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Stimulation of Optical Phonons in Deuterated Palladium

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Progress made since 2007 in the triggering of excess power by terahertz stimulation of deuterated palladium is reported. The stimulation was provided by tuning dual lasers to one of three specific beat frequencies corresponding to the known optical phonon frequencies of deuterated palladium (8, 15, 20 THz).

Results imply that optical phonons may be involved in the Fleischmann-Pons effect, giving preliminary support to Hagelstein's phonon theory. The importance of laser beam polarization is also demonstrated, confirming earlier work reported by Violante et al., and by Letts and Cravens.

1. Introduction

As is well known by now, Fleischmann, Pons and Hawkins first proposed the idea that nuclear reactions might be induced in deuterated palladium on March 23, 1989 [1]. The idea was controversial from its inception and sought scientific legitimacy from experimental results, not from established nuclear theory.

The experiments of Fleischmann and Pons showed electrode power densities and figures of merit normally associated with nuclear reactions but few indications of the required nuclear ash. Their claim for nuclear reactions induced in the solid state at room temperature rested mainly on the fact that known chemistry could not yield the observed power and energy densities. Their 1989 nuclear claim would take several years to confirm experimentally.

In 1993 Miles and his collaborators reported the presence of 4He in roughly the amount expected from D-D fusion and was commensurate with the excess power observed [2]. ^{4}He and excess power were also reported by Apicella et al. in 2004 at ICCF 11 [3] and by Violante et al. in 2005 at ICCF 12 [4]. There is now enough diverse experimental evidence to suggest that nuclear reactions really are possible in the solid state at room temperature.

1.1. Hagelstein's Phonon Theory

From the beginning, Hagelstein pondered the role of phonons in the solid state fusion of deuterium. His early work proposed a coherent phonon-photon mechanism as described in reference [5], presented at the ASME meeting December, 1989. Hagelstein proposed that the large nuclear energy release might be radiated into the lattice phonon field "one phonon at a time." By 2003, Hagelstein modified the details of his phonon theory to favor a phonon exchange process as reported in his ICCF10 conference paper, reference [6] but the role of phonon coupling remained an important part of his overall theory. In his conjecture 4, page 847 of reference [6] he states that "Anomalies in metal deuterides are stimulated by strong phonon excitation." In 2007 Hagelstein refined his phonon theory further in reference [7]; in this paper, Hagelstein proposed once again that phonons are involved in the transfer of 24 MeV quanta from the D+D → ^{4}He reaction to the lattice in the form of heat. The transfer is conjectured to be accomplished in a series of smaller quanta mediated by phonons. Hagelstein suggests that the optical phonon modes are the most likely candidates – especially the modes with low group velocity typically located at the edge of an optical phonon mode. In palladium deuteride, the band edges occur near 8 and 15-16 THz [14 & 15].

2. Experiment Meets Theory

The work discussed in this paper began in March 2007 as a series of experiments conducted by Letts and Cravens in collaboration with Hagelstein. Our goal was to see if an experimental connection could be made with the phonon aspects of Hagelstein's theory. Hagelstein's theory is complex but our experimental approach was simple – we used dual lasers in beat mode to create beat frequencies near the three known optical phonon modes for palladium deuteride. We had data for palladium hydride but guessed that the deuteride phonon modes would be similar. Figure 1 shown below was our guide for all of the initial experiments and is still in use as more data is accumulated in continuing experiments. Before experiments were run, Hagelstein predicted that the edges of the optical phonon band would be the best candidates for stimulation to produce excess power. This region is where low group-velocity compressional phonon modes exist. This is consistent with our observations near 8 and 15 THz; but the response near 20 THz requires an alternate explanation. Perhaps the simplest conjecture for this higher frequency response is proton contamination, which might be expected to produce a zero-group velocity band edge near 20 THz. Such a conjecture may be confirmed in future experiments in which the proton contamination is better controlled, and from phonon band calculations done for palladium deuteride contaminated with hydrogen.

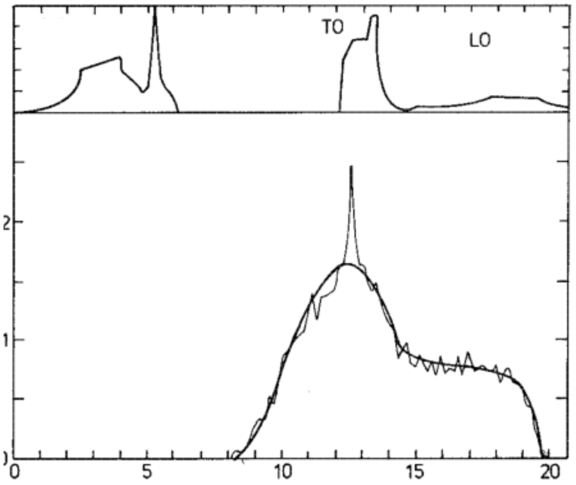


Figure 1. The PdH density of states from Ref. [8], where the horizontal axis is frequency in THz.

2.1. Instrumentation and Calorimetry

This work covers 19 tests from 3 cells; two time periods are involved – March 2007 to May 2007 and then April 2008 to the present. The goal of this work is the creation of a beat frequency versus excess power graph to determine if stimulation of the three optical phonon modes of palladium deuteride leads to the observation of excess power. If phonon modes are involved with the production of anomalous heat, then such a graph might show elevated excess power production clustered about the three phonon mode frequencies.

All experiments were conducted in Austin, Texas. The experimental setup is shown below in figure 2. Isoperibolic calorimetry was used on all tests. Lab temperature is fairly stable at 26 ±1°C. The temperature enclosure (the black box shown in figure 2) is controlled by Labview and held at 25 ±0.03°C. Cell power is provided by a digital HP E3632A power supply. Cell power is held constant by Labview to within 10 mW. Cell power is typically 7 - 10 watts with current up to 1.25 to 1.5 amps. Current and cell power are held constant. See figures 1a-1f below for experimental details.

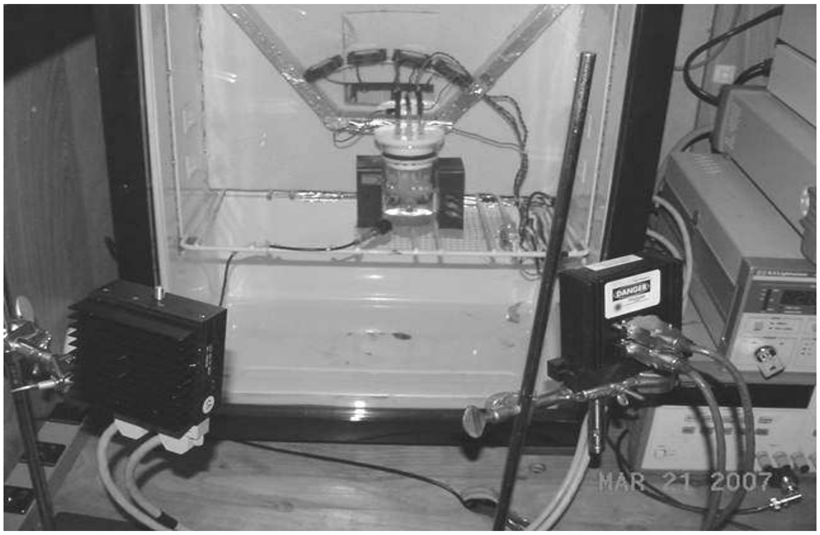
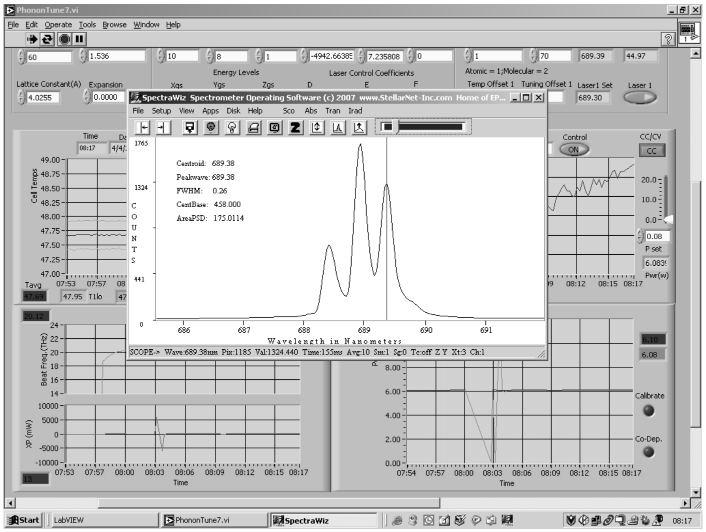


