Eu:YSO Spectroscopy Analysis

ZJS

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Contents

1 Absorption Spectroscopy

Absorption spectroscopy hasn't worked so far. For one, it's been difficult to produce green exactly where we want it. We've tried a few different methods, mostly employing some combination of femtosecond laser, photonic crystal fiber (PCF), and nonlinear doubling crystal. See fig. 1.

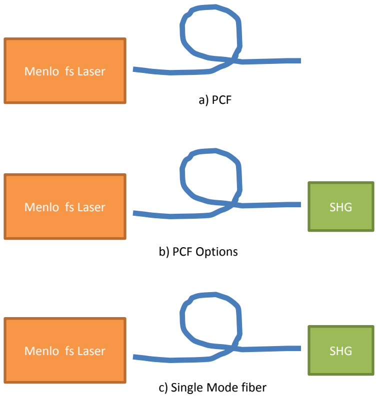

Figure 1: Green Light Generation Schemes

Photonic crystal fiber is very interesting. Instead of a core and cladding with slightly different refractive indicies as in a 'normal' optical fiber, PCF more resembles a glass rod suspended in air. This is accomplished by constructing the photonic crystal fiber from a stack of glass capillary tubes with a solid rod in the middle. When the PCF is drawn, the core is surrounded by a honeycomb of holes, see fig. 2. This construction gives a huge effective index step between core and 'cladding' region and as result gives the fiber interesting properties. The property that we are interested in is that the fiber is very highly nonlinear. Shooting a temporally very short optical pulse through this highly nonlinear media, with very tightly confined mode (it has a small core of a few μm) results in very significant spectral broadening.

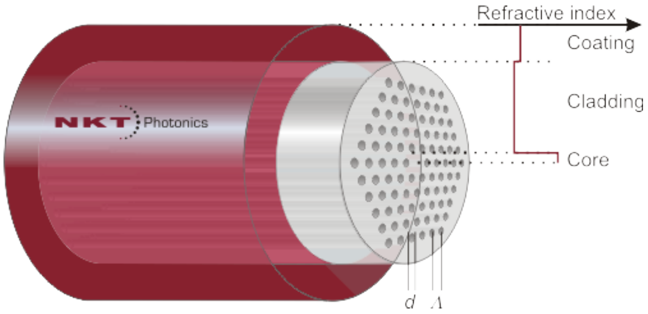

Figure 2: Cartoon of PCF from NKT

Originally we thought that we would be able to broaden our fs laser (Menlo Orange, with compressor) sufficiently to reach the green, i.e. fig. 1 a). However, this was shown to not be the case. Although we were able to achieve hundreds of nm of broadening, it was not sufficient to reach such a short wavelength. See fig. 4. The max bandwidth we were able to achieve was from about 900 to 1200 nm. This is shown in the 'direct-coupled' case in fig. 4. This corresponded to about 100mW of input power. We were able to achieve good coupling, ~40%, by using a very nice flexure fiber launch stage and very short aspheric coupling lens. Many thanks to Dave Campos over in Med Physics for helping cleave the PCF with his fiber cleaver. Interestingly, you can even see some of the hexagonal structure of the fiber when looking at the output when it's well coupled.

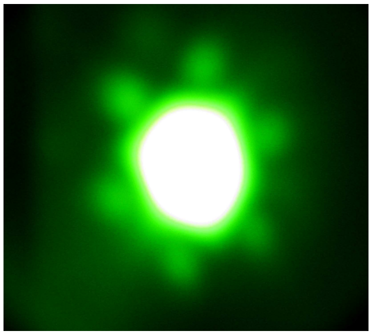

Figure 3: PCF output mode pattern showing hexagonal structure

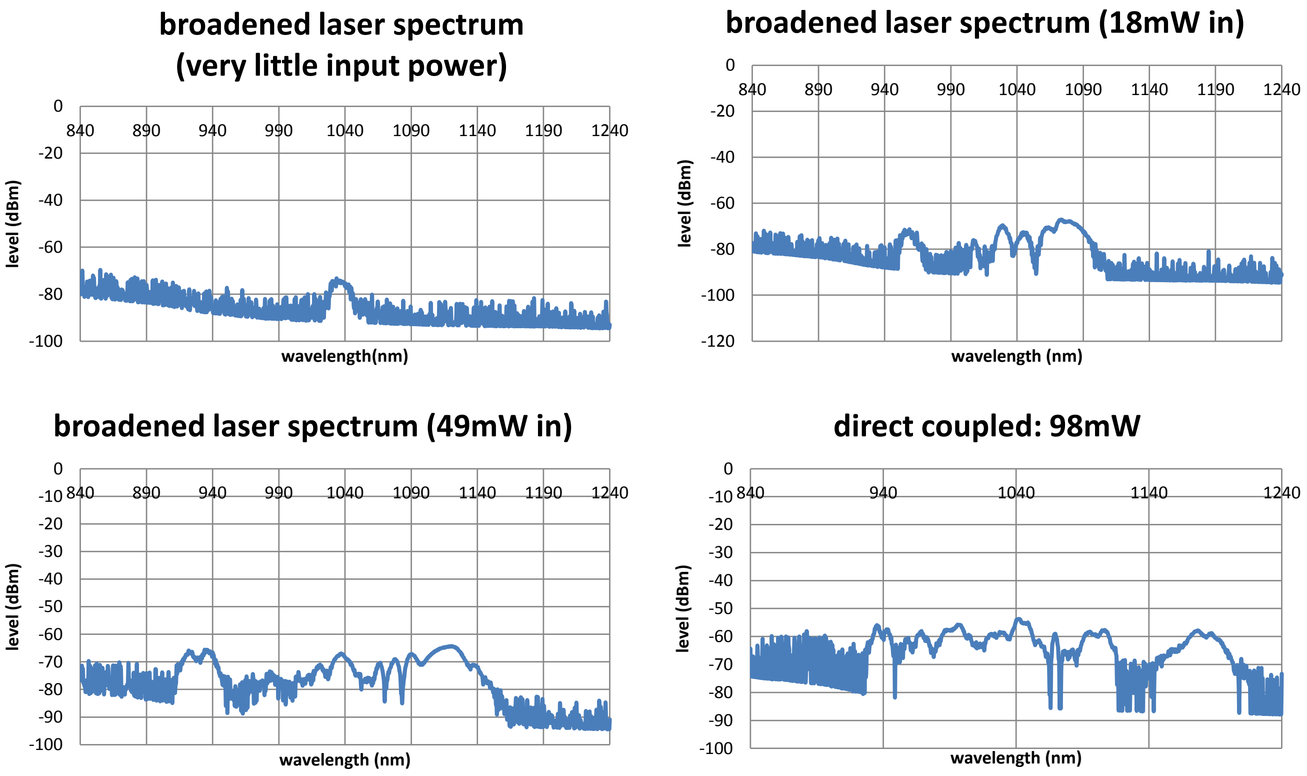

Figure 4: Observed Spectral Broadening via PCF

I should mention that the output spectra that we see agree, at least qualitatively, with simulated spectra generated from a modified version of a program found online[1].

