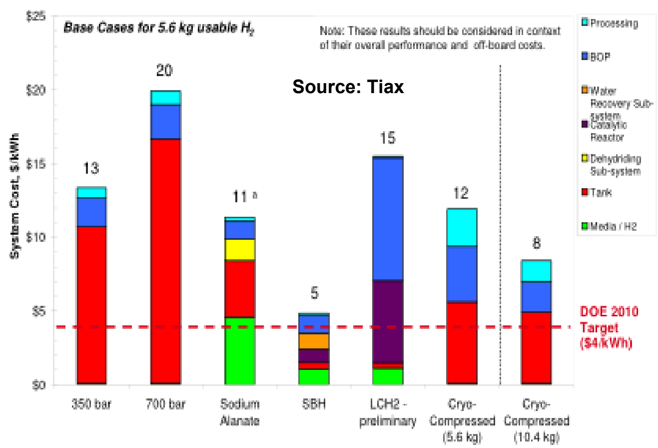
- *We currently fill at low pressure* from a conventional LH_2 storage vessel
- *A high pressure LH_2 pump* offers rapid single phase refueling without boil-off
- *Single flow refueling* can be reliable and cost effective
- *Site Permission and Utilities granted.* Will also serve for high pressure cryogenic H_2 testing
- *For full details*, attend PD074 tomorrow (Wed) at 1:45 pm

H_2 liquefaction is energy and capital intensive, but total user energy and cost is what matters