Figure 1a. Cell in temperature controlled enclosure stimulated by dual lasers. Note optical spectrum analyzer detector in front of cell to check laser calibration during the experiment.



60 1.536 10 8 1 -4942.66385 7.235808 0 1 70 689.39 44.97

Lattice Constant(A) 4.0255 Expansion 0.0000 Laser1 Set 689.30

Time 08:17

Centroid: 689.38
Peakwave: 689.38
FWHM: 0.26
CentBase: 458.000
AreaPSD: 175.0114

Tavg 47.69 47.95 T1lo

0.08 P set 6.083 Pwr(w)

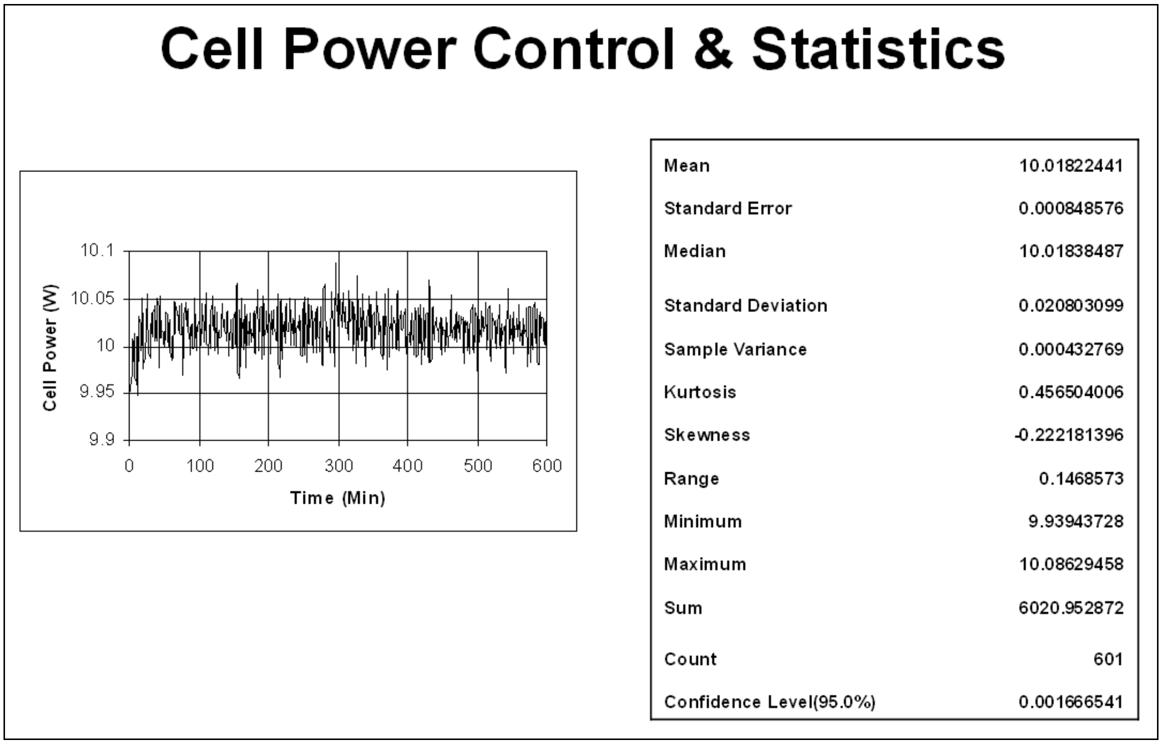
20.12

6.10
6.08

13

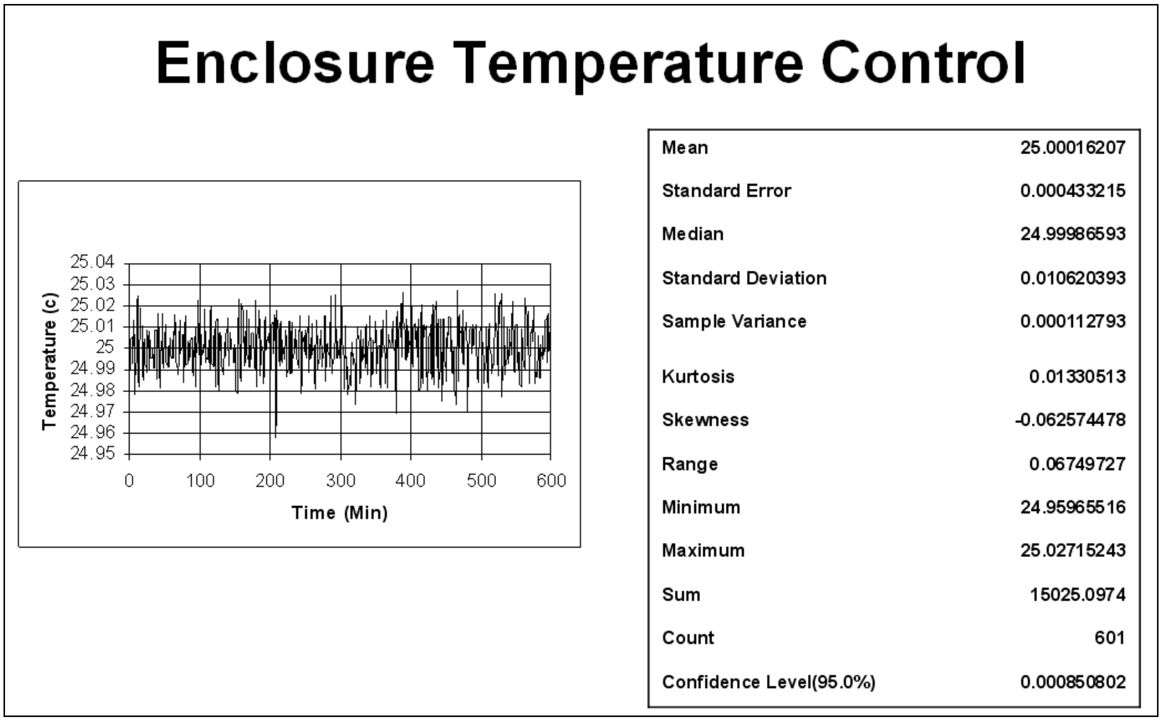
SCOPE-> Wave:689.38nm Pix:1185 Val:1324.440 Time:155ms Avg:10 Sm:1 Sg:0 Tc:off Z Y Xt:3 Ch:1

Figure 1b. Measurement of the laser spectrum as the experiment proceeds. Laser wavelength measurements have a precision of about 0.25 nm.