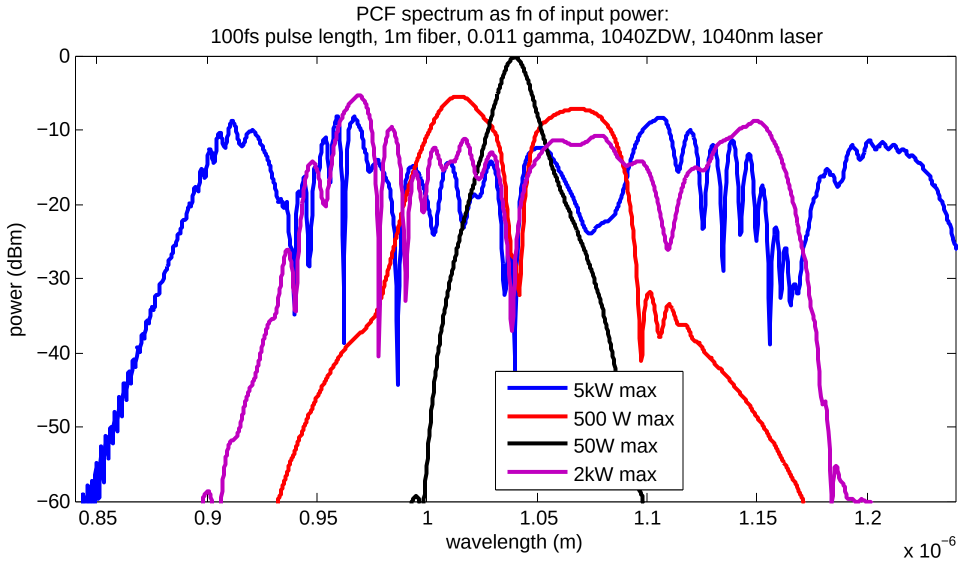

Figure 5: Simulated PCF Output Spectra

Another tool in our arsenal was to use SHG a doubling crystal. Since the SHG is so inefficient, we would need to broaden and then frequency double. See fig. 1b). We tried many different combinations of PCF. For example,

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[1] credit goes to Laurence McGlashen, see: http://lrm29.github.io/files/Laurence_McGlashan_CETIIB_Research_Project_Report.pdf

using the original long piece (~1m) provided too much broadening. Too much of the power was diverted to colors that would not give us green when doubled, or anything actually since the crystal is designed to double around 1040nm. Unfortunately, as can be see in fig. 4, the broadened spectra are not flat, although they cover a great deal of bandwidth. Because of the intensity-squared dependence of SHG, the spectral features that are large tend to dominate the SHG. Since we don't have control over exactly what the broadened IR spectra looked like, it was very difficult to get coverage at 1055nm and also make that the peak. We tried shorter pieces, even a very short piece (~10cm), but broadened IR spectra was not optimal for green at 527nm. With small spectral broadening, usually the peak of the spectra would remain centered around 1040nm (the peak of the Menlo laser output) resulting in green generation centered around 510-520nm, not covering our region of interest.

One approach that was relatively promising was to use a fiber with comparatively little broadening compared to the PCF, i.e. declare defeat and abandon our super-awesome PCF for a piece of normal single-mode fiber, fig. 1 c). This gave a relatively smooth broadened IR spectra but still suffered from the issue that peak of the IR power was at too short a wavelength. The best we were able to achieve was to have the edge of the IR output at 1055. This lead to relatively small amount of power at 1055nm and as a result a very small amount of green in the vicinity of 527nm despite best efforts to phase-match at 1055nm.

Another issue was technical. We had difficulty reading out data from the optical spectrum analyzers. Our spectrum analyzer didn't go below 600nm, so we borrowed two spectrum analyzers from quantum computing. One of the spectrum analyzers,Ando AQ6310, couldn't be interfaced with the computer. The other, Anritsu MS9701B/MS9030A , had a broken front panel, but was able be controlled remotely via a Matlab program.

Ultimately we've come to the conclusion that it's very difficult to see a tiny dip in green on top of a large background when we are unable to easily/reliably produce much green light and when that green light is not centered at the wavelength of interest. Also, the Menlo fs laser broke and had to be sent back to the manufacturer for repair, putting Eu:YSO absorption spectroscopy experiments on hiatus. Should we come back to it, one thing that we would like to try is introducing a long-pass filter at 1050nm to help us separate out the part of the IR spectra that we want to double.

2 Fluorescence Spectroscopy

Initial investigations: We acquired some high power UV LED (~100mW centered at 365 and 385nm) sources, from a company called Mightex, to use excite the Eu:YSO crystal. Initially we tried using them in conjunction with a grating spectrometer set-up from the 625 lab as well as a borrowed monochromator set-up. No green or yellow features were discernible with the grating spectrometer, presumably it is too optically inefficient. The monochromator yielded some hint of a feature. We were able to see a small amount of green and tried to map it out using a photon counter, but the feature was very small. These instruments were insufficiently precise and inadequate to find the 527nm feature we were looking for.

2.1 Analysis Procedure

Our colleague Mike Wood came to the rescue. He let us use his 3m grating spectrometer which was able to see the features that we were looking for. However, the data analysis from this instrument was relatively sophisticated and required writing some code to analyze the output CCD images.

There were a number of issues that had to be resolved in order to get the program working. See fig. 6 for a cartoon of the general flow of the analysis. Explanation is below, here is a list of issues:

1. Absolute reference line required to calibrate the spectrometer
2. Day to day order location drift on CCD
3. Multiple CCD exposures are required to acquire a gap-less spectrum: vertical overlap and horizontal offset of CCD images needs to be determined
4. Order curvature and changing order spacing
5. Order bleed through: light from a bright spot can contaminate an adjacent order and create a spurious feature