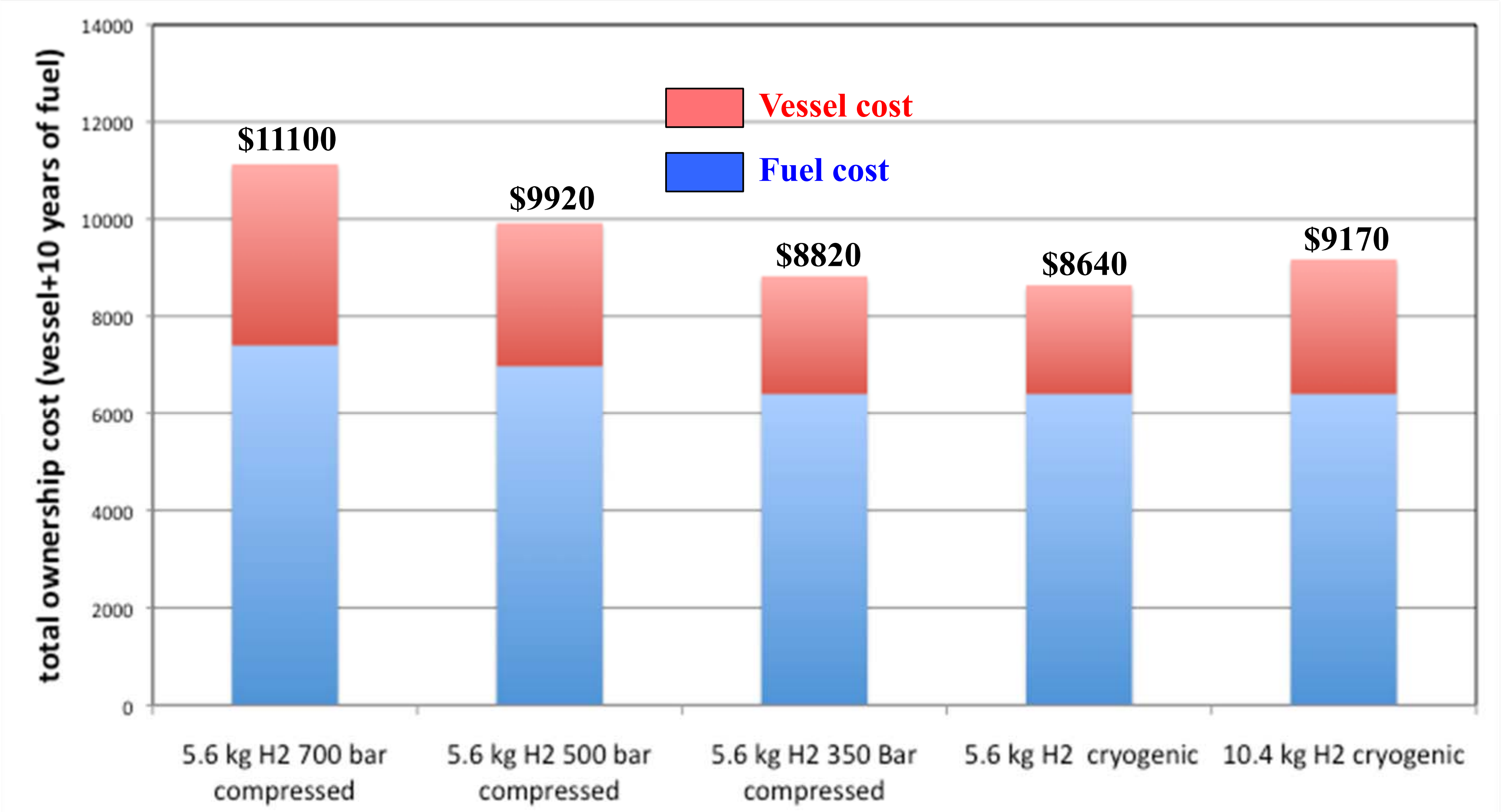


- **Liquefaction energy 4x greater than compression energy.** Direct energy cost advantage for compression

- **LH_2 delivery cost comparable** to 350 bar Liquefaction costs balanced by lower station costs.

- **LH_2 lowers onboard costs:** 2-4x less carbon fiber reduces overall cost. *Substantial* cost reduction with higher capacity

The energy cost of H_2 liquefaction is outweighed by onboard storage & refueling savings, with superior range/volume



System vol.	**224 L**	**262 L**	**329 L**	**160 L**	**231 L**
Drive range	**300 mi**	**300 mi**	**300 mi**	**300 mi**	**560 mi**