Cell Power Control & Statistics

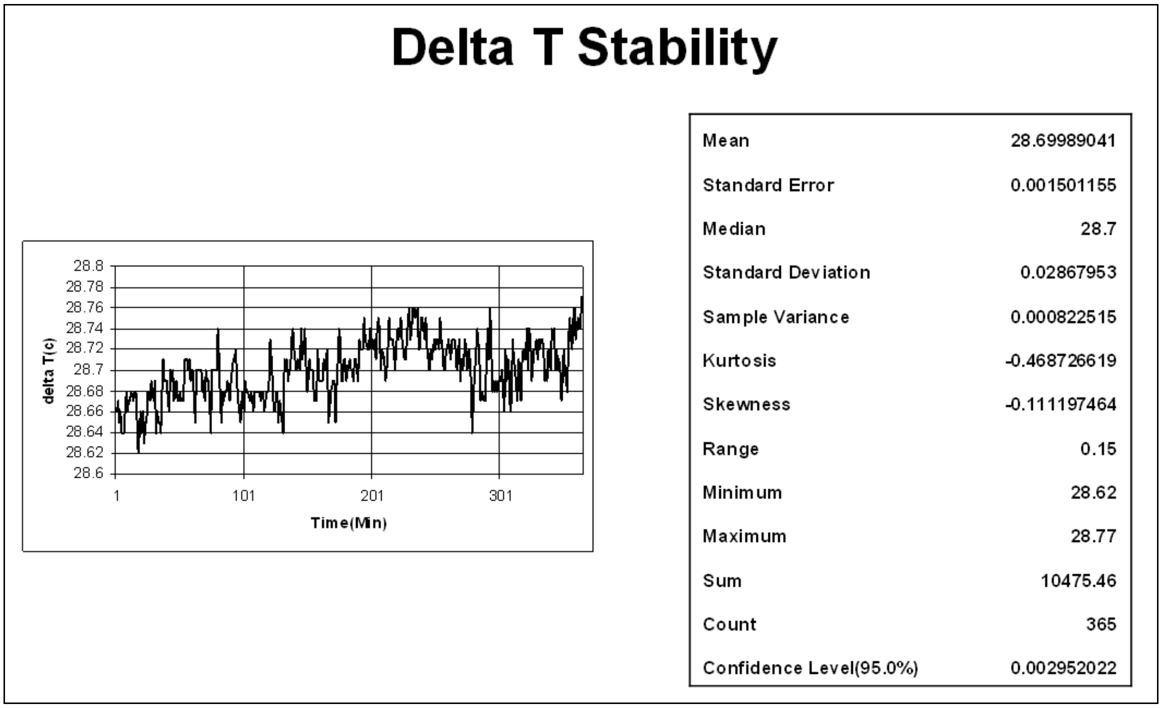
Mean	10.01822441
Standard Error	0.000848576
Median	10.01838487
Standard Deviation	0.020803099
Sample Variance	0.000432769
Kurtosis	0.456504006
Skewness	-0.222181396
Range	0.1468573
Minimum	9.93943728
Maximum	10.08629458
Sum	6020.952872
Count	601
Confidence Level(95.0%)	0.001666541

Figure 1c. Cell power is held constant with a variation of ±0.02 W. Current is held constant and voltage is varied to maintain the power set point.


Enclosure Temperature Control

Mean	25.00016207
Standard Error	0.000433215
Median	24.99986593
Standard Deviation	0.010620393
Sample Variance	0.000112793
Kurtosis	0.01330513
Skewness	-0.062574478
Range	0.06749727
Minimum	24.95965516
Maximum	25.02715243
Sum	15025.0974
Count	601
Confidence Level(95.0%)	0.000850802

Figure 1d. The cell’s ambient temperature variation is about ±0.02°C.



Mean	28.69989041
Standard Error	0.001501155
Median	28.7
Standard Deviation	0.02867953
Sample Variance	0.000822515
Kurtosis	-0.468726619
Skewness	-0.111197464
Range	0.15
Minimum	28.62
Maximum	28.77
Sum	10475.46
Count	365
Confidence Level(95.0%)	0.002952022

Figure 1e. Tight cell power and ambient temperature control results in a stable temperature difference between the cell and its environment

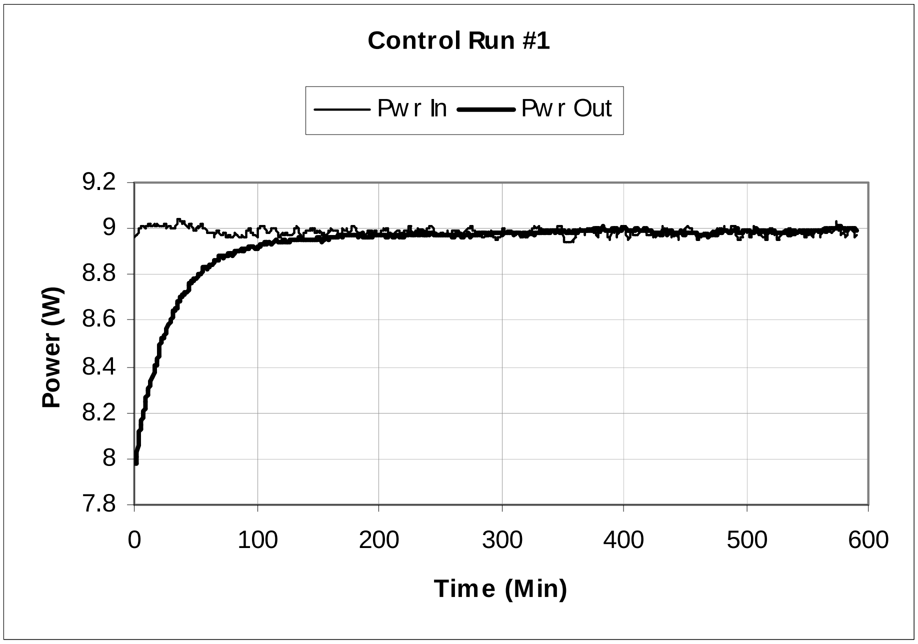


Figure 1f. The isoperibolic calorimeter demonstrates good long-term stability when the cell is not producing excess power. Most experiments run for 10 hours or less, so the calorimeter is stable over the time scale of the experiments.

Figure 2. A typical equipment setup for this work; data is collected by a Labview-controlled Agilent 34970A and all data is displayed and stored on a PC.

Lasers are controlled by an ILX 3722B and an Optima laser controller. The laser controllers typically keep the lasers within 0.25 nm of tuning set point. Data is displayed on a PC and all data is recorded to a spreadsheet. The lasers are kept in tune by checking with an optical spectrometer.

2.2. Experimental

A typical cell is shown in figure 3 below. Two thermistors record cell temperature. One probe is placed slightly above the cathode and one probe is placed slightly below the cathode. The average of the two probes is compared to enclosure temperature in computing excess power. Cell is not mechanically stirred. 100 grams of 0.5 M LIOD is used as electrolyte. Platinum coated alumina pellets are used as recombiners, providing a closed electrochemical cell.

Figure 3. Typical cell configuration. Magnets as shown provide a 700 gauss field across the cathode face. In the foreground is the optical spectrometer detector used in tuning the lasers within 0.25 nm. Air is vigorously stirred within the temperature-controlled enclosure.