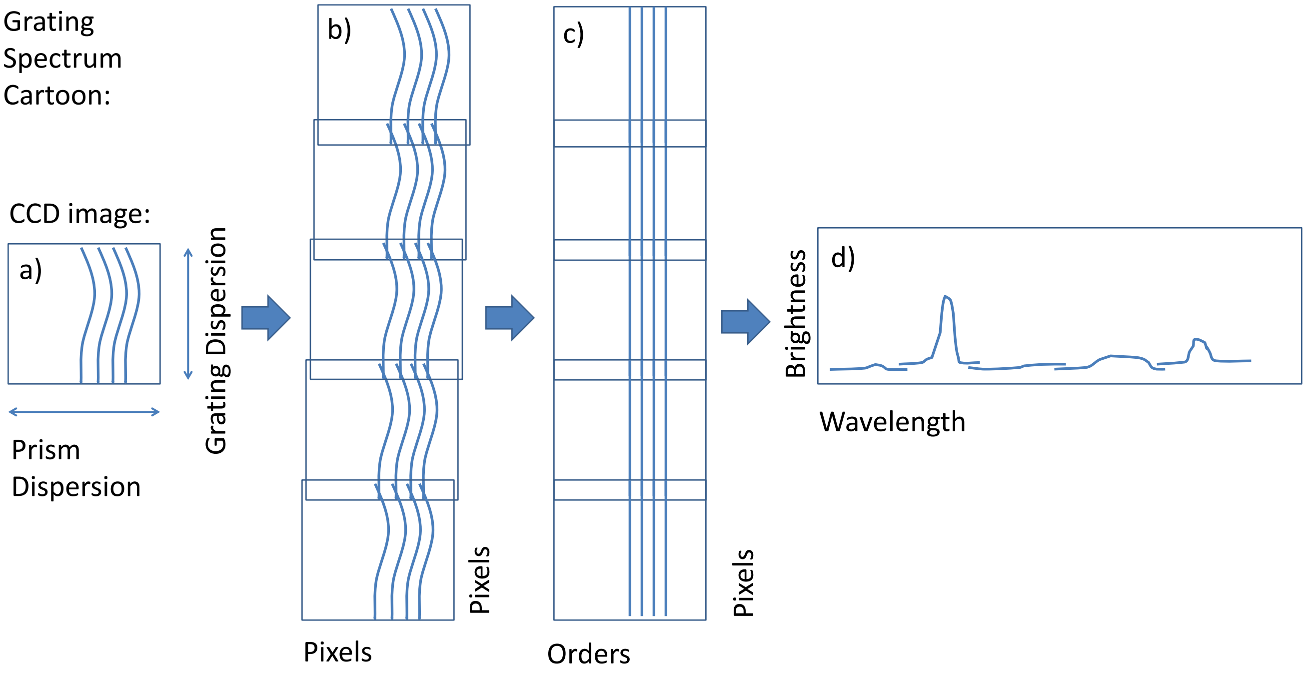

Figure 6: 2D Spectrum Analysis Cartoon

Instead of spitting out a line-spectrum as scanning a monochromator would produce, Mike's grating spectrometer output is folded in 2D and the output recorded onto a large CCD (2048x2048). Each image shows multiple orders, depicted by the blue curved lines in fig. 6 a). This allows for a tremendous amount of data to be acquired in a single CCD exposure. Combined with a known line from an atomic source, it is possible to identify the wavelength of all features on the CCD image.

There are a few wrinkles however. One issue is that there can be a slight drift in the pixel position of all the orders from day to day. We took calibration spectra the day after our Eu data and found that their order pixel positions were different by about 6 pixels. That is, the x-positions of all the orders on the CCD differed by about 6 pixels from one day to the next. This is an issue that needs to be taken into consideration when the orders are only ~10 pixels wide. Incorrectly locating the center of the order exaggerates artifacts in the data. A spectral line that is nicely centered and appears in one order can appear as two approximately equal lines in adjacent orders if the locations of the orders are incorrect, muddling the data. This is related to order bleed-through, where a very bright feature can contaminate the same y-position on an adjacent order. Incorrectly identifying the order positions only exacerbates this.

Another issue is that the grating disperses colors so much that a single CCD image cannot capture the whole order. As a result, multiple shots at different grating positions must be acquired to cover the whole spectrum, as seen in fig. 6 b). For our Eu:YSO analysis we used 6 grating positions: 7910, 7952, 7994, 8036, 8078, 8120. The amount of pixel overlap between frames (i.e. the vertical direction in b)) has to be figured out as well in order to get an accurate spectrum and get features that appear in more than one frame to line up. The offset was determined to be approximately 1552 pixels after which the two frames would overlap. This was determined by trial and error to see what offset gave the best overlap.

Another issue is that the x position of the orders changes as a function of the grating tilt. For each grating position, the positions of the orders were observed to move side-to-side by approximately 4 pixels. This is represented by the CCD frames being offset horizontally in fig.6 b).

Another issue is that since these are high orders, large m, they all would overlap were it not for a prism used to disperse them. The prism dispersion isn't flat, but of course depends on wavelength, so the orders in the image are not evenly spaced. Also, because of the prism or potentially other aberration issues, the orders are curved. This is represented by the curved lines representing the orders in fig. 6 b). These corrections have to be taken into account if your spectra is going to match up correctly when you try and stitch them together.

The general procedure is as follows. First a couple of calibration scans are needed: a Mercury and Tungsten spectra. The Hg has a bright narrow line at 546.0750nm, that can be used to locate a pixel and identify its order and wavelength. We know from Mike and their previous calibrations that this line appears in order 141. A broadband source, the Tungsten, helps us identify the positions of all the orders of interest bench-marked to the location of the known order tagged with the Hg line. Using these calibrations, and Nick Brewer's order finder routine, this let's us label the position of all orders of interest in the CCD frame or to put it another way, let's us know the wavelength associated with pixels on the CCD frame.

Mathematically a couple pieces of information are needed. One is the relationship between adjacent orders, m's; smaller orders correspond to longer wavelengths and go as the ratio of order numbers.

$$\lambda_{target} = \lambda_{known} \frac{m_{known}}{m}$$

The other required piece of information is the wavelength spreading in y. This depends on order number, m, as well as the grating and optics which has been calibrated to a number of pixels. The change in pixels is the difference between the y pixel number and the position of the known Hg line.

$$\Delta\lambda_y = \frac{0.75 Angstroms}{m} \Delta pixels$$

Taking into consideration any day to day pixel shift, as mentioned above, this lets us locate the positions of the orders in a Eu frame, our actual data. Next, we need to take enough frames at different grating positions to cover the entire order. Accounting for the change in order locations with grating position, the overlap between CCD frames, as well as order curvature and changing line spacing (as mapped out with the W spectrum), this let's us build a table of orders, fig.6 c). The y dimension contains all the pixels along the order, concatenated from the different CCD frames and the x dimension contains the orders. At this point, a choice is made as to how many pixels in the x direction are included in the calculation of the value for each order at that y pixel position. Finally, since there is enough coverage in y to span the whole order and orders overlap without gaps, the 2D spectra can be unfolded producing a single spectra. Since the orders overlap, i.e. the top of one order overlaps with the bottom of the next, the sections in the final output spectrum in fig. 6 d) are depicted to overlap.

2.2 Results

2.2.1 Gross Structure

After analysis we can compare the output spectra to what we expect from a couple of previous investigations. First let's look at the general structure. From Shen and Kachru's 1993 paper[1], they show an Eu:YSO fluorescence spectra between about 525 and 710nm. See fig. 7.