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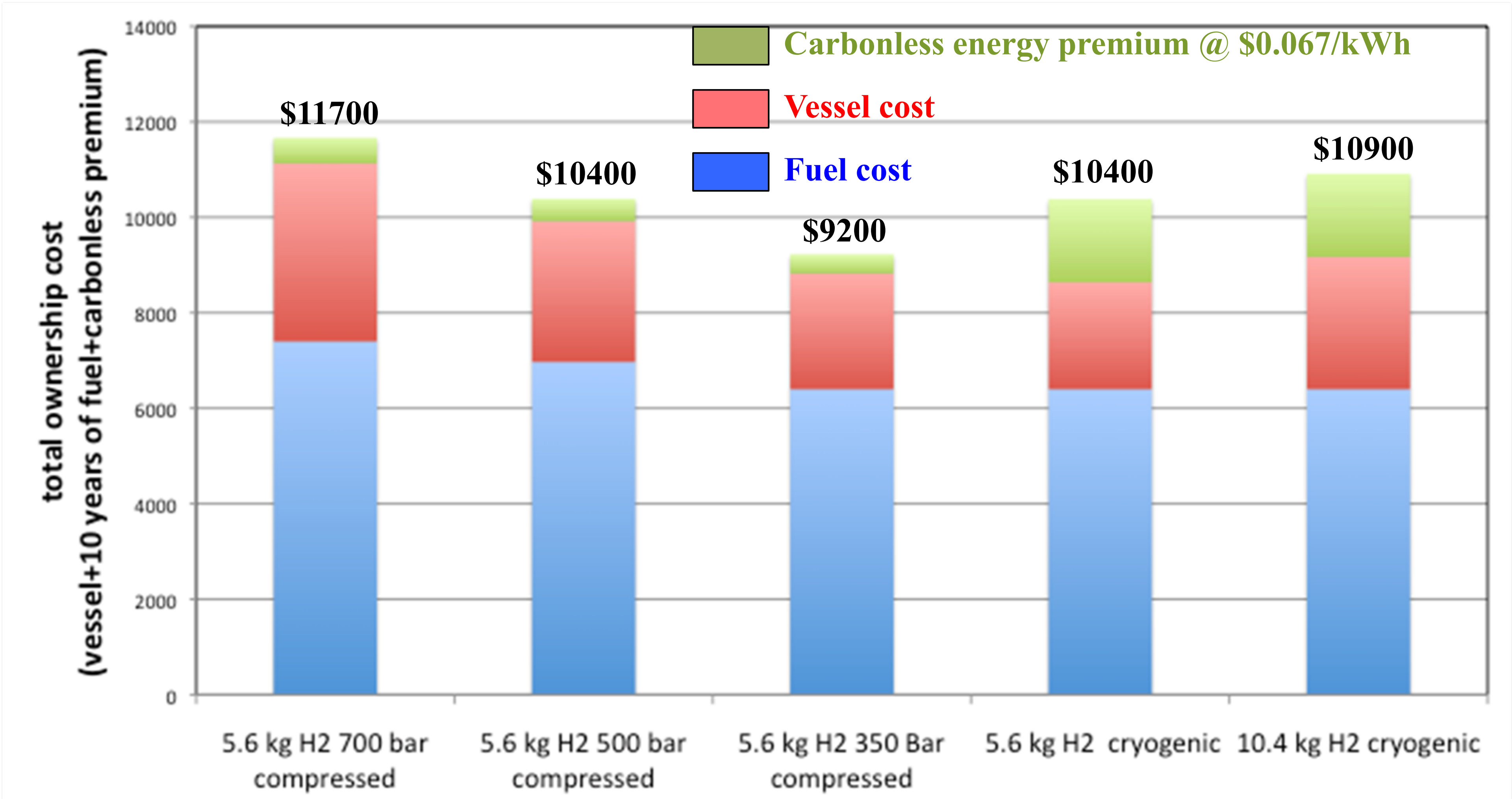
When considering CO_2 emissions from liquefaction, total energy cost savings offset carbonless energy *premium*