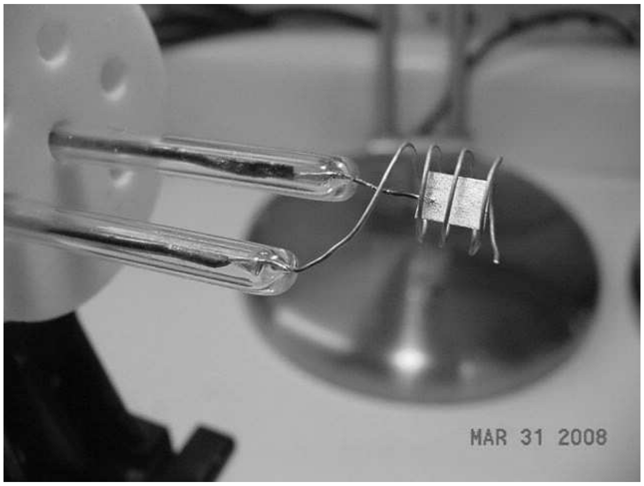


Figure 4. A typical cathode and anode assembly; cathode is typically a Pd plate 8 mm × 10 mm × 0.2 mm with a Pt anode coil. Pt wires are sealed inside soft glass 5 mm tubes. Cell lid is Teflon.

Table 1. 48 data points from 19 experiments taken from 3 cells tested in 2007 and 2008. Cells in table 1 were tested at ~ 50-60°C. Two high temperature tests were made and are discussed in 2.2.5 below.

No.	Experiment	Date	Freq. (THz)	XP(mW)
1	662n	3/25/2007	3.12	0
2	662n	3/25/2007	3.81	0
3	662n	3/25/2007	4.50	0
4	662n	3/25/2007	5.18	0
5	662n	3/25/2007	5.86	0
6	662n	3/25/2007	6.33	15
7	662n	3/25/2007	6.80	25
8	662i	3/21/2007	8.00	80
9	662g	3/20/2007	8.30	125
10	662k	3/22/2007	8.40	130
11	662i(2)	3/21/2007	8.48	80
12	662i(2)	3/21/2007	8.61	90
13	662i(2)	3/21/2007	9.06	60
14	662i(2)	3/21/2007	9.65	40
15	662i(2)	3/21/2007	10.95	30
16	662i(2)	3/21/2007	12.31	40
17	662i	3/21/2007	13.62	0
18	662i(2)	3/21/2007	13.68	20
19	662i	3/21/2007	14.23	70
20	662i(2)	3/21/2007	14.36	20
21	662f1	4/13/2007	14.50	140
22	662j1	4/15/2007	14.70	70
23	662w	3/31/2007	14.70	70
24	662y	4/2/2007	14.70	120
25	662a1	4/4/2007	14.70	80
26	662j1	4/15/2007	14.70	150
27	662s1	4/23/2007	14.70	66
28	662i(2)	3/21/2007	14.88	80
29	662f1	4/13/2007	15.20	160
30	662a1	4/4/2007	15.30	200
31	662f1	4/13/2007	15.82	140
32	662b2	5/5/2007	15.90	50
33	662w	3/31/2007	16.02	40
34	662f1	4/13/2007	16.45	80
35	662f1	4/13/2007	17.09	0
36	662i2	3/21/2007	18.23	0
37	662c2	5/5/2007	18.40	100
38	662w	3/31/2007	18.56	70
39	662t1	4/25/2007	18.80	50
40	662i2	3/21/2007	18.87	0
41	670a	6/6/2008	19.28	100
42	662o	3/25/2007	19.40	200
43	662i2	3/21/2007	19.50	30
44	669u	4/30/2008	20.00	250
45	662x1	4/29/2007	20.50	250
46	662o2	5/17/2007	20.70	300
47	662i2	3/21/2007	21.40	130
48	669a1	5/8/2008	22.11	0

The work reported in this paper began on March 20, 2007 with experiment 662G (see table 1 above); the cathode stock was palladium made from a billet provided by Scott Little of Austin, Texas. The palladium was taken from a large palladium target from Texas Nuclear. The target was unused and of unknown purity but thought to be at least 0.995. The cathode was prepared following a 17 step protocol described previously [9]. The cathode was cold-rolled using a 90 degree rotation with each pass. This is thought to minimize stress build-up in any one direction. The cathode was 5 × 12 × 0.2 mm and was loaded at 75 mA/cm^2 for 120 hours. Electrolyte was 100 g of 0.5M LIOD. Excess power was not produced until gold was plated onto the cathode, magnets were in place around cell at ~ 700 gauss and dual lasers were applied with a beat frequency of 8.26 THz. Cell resistance also declined sharply as the Fleischmann-Pons heat effect appeared. Cell power dipped slightly just before cell temperature increased, as was reported in the Guruswamy experiment [10] and the SRI experiment [11] in 1990. See figure 5 below.

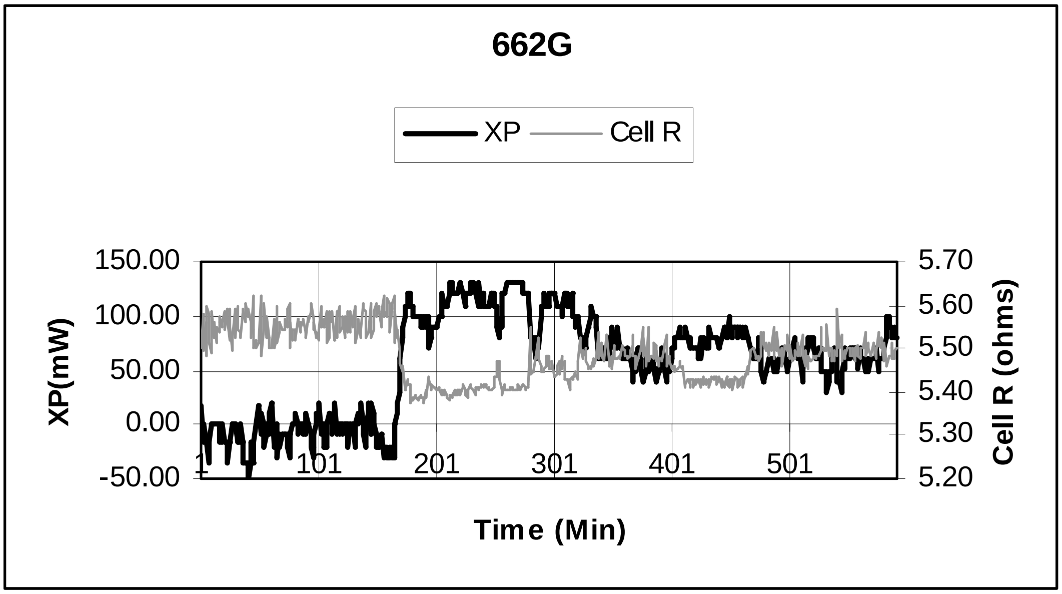


Figure 5. The apparent small endothermic response that precedes the exothermic response has been observed in other experiments since 1990. Cell resistance also declined quickly as the cell triggered.