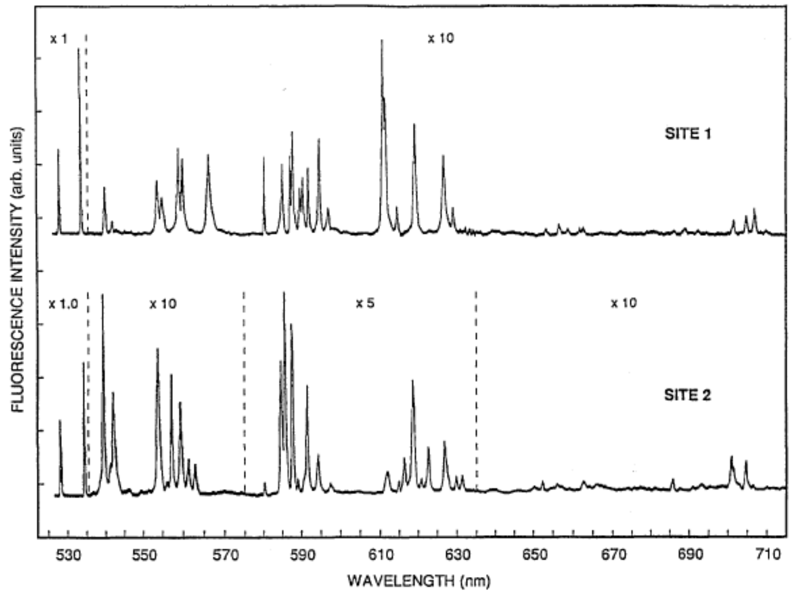

Fig. 2. Fluorescence spectra at ~8 K obtained by excitation of Eu ions to the lowest Stark level in the $^5D_1$ state.

Figure 7: Shen and Kachru Eu:YSO fluorescence spectrum

There is also a small figure in another paper by Yano, Mitsunaga and Uesugi[3] that identifies the transitions related to the different line groups. See fig. 8.

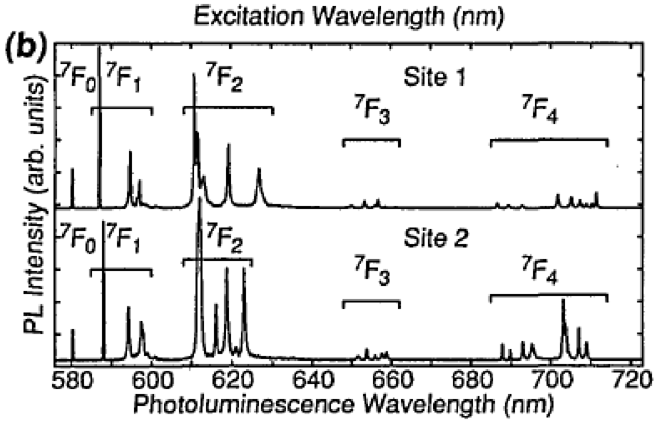

Figure 8: Yano, Mitsunaga, Uesugi Eu:YSO fluorescence peak groups

We observe something similar, where we can also clearly identify the different peak groups, fig. 9.

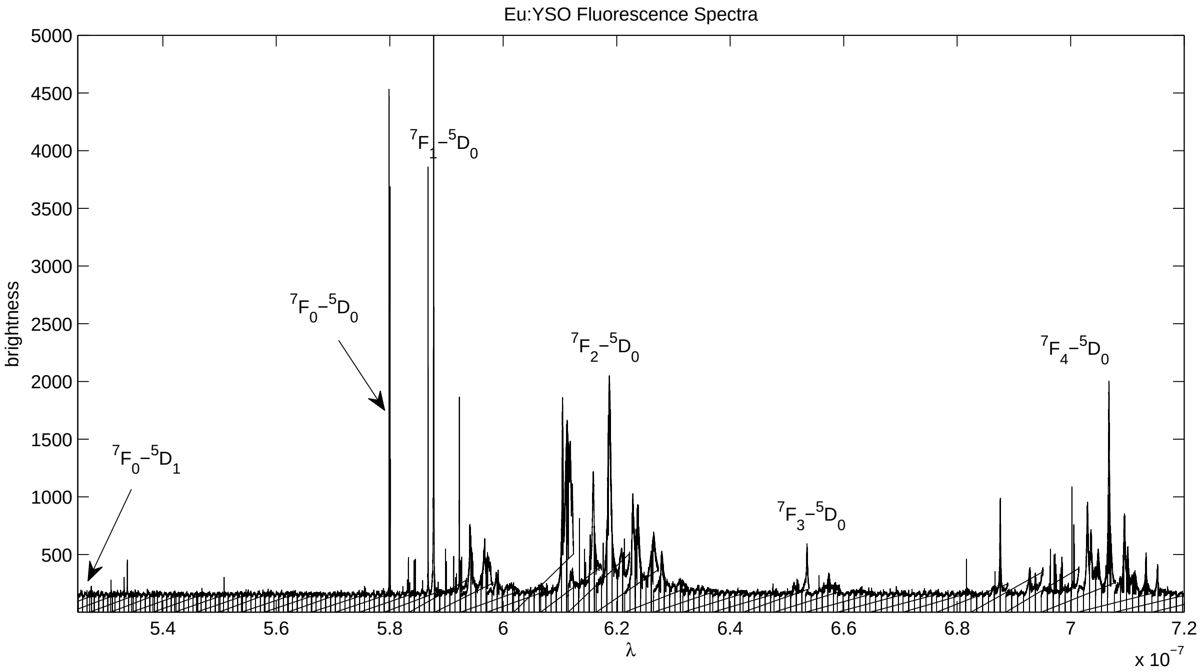

Figure 9: Our Eu:YSO fluorescence spectrum

We can see there are a lot of similarities between the spectra we observe and what is in the literature. Some observations:

- Interestingly we observe no features between about 535 and the 580nm group, whereas in fig. 7, they observe lines in that wavelength range. What is different between our experiments that would cause this?
- Interestingly the 580nm group is relatively small in the investigations in the literature, but we observe it to be rather bright.
- It makes sense that the $^7F_0 -^5 D_0$ transition is very narrow, as that is a J=0 to J=0 forbidden transition.
- It also seems to hold, as Thiel mentions, that sharpest lines are expected between the lowest lying ground state and the lowest lying line of the excited manifold as higher lying levels will be broadened by non-radiative transitions within the manifold to the lowest lying excited state[2]. Apparently the non-radiative relaxation is quite strong. See pg. 354. This would seem to relate to why the $^7F_0$ is narrower than the $^7F_1$, the $^7F_1$ is narrower than the $^7F_2$, etc, although we're talking about the ground states in this circumstance. Since we're talking about the ground states, this argument is not as clear to me; does this imply something about the relaxation among ground states?

We can also examine some of the particular transition groups and see how they compare to what is cited in the literature. For example, looking at the red transitions, the $^7F_2$ group, we can compare the lines present with the stark levels identified in [3] Table 1. The black is a zoom-in on our experimental spectra between 605 and 630nm. The red and blue lines are the estimated positions of the various Stark levels for site 1 (blue) and site 2 (red). The line groups are referenced off the highest energy line, i.e. the shortest wavelength peak is picked and the stark splitting mapped onto the spectrum. The features labeled as *'artifacts?'* are lines that were identified as being potential fake features from order bleed-through. As we can see, correspondence is not perfect. Some lines are apparently not present or appear to sit where a suspected artifact lies. However, the general spacing seems reasonable and it seems some of the stronger lines are probably legitimate Stark levels. Compare to the $^7F_2$ group in fig. 8.