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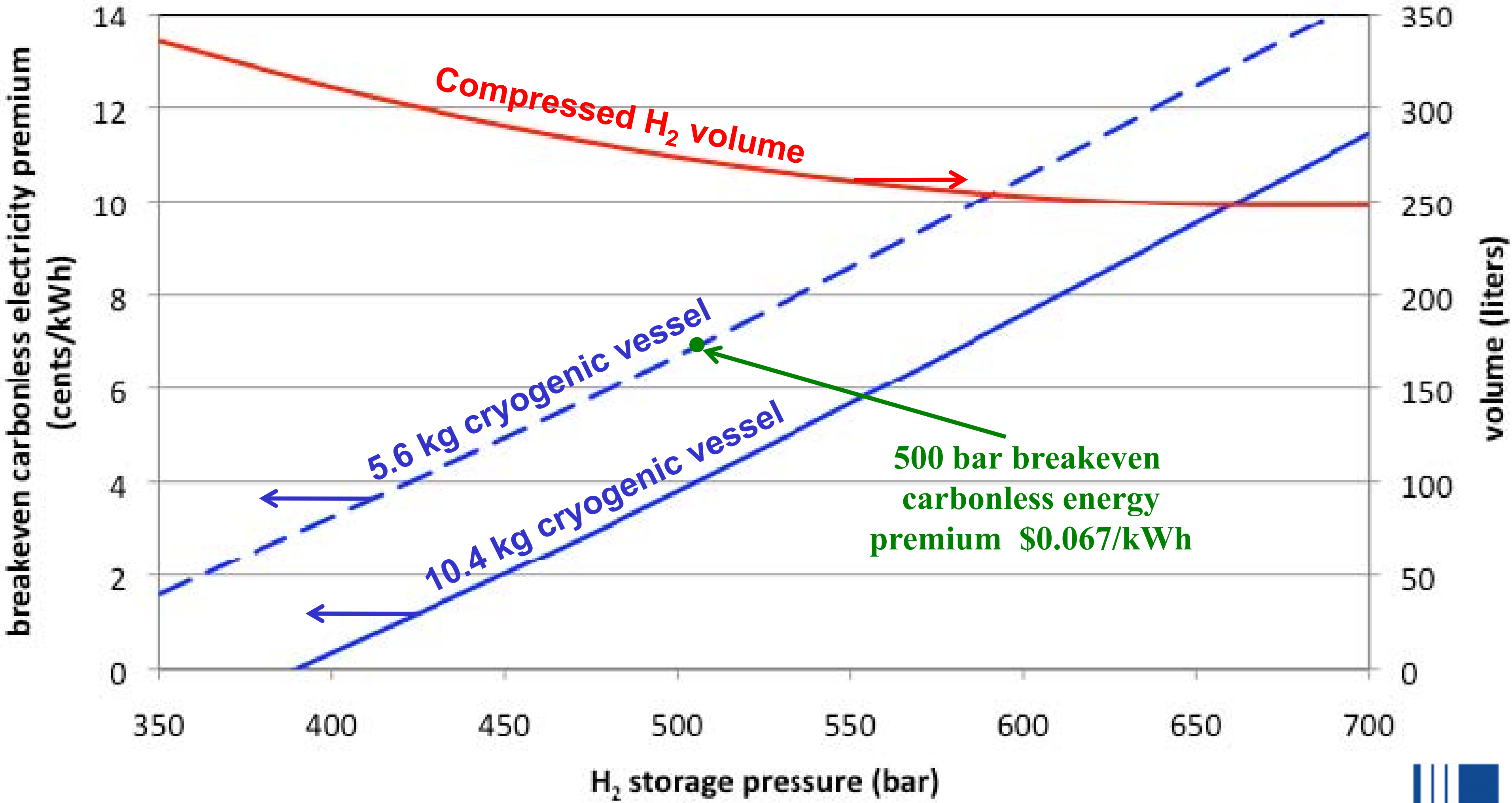
For every storage pressure there is a *reasonable breakeven* carbonless energy premium. Cryogenic pressure vessels maintain volume/range advantage



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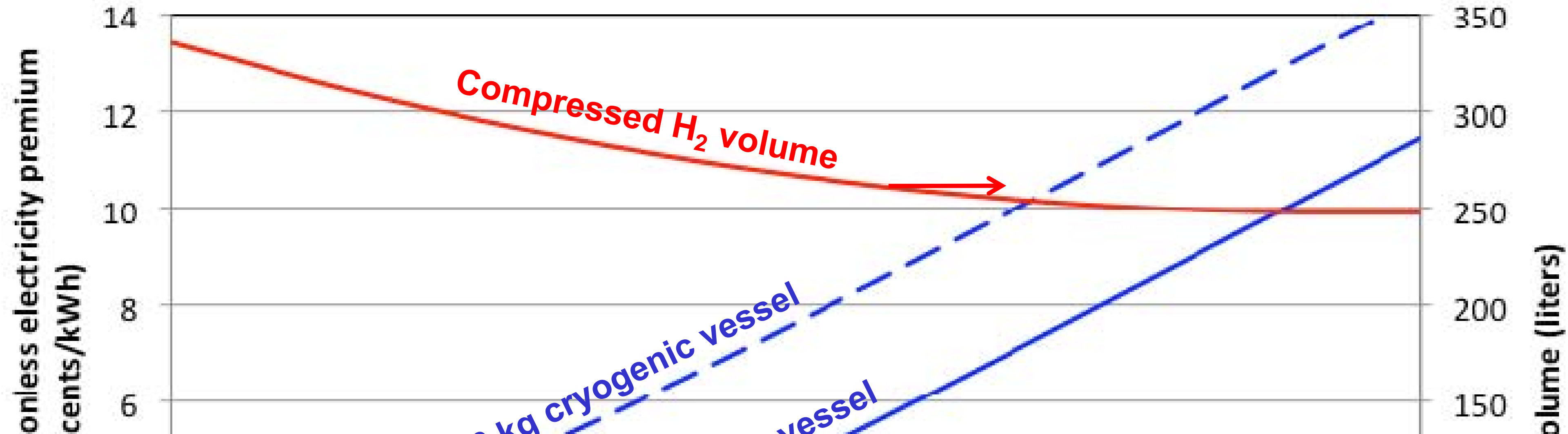