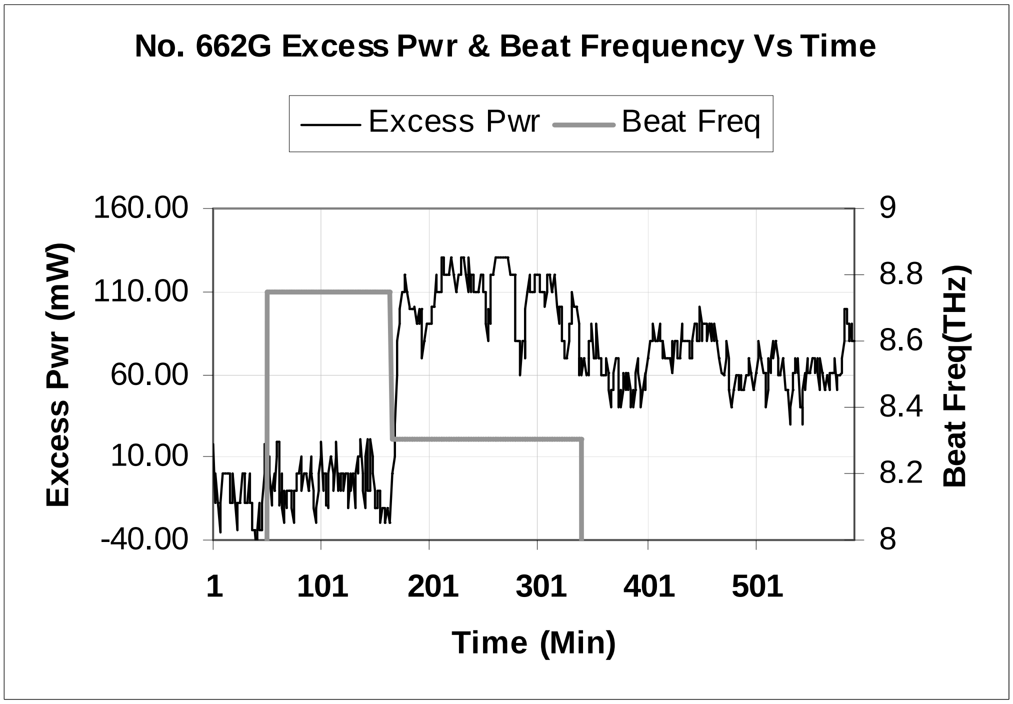


Figure 6. Plot shows the lack of a thermal response at 8.75 THz followed by an immediate thermal response at 8.26 THz. This highly selective frequency sensitivity was observed throughout this experimental campaign.

The dual lasers were tuned to 664.59 nm and 677.74 nm for a beat frequency of 8.75 THz. and held for 114 minutes. There was no thermal response. Lasers were then tuned to 664.61 nm and 677.01 nm for a beat frequency of 8.26 nm. Cell temperature increased immediately and cell resistance declined. The cell's thermal response to beat frequency is shown in figure 6 above.

2.2.1. The Null Experiment

In the first five days of this campaign, excess power continued to be observed around 8 THz. By March 25, 2007 we began to wonder if we could produce a null result by scanning the beat frequency over the range 3 to 7 THz, stopping just short of the 8 THz optical phonon frequency for $PdD_{0.9}$. The lasers were tuned to 3.12 THz and scanned to 6.8 THz in steps of 0.7 THz with a hold time of one hour at each step. Hagelstein's phonon theory suggested that only optical phonons are involved in producing the heat producing Fleischmann-Pons effect – so it was important to *not* see an exothermic response when the beat frequency was below 8 THz. This was observed in experiment 662N, shown in figure 7 below.

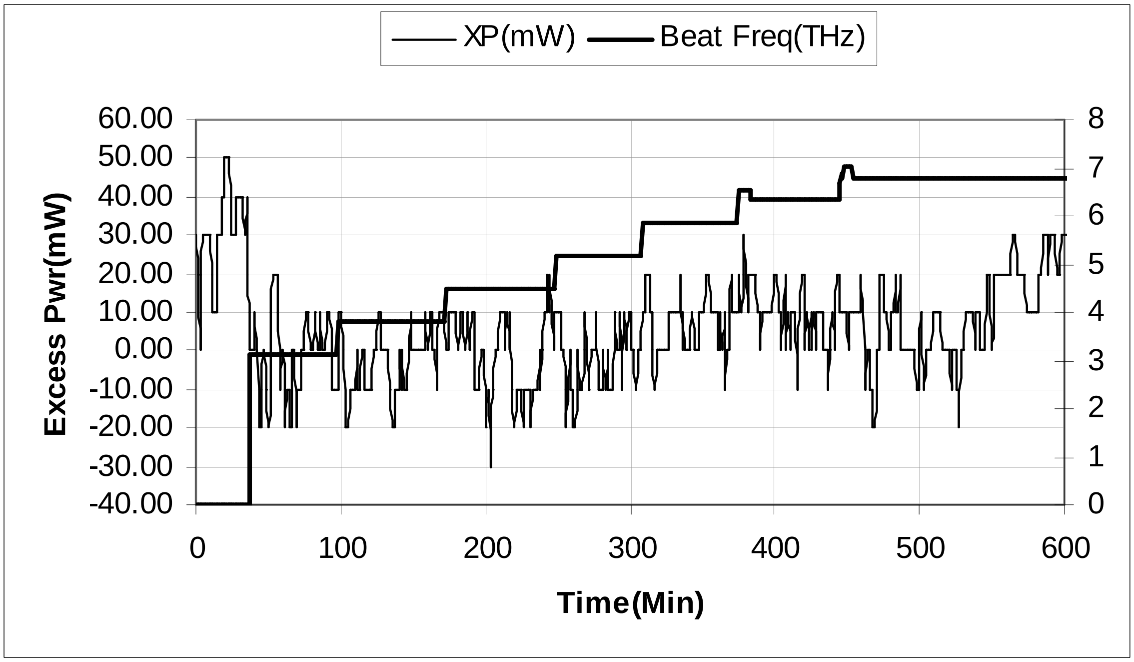


Figure 7. This shows that no excess power is produced when the beat frequency was scanned from 3 – 7 THz. This graph also shows that the calorimeter is stable over 10 hours with a power variation ~ 10 mW. Laser power of ~ 40 mW is not seen by the calorimeter when the beat frequency is off resonance.

2.2.2. Other Phonon Modes

By March 25, 2007 it appeared that the lowest $PdD_{0.9}$ phonon mode had been fairly well explored around 8 THz. We then wondered if either of the two other known palladium deuteride phonon modes would be thermally responsive. Experiment 662O was started with lasers tuned to 632.8 nm and 659.83 nm to produce a beat frequency of 19.4 THz. Cell temperature began to increase within 20 minutes of turning on the dual lasers. Cell temperature increased 0.8 degrees over 200 minutes to produce an excess power signal of 200 mW. The lasers were left on for about 10 hours and excess power continued to be observed. After about 10 hours the lasers were turned off and excess power declined to ~ 0 W. See figure 8 below.