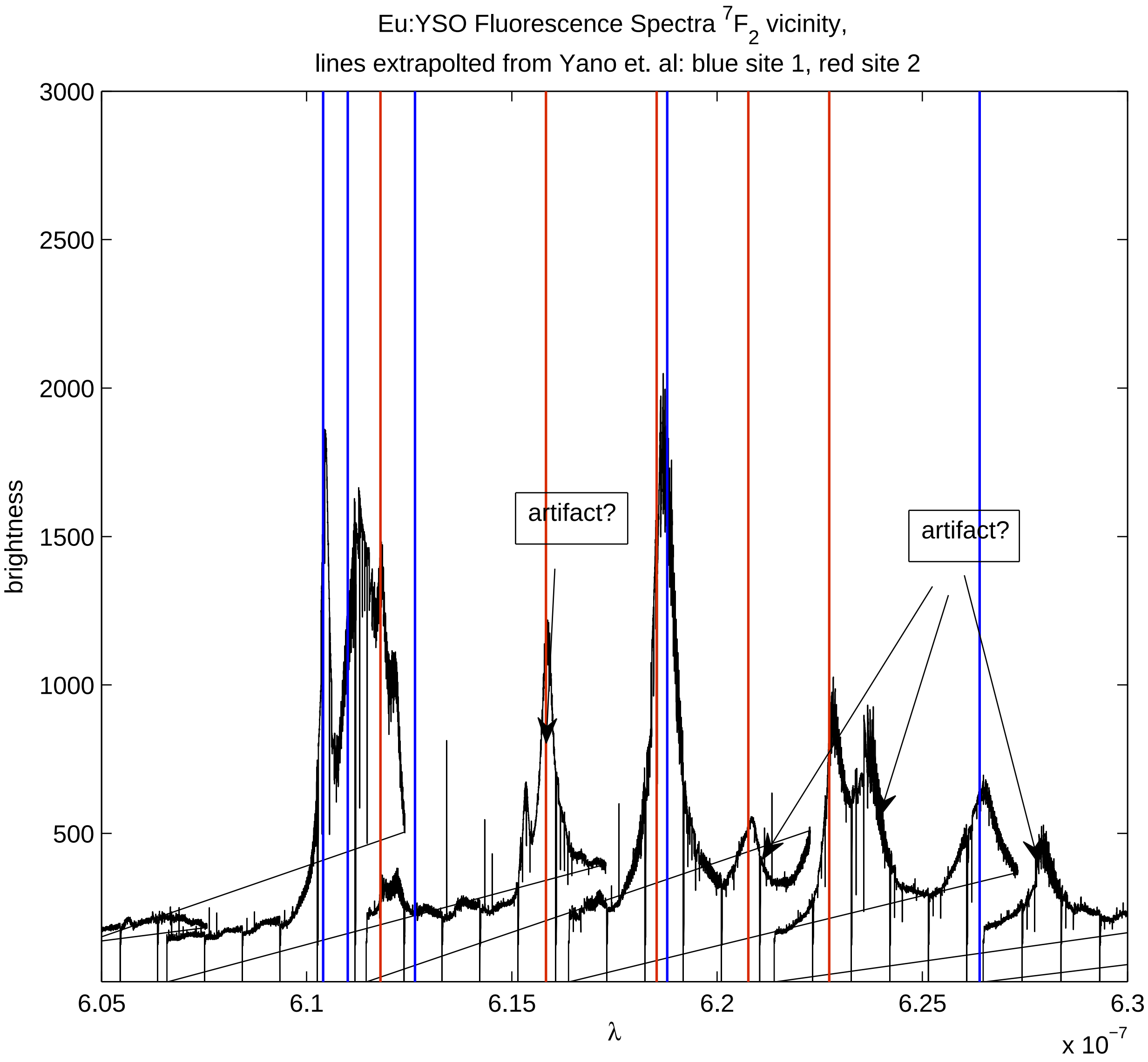

Figure 10: Our Red $^5D_0 - {}^7F_2$ Lines

We can perform the same kind of procedure for the $^7F_1$ group, see fig. 11. This region is less muddled with only 2 groups of 3 lines. In this region, it appears that the Stark levels could reasonably correspond to the observed features. However, one issue is that spacing between the highest energy lines (two sites) is not the same as is quoted in the literature. Yano identifies it as being about $21cm^{-1}$, but the spacing between these two experimental lines is more like $29cm^{-1}$, This raises a couple of questions:

- Could the discrepancy in spacing between the two highest energy lines, i.e. two sites, be temperature dependent? We did this observation at around 77K, whereas Yano was working at 6K. Their paper seems to show lines move between room temp and 6K, but the spacing between sites seems to be constant.
- Why are the highest-energy components so much narrower and brighter than the other Stark levels? Note: the line at 588 goes off the scale to something like 10000. Is there some simple explanation based on the energy structure that could account for this? The different Stark levels are the consequence of a static electric field from the crystal splitting the levels of different m_j. If there were some reason that the highest lying Stark level was prevented from decaying non-radiatively to the $^7F_0$, perhaps that could explain the line sharpness, a lack on non-radiative broadening. Would this require a Stark-level dependent condition, and can we come up with a Stark-level dependent condition on non-radiative decay? What does non-radiative decay mean in

the ground states? Is it a significant issue? If one were working on the ${}^7F_1$ group, would it be possible to manipulate this distribution, say with optical pumping to preferentially put population in the non-broadened site? Does any of this have any relevance or implications for the transition that we're interested in, ${}^5D_1 - {}^7F_0$, that has no Stark structure in the ground state, but does in the excited state? This is something that would be nice to nail down, understand better.