cost analysis compressed vs. cryogenic	5.6 kg H2 350 Bar compressed	5.6 kg H2 500 bar compressed	5.6 kg H2 700 bar compressed	5.6 kg H2 cryogenic	10.4 kg H2 cryogenic
system weight, kg	95	106	119	102	149
system volume, L	329	262	224	160	231
hydrogen volume, L	258	192	149	81	151
volumetric efficiency	0.78	0.73	0.67	0.51	0.65
hydrogen density, kg/m3	23.2	30.7	39.1	70.7	70.7
H2 mass, kg	6.0	5.9	5.8	5.7	10.7
Usable H2 mass, kg	5.6	5.6	5.6	5.6	10.4
Usable kWh hydrogen	186	186	186	186	346
onboard system cost, $	2420	2950	3730	2240	2770
10 year fuel cost, $	6400	6970	7400	6400	6400
total cost, $	8820	9920	11100	8640	9170
10 year storage energy, kWh	6000	7000	8000	26000	26000
breakeven carbonless electricity premium, cents/kWh	-	0.000	-	0.067	0.039

Future work: explore performance limits of vessel and cryogenic H_2 behavior: shape, scale, refueling speed, and energy efficiency

- *Pressurized LH_2* offers rapid, efficient refueling and is likely necessary to achieve ultimate DOE H_2 storage goals
- *Full-scale para-ortho conversion kinetics* experiments will enable us to determine optimal vessel design parameters as well as whether liquefaction energy and cost can be reduced
- *Generation 4 vessel* design to maximize dormancy across the full spectrum of onboard H_2 capacities
- *Multiple Volume Vessels* offer flexible blend of capacity, weight, cost, shape, and dormancy over a single state H_2 storage vessel. Multiple H_2 storage states do add complexity

Collaborations:
We established cooperative research & development (CRADA) agreement with automaker and pressure vessel manufacturers

- ***CRADA with BMW*** **started June 2008 to investigate vacuum stability, conduct cryogenic pressure cycling, and study conversion to *ortho*-H_2. BMW provides great automotive focus to our experimental and demonstration efforts.**

- ***CRADA with Structural Composites Industries (SCI)*** **uses LLNL's thermal/mechanical analysis capability and H_2 experience as well as SCI's composite cylinder design & manufacturing expertise to develop efficient and lower cost pressure vessels designed specifically for cryogenic H_2 storage.**

Summary: Cryogenic pressure vessel dormancy and volume advantages have been demonstrated. We are studying vacuum, as well as cryogenic H_2 behavior and refueling

- ***8+ day dormancy*** **(zero evaporative losses) was demonstrated. Our 10.4 kg capacity vessel retained 7.5 kg H_2 after a *month*.**
- ***Conversion of para-H_2 to ortho-H_2*** **doubled dormancy for a nearly full vessel**
- ***Composite vessel outgassing experiments*** **produced information necessary to select appropriate getters**
- ***Pressurized LH_2 refueling capability*** **will enable rapid refueling with minimum evaporative losses and potentially higher capacity fills**