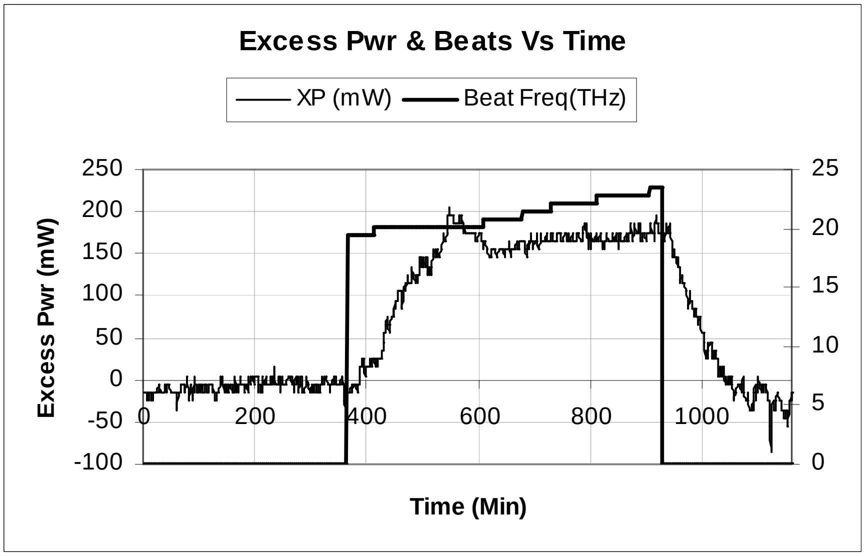


Figure 8. This graph demonstrates that the highest frequency palladium deuteride phonon mode at ~ 20 THz is also response to beat frequency stimulation.

Figure 8 above shows that a beat frequency stimulation of 19.40 THz triggers an exothermic reaction in palladium deuteride. This provides a comforting connection with some established physics in that the literature [8] shows the upper edge of the highest frequency optical phonon mode in PdH to be near 20 THz. See figure 1 above.

The middle optical phonon frequency near 15 THz was tested April 2 – April 23, 2007 in a series of nine experiments under various conditions of cell temperature and current densities. All nine experiments produced excess power, ranging from 66 mW to 200 mW. Figure 9 below shows the thermal response of the cell to stimulation near 15 THz.

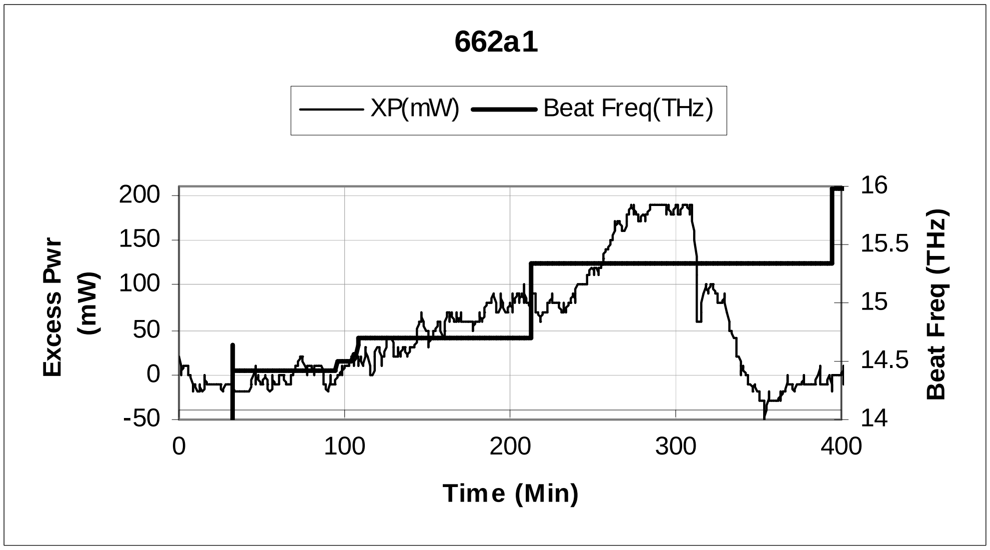


Figure 9. The cell responds thermally to the middle optical phonon frequency near 15 THz. Excess power increases as the beat frequency approaches 15 THz.

As figure 9 above shows, the excess power signal strengthened as the beat frequency approached 15 THz. However, the excess power signal saturated after 5 hours and returned to zero, even with the dual lasers on.

2.2.3. Laser Polarization Angle

In 2003 Letts and Cravens reported that single laser beam polarization seemed to be an important factor in stimulating deuterated palladium cathodes [9]. When the laser beam polarization was at a 90 degree angle with respect to external magnetic field lines, excess power production was maximized. When the polarization angle was at a zero angle with respect to the external magnetic field lines, excess power production stopped.

In 2004, Apicella and his collaborators advanced our understanding of the importance of laser polarization in reference [3]. In this paper, P polarization was shown to be enabling for the production of excess power, while the S polarization was not. The P polarization effect as reported by Apicella was with respect to the cathode surface only, not an external magnet field as reported by Letts and Cravens [9]. Apicella and his collaborators proposed that the P polarization was effective in triggering excess power due to its ability to create charge separation on the cathode surface. P polarization means that some or all components of the electric field of the laser beam are perpendicular to the cathode plane.

2.2.4. Optical Phonon Mode Bandwidth

After a few scans of the beat frequencies across the three optical phonon mode edges, it became apparent there was a very narrow band that would trigger excess power. It quickly became a goal to delineate the bandwidth of the sensitive regions. One example of the left edge of the 20 THz sensitive region is seen in experiment 662t1 shown in figure 10 below.

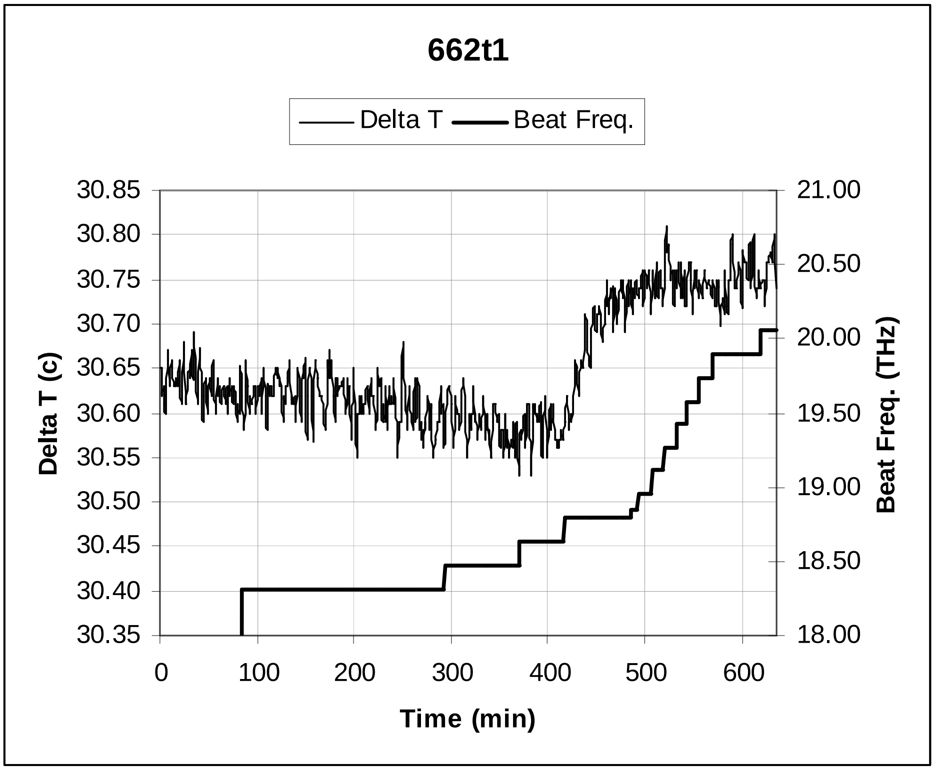


Figure 10. The possible left edge of the optical phonon mode that triggers an exothermic reaction in palladium deuteride.