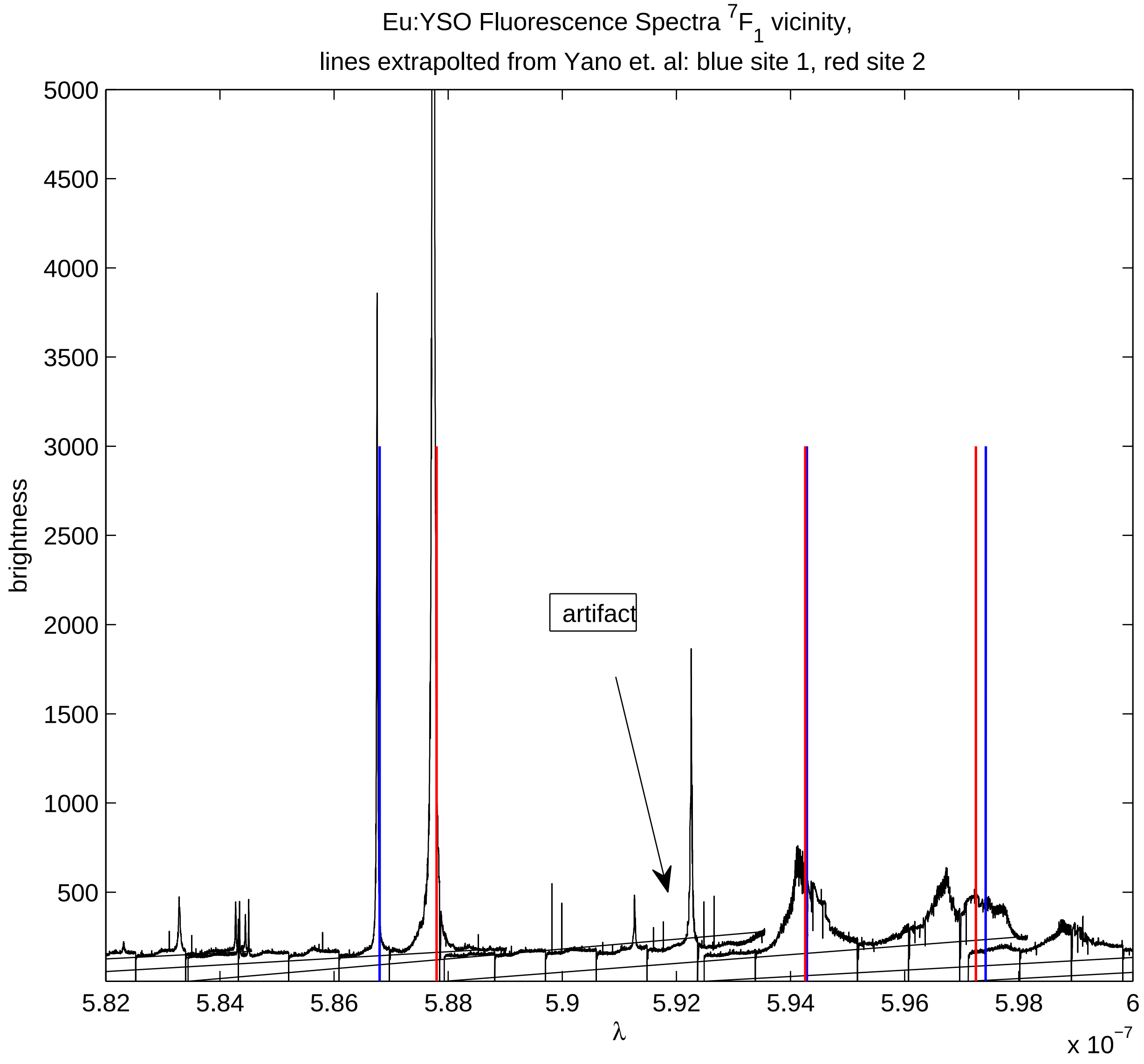

Figure 11: Our Yellow${}^5D_0 - {}^7F_1$ Lines

2.2.2 ${}^7F_0 - {}^5D_0$ Transition

Let's next look at the yellow transition at 580nm that's in all the papers. Side note, since the two yellow lines appeared in two adjacent orders, they provided a really good way to match up the spectra and figure out the CCD frame overlap to about 1552 pixels. Interestingly there is a slight difference between what we observe and where the peaks are supposed to be in wavelength. Our measured peaks are about 1/3-1/2 of an angstrom longer in wavelength than we expect. The spacing between the lines looks excellent. Perhaps this is just the limit of our measurement or maybe there is a difference. Note, these lines are quoted in [3].

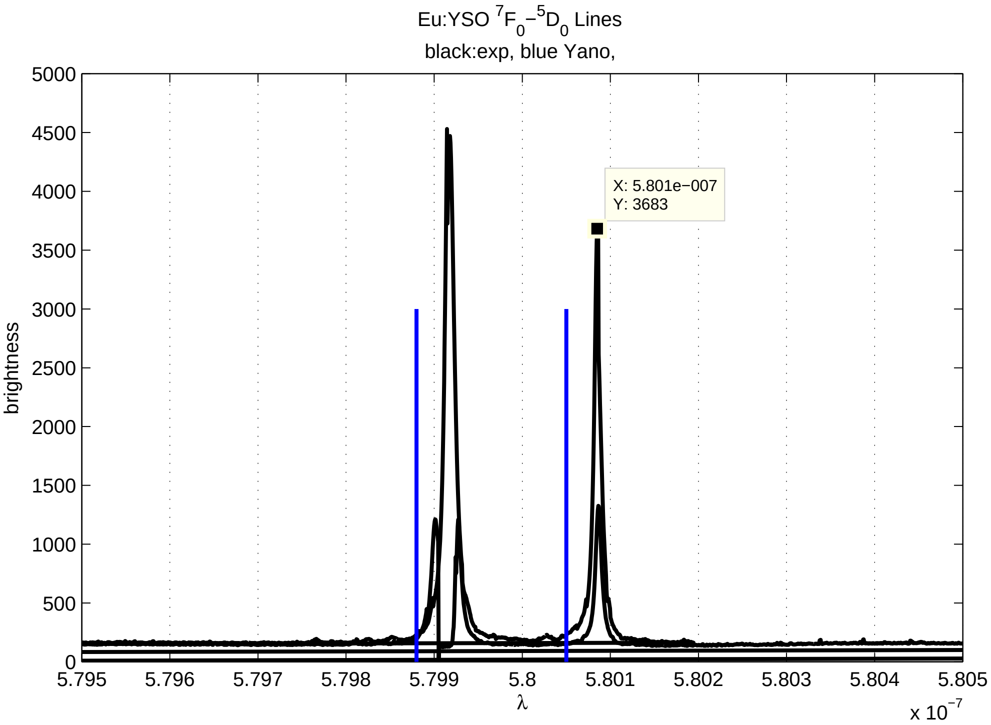

Figure 12: Our 580nm Yellow $^5D_0 - {}^7F_0$ Lines

Let's try and fit the transitions and compare to what is quoted about the transitions.