The strategy was to begin scanning the beat frequency below the suspected left edge of the 20 THz optical phonon mode. In figure 10, the scan started at 18.31 THz and advanced in steps of 0.16 THz. When the scan reached 18.79 THz, an exothermic cathode response was observed as cell temperature increased sharply. The edges of the optical phonon bands may vary with loading, cell temperature or other factors not yet known. This particular experiment showed the left edge to be at 18.79 THz. Two experiments tested 21.40 THz and 21.70 THz and both tests triggered excess power, suggesting that the band edge is above 22 THz. Figure 10a below shows that the right edge of the 20 THz mode appears to be near 22.11 THz.

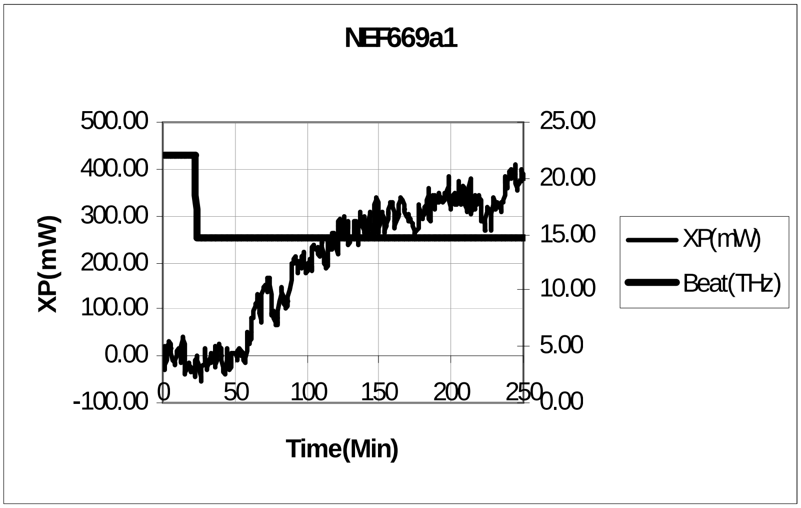


Figure 10a. A beat frequency of 22.11 does not trigger excess power, suggesting that the right edge of the highest frequency optical phonon mode is slightly to the right of 22 THz.

Using a similar strategy for the other two optical phonon modes lead to a series of graphs that identified the edges of all three modes for deuterated palladium. Figure 10b below shows a composite graph of all three modes. The mode near 8 THz is centered at 8.3 THz and has a mode width from 7 - 9 THz at its half maximum. The mode near 15 THz is centered at 15.3 THz and has a mode width from 14 - 16 THz. The mode near 20 THz is centered at 20.5 THz and has a mode width from 18 – 21 THz.

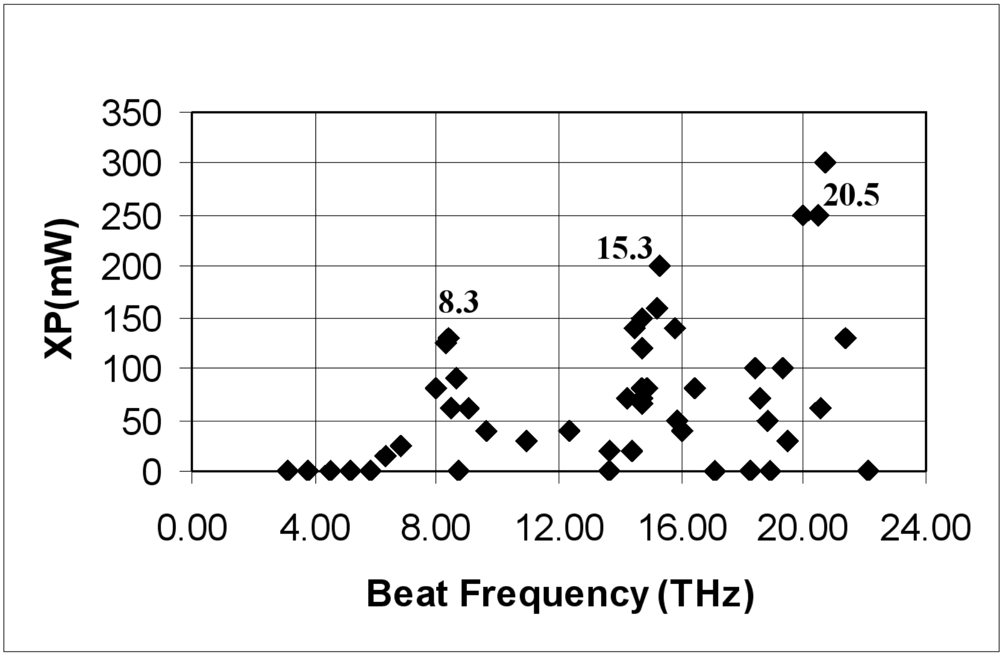


Figure 10b. All three frequencies that trigger excess power in a Fleischmann-Pons cell.

Data from the left side of each optical phonon mode was put into Excel and an excess power versus frequency correlation was performed. The results are shown in figure 10c.

Correlation of Excess Power and Frequency

Frequency Range		Correlation
3-8	THz	0.85
13-15	THz	0.82
17-21	THz	0.83

Note: to get meaningful statistics, only data from the left edge of the mode to its peak was correlated.

Figure 10c. There is a high degree of correlation between excess power and beat frequency

Various researchers have reported that excess power production is often larger when cell operating temperature is elevated. Hagelstein proposed that this is due to the energy required for the formation of molecular D2 near Pd vacancies. Our results are qualitatively consistent with this, as increasing cell operating temperature from 62°C to 73°C increased excess power production from 225 mW to 900 mW, a 400% increase. This increase of excess power with temperature is a larger effect than has been reported by Storms (the activation energy in Storms experiment was meV, while the activation energy that would correspond to the present result is 1.5 eV). Results from experiments 669u and 669v are shown in figures 11 and 12 below.

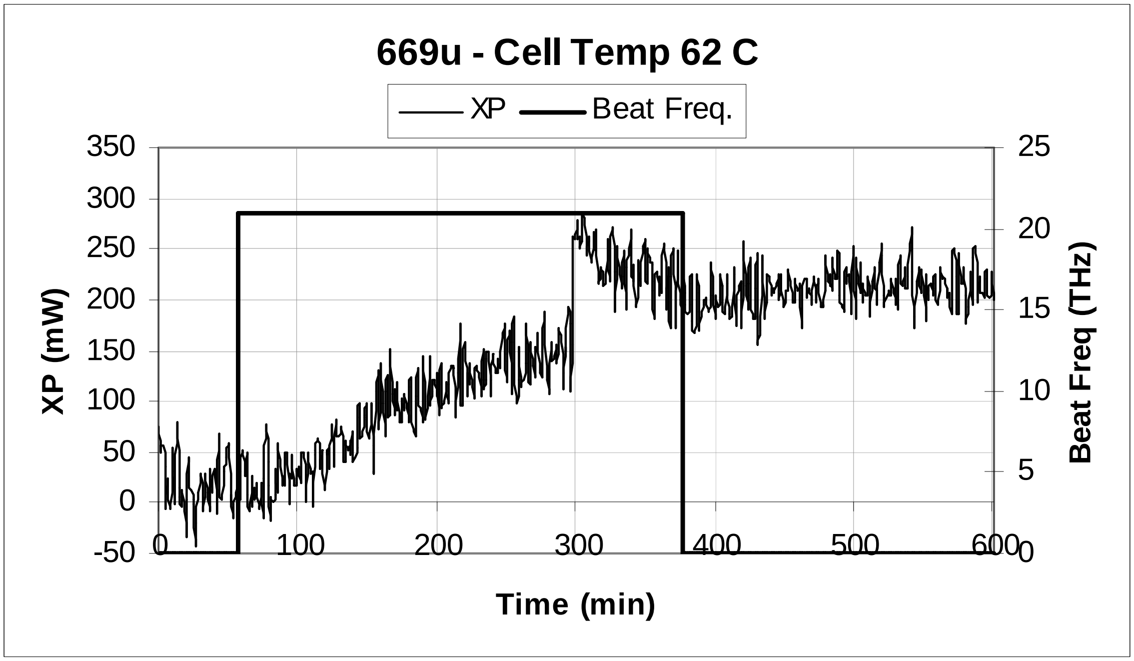


Figure 11. A 21 THz beat frequency triggers excess power of 225 mW at a cell temperature of 62°C.

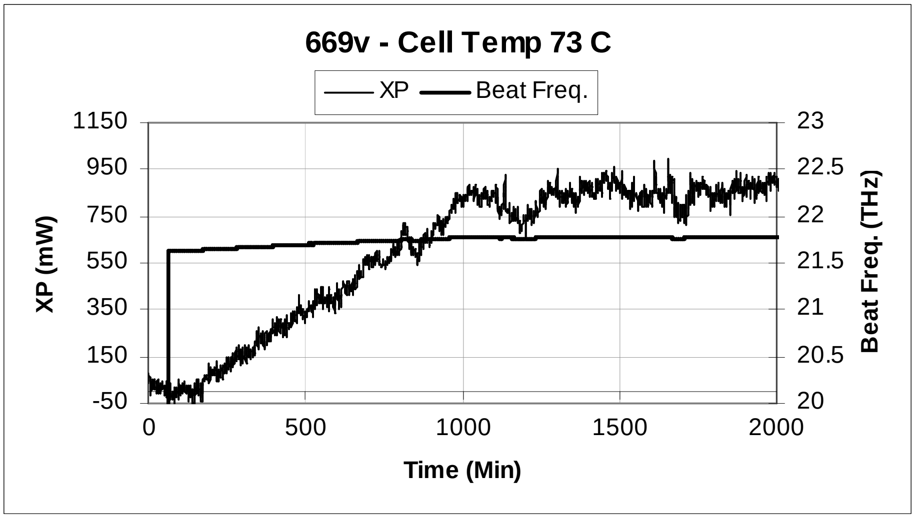


Figure 12. The cell triggers at about the same beat frequency as 669u but the thermal response at 73°C is 4 times greater than at 62°C.

3. Improved Reproducibility with Dual Laser Stimulation

The use of dual lasers to produce beat frequency stimulation near 8, 15 or 20 THz has resulted in high reproducibility (>90%); we don't know if this is a permanent benefit but for the last year cathodes made from several palladium sources have produced excess power when stimulated at one of the mode frequencies reported in this paper. An example of this reproducibility is shown in figure 13 below.

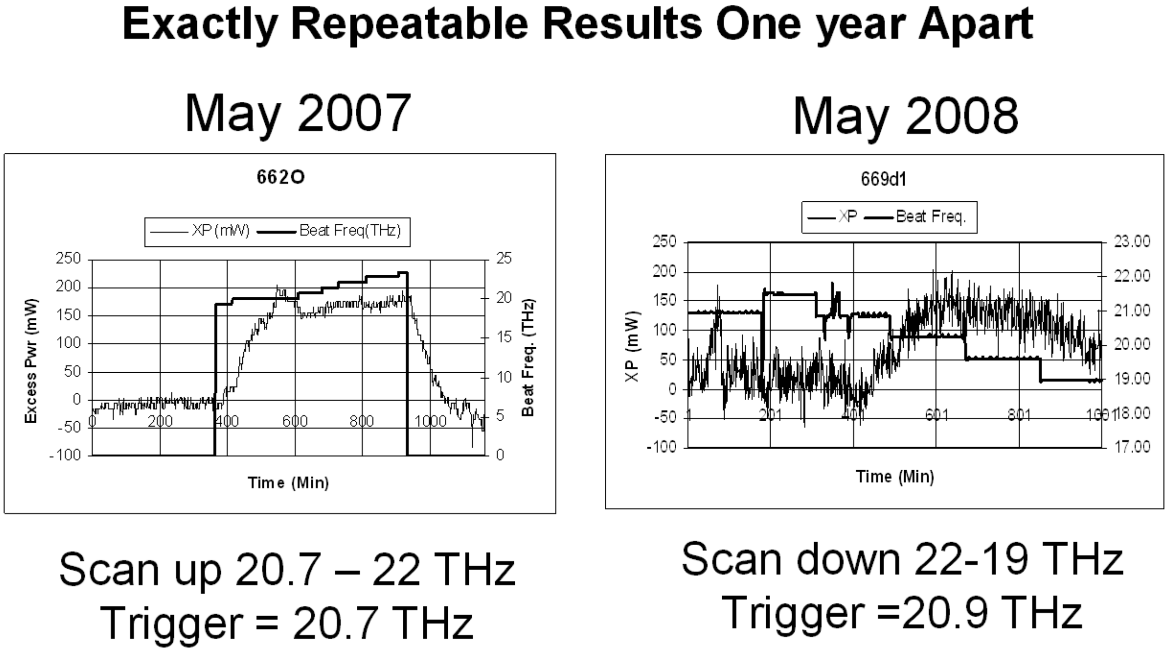


Figure 13 Two experiments were conducted one year apart. When stimulated with beat frequencies near the 20 THz optical phonon mode for palladium deuteride, both cells responded nearly identically. Excess power produced in both cells was ~ 175 mW.

5. Discussion

Can these experiments connect with any known physics? On the face of it, the observation of a thermal response at the specific beat frequencies 8, 15 and 20 THz [shown in Figure 10(b)] combined with the observed dependence on polarization implicates compressional optical phonon modes in PdD as participating in the physical process responsible for excess heat production in the Fleischmann-Pons excess heat effect. The lower two specific beat frequencies observed (8 and 15 THz) are consistent with the interpretation of optical phonon modes with low group velocity in PdD. The higher frequency response (20 THz) represents a conundrum for a PdD explanation, since it lies above the LO band edge. One possible resolution of this is to assume that H is present as a significant impurity, and that 20 THz is due to an LO band edge associated with hydrogen in mixed PdDxHy. Whether this is the case or not can be determined in future experiments where the hydrogen content of the heavy water is better controlled. Additionally, our results motivate theoretical studies with mixed hydrogen and deuterium loading to verify under what conditions, if any, a splitting of the LO band near the band edge occurs.

Although gold does not form a hydride, it should be noted that the gold overlayer has not been ruled out as the site for the exothermic reactions observed during this campaign. It has been conjectured that the reaction site is in the palladium deuteride but this has not been proven. This will be addressed in experiments to be conducted in 2008-2009. The D/Pd ratio was not measured during these experiments. The cathode was loaded for 120 hours at a low current density and then loaded for an additional 24 hours at 1 amp. This loading protocol usually produces a cathode that is responsive to dual laser stimulation.

While the present work is suggestive, it is not complete – work is underway now to collect more data points between 3 and 25 THz in the coming year. It is hoped that this work will give theorists some useful data and motivate our experimentalist colleagues to collaborate more closely with theorists to advance our understanding of Condensed Matter Nuclear Science.

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