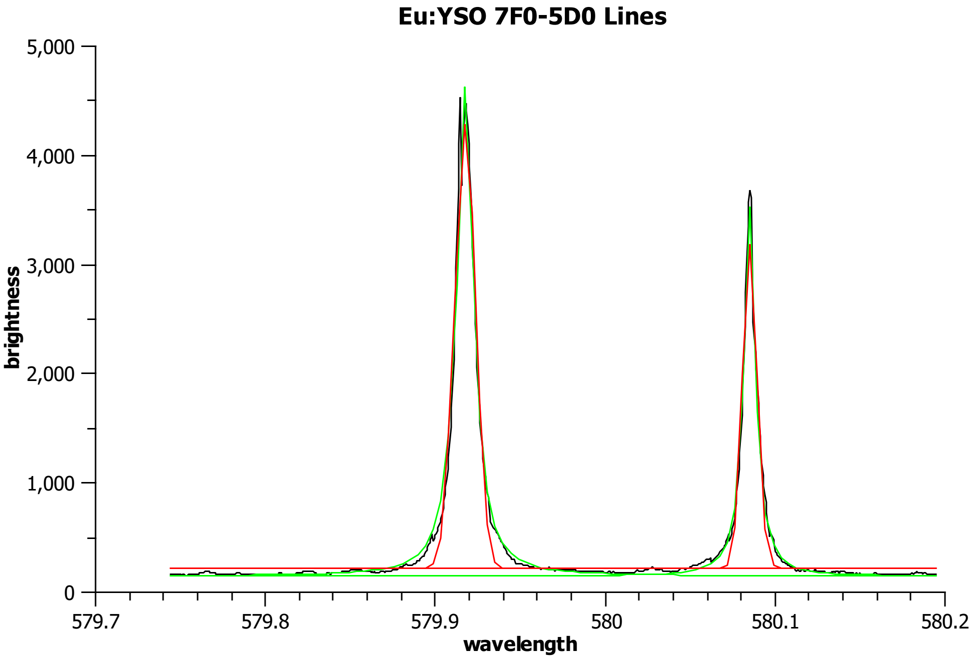

Figure 13: Yellow Line Fits

The Lorentzian fits (green) of these two lines look excellent, $R^2 > 99\%$. The red curves are Gaussian fits. Some observations:

Line	measured λ (nm)	expected λ (nm)	λ difference (nm)	measured Γ (GHz) @ 77K	expected Γ (GHz) @ 1.4K[2]	expected Γ (GHz) @ 8K[3]	expected Γ (GHz) @ room temp[3]
Site 1	579.9175	579.879	0.0385	21	1.7	8.6	94
Site 2	580.085	580.049	0.0360	15	1.4	5.6	53

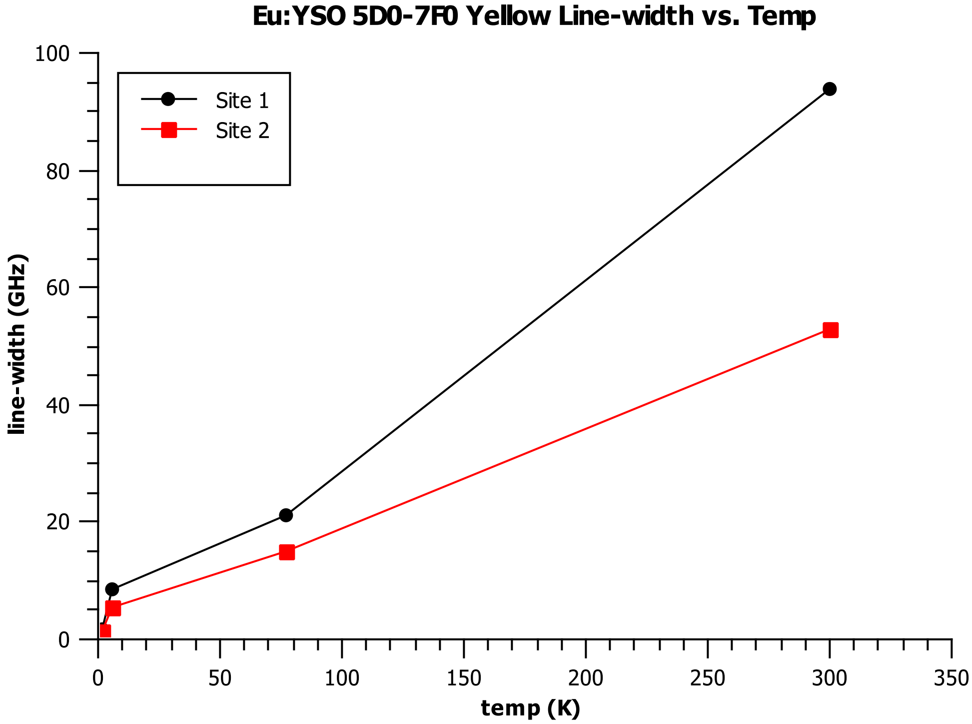

Table 1: 580nm Yellow Line Fit Parameters and Line-width vs. Temp

- There seems to be a systematic shift between our lines and where they are supposed to be of about 0.37nm. Perhaps this is a calibration issue. It's also suggested in Yano that the lines move some with temperature, but this effect does not appear to fix the discrepancy. As a side question, why would the lines move with temp?

- The spacing between the two site lines is supposed to be about 0.17nm, we measure basically the exact same value at 0.1675nm. I guess this could be related to the crystal field splitting. Perhaps the lowest order effect is a static spacing between the two lines, the higher order effect inhomogeneous broadening. Since the inhomogeneous broadening is non-temp dependent, maybe the line spacing isn't either. However, i don't know how this relates to the fact that the shift in the pair of lines, the offset not the spacing between them seems to be temperature dependent.

- Lorentzian fits are better than Gaussian fits, see fig. 13. Lorentzian lineshape indicates homogeneous broadening, apparently due to phonon coupling and fluctuating spins[2]. If there were significant inhomogeneous broadening, we would expect more of a Gaussian lineshape. Apparently at LN2 temps, the phonon homogeneous broadening overwhelms the inhomogeneous linewidth. Presumably, our linewidth is temp limited, we're seeing a lot of phonon broadening. We would have observed a more Gaussian lineshape due to the crystal broadening had phonon effects been small enough. This is also consistent with Thiel's quoted $\Gamma_{inh}$of a ~2GHz, as we're about 10x larger. However, Thiel also notes on pg 354 that inhomogeneous broadening by dilute defects can cause a Lorentzian lineshape. Also, another paper by Yano and company goes into some of the details of the contributions to the linewidth[2]. Need to think about this some more.

- Interestingly, our linewidth measurements at 77K temperatures lie in between the line-widths cited by Yano at 6K and room temp respectively, see 1. This seems very reasonable.

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[2] Yano,Mitsunaga, Uesugi. J. Opt. Soc. Am. B/Vol. 9, No. 6/June 1992.

2.2.3 $^{7}F_{0} -^{5} D_{1}$ Transition

Next, let's take a look at the transition group that we're actually interested in, the strong magnetic dipole transition in the green at about 527nm.

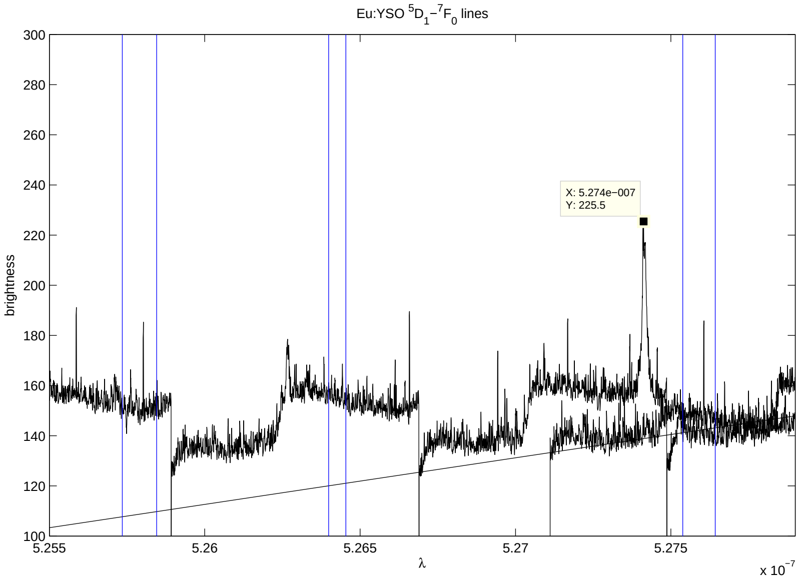

Figure 14: Our 527nm Green $^{5}D_{1} -^{7} F_{0}$ Lines

It appears we can make out the two brightest features, one at about 526.3, another at about 527.4nm. This compares favorably with Shen, fig.[fig:Expected-Green-Features].

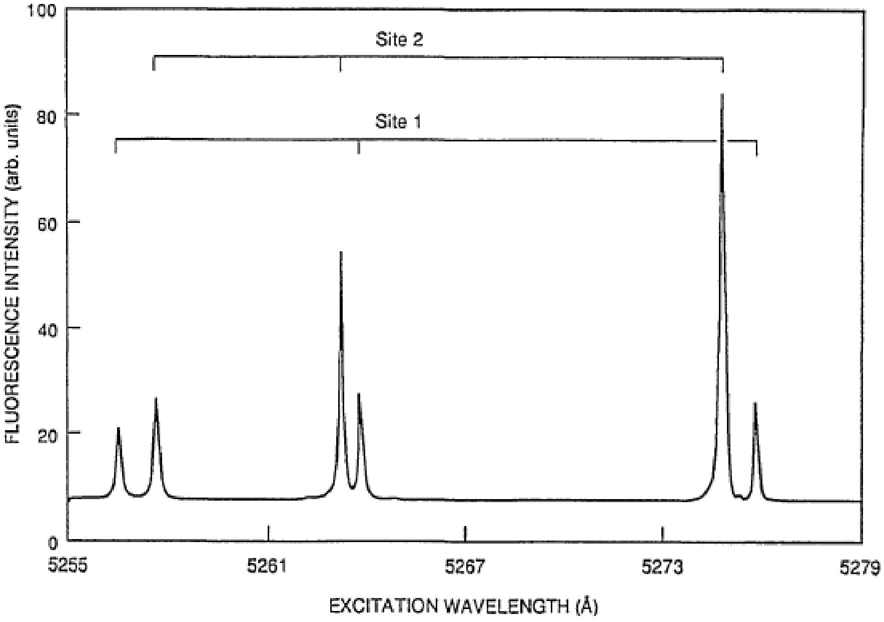

Figure 15: Shen and Kachru, Expected Green Features

Let's zoom in on the brightest features in our experimental data.

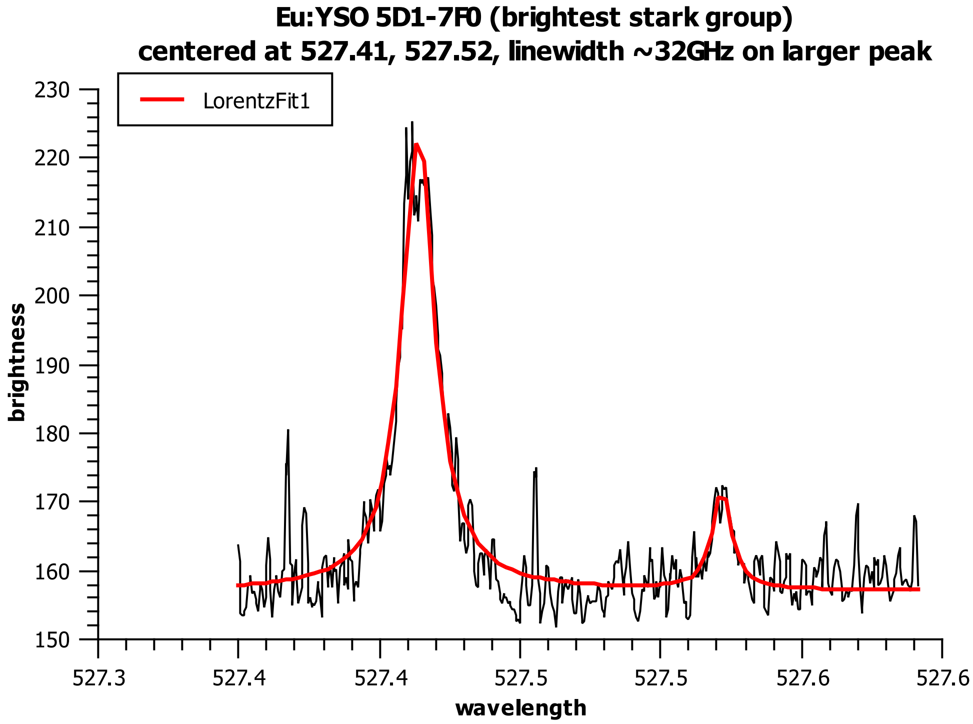

Figure 16: Our Brightest 527nm Feature

Stark Level	Site	expected λ(nm)	measured λ(nm)	difference (nm)	expected Γ(GHz) @ ~3K	measured Γ(GHz) @ ~77K
1	1	527.6426	527.52	0.1226	2.3	-
	2	527.5381	527.41	0.1281	2.7	32
2	1	526.4543	-	-	-	-
	2	526.3989	526.27	0.1289	-	-
3	1	525.7347	-	-	-	-
	2	525.8453	-	-	-	-

Table 2: 527nm Lines Data Comparison

When we zoom in, the tiny adjacent peak from the other crystal site becomes visible, fig. 16. Shen locates the two longest peaks at 527.54 and 527.64nm. As we can see our peaks appear to be shifted by about 0.13nm or so compared to this. Additionally we can measure the width of the brightest feature and get about 32GHz. This is significantly broader than the width Shen measures at 3K of about 3GHz, but it should be as we're at a higher temp; it's also consistent with our measurements of the 580nm line broadening.

3 Next: Laser-scanning absorption spectroscopy

4 Judd-Ofelt Studies with RELIC

References

[1] X. A. Shen and R. Kachru. 7f0-5d1 transition in eu3+:y2sio5. *J. Opt. Soc. Am. B*, 11(4):591–596, Apr 1994.

[2] C.W. Thiel, Thomas BÃ¶ttger, and R.L. Cone. Rare-earth-doped materials for applications in quantum information storage and signal processing. *Journal of Luminescence*, 131(3):353 – 361, 2011. Selected papers from DPC'10.

[3] Ryuzi Yano, Masaharu Mitsunaga, and Naoshi Uesugi. Ultralong optical dephasing time in eu3+:y2sio5. *Opt. Lett.*, 16(23):1884–1886, Dec 1991.