Detonation Spectroscopy: Results, Problems, and Directions

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1 Purpose

Presented here are some notes and results of efforts to acquire and analyze spectra from detonations. It builds and extends work performed by Bill Ward as a SURF student during the summer of 1997.

Ideally, measuring the spectra of detonations should take the following steps:

1. Obtain spectrum of event.
2. Digitize or record wavelengths of lines and bandheads, perhaps also their intensity.
3. Consult spectral atlases to identify features, yielding information about species present.
4. Analyze relative intensities of bands to determine rotational / vibrational temperature. With additional fluorescence lifetime or emission probability data, compute relative concentrations of species.
5. Evaluate natural radiation and infer state populations to predict the efficacy of different laser induced fluorescence strategies and relate emission intensity in given wavelength ranges to particular species.

Work under this strategy was begun using a Jarrell-Ash Wadsworth mounting grating film spectrometer as described in Bill Ward's report. Although the resulting spectra are remarkable and clearly show some expected and some unexpected phenomena, our attempts to identify a significant number of lines or otherwise obtain useful information from them have been frustrated.

Among the directly useful results are the following:

- We can roughly quantify the spectral content of detonation radiation and predict the usefulness of various filters to reduce background during laser induced fluorescence experiments. In particular, large amounts of red and yellow light are emitted by C_2 and Na impurities in all experiments (including H_2-O_2 detonations with no oxy-acetylene driver).
- Striking differences are evident between detonations and flames. While the specific differences have not yet been completely analyzed, it is apparent that further investigation should yield interesting results.

2 Background

Little or no work on detonations seems to have been performed until now. The most typical radiation sources for spectroscopy are arcs, sparks, and discharges, with flames also being popular for molecular spectroscopy. Spectroscopic investigation has been made of emission and absorption from shock tubes, including some experiments that may be interpreted as detonations (Gaydon 1957). However, direct data (graphical spectra) from bona fide detonations have been difficult to locate. These type of data are important particularly as laser induced fluorescence techniques are being increasingly applied to detonations. The natural radiation present in detonations can have a profound impact on signal to noise ratio, and quantitative laser induced fluorescence is based on theories that beg to be tested under the conditions peculiar to detonations (high pressure, high temperature, and possibly nonequilibrium).

For a general introduction to spectroscopy, a number of books are useful. Walker and Straw (1961) and Walker and Straw (1962) are good general discussions of spectroscopy, including descriptions of techniques. Richards and Scott (1985) is a good introduction to the theory of molecular spectra, while Herzberg (1937) and Herzberg (1971) are more technical discussions of atomic and molecular spectra and structure. Bradley (1962) pertains to shock wave physics and chemistry, including some discussion of radiation. Spectroscopy of flames is discussed in Gaydon (1957) and Gaydon and Wolfhard (1970). Some discussion of shock tube spectroscopy is given in Fairbairn and Gaydon

(1957). Spener and Wagner (1954) seems to include actual spectra from detonations, but unfortunately is in German. A very comprehensive compilation of atomic spectral lines is found in Harrison (1969) (100,000 lines), while Zaidel et al. (1970) is an abridged list (52,000 lines) more convenient for reference. Pearse and Gaydon (1963) contains a list of bandheads and individual bands. A number of these references contain photographic spectra that can be very helpful for identifying spectra on films.

3 General Problems

1. Wavelengths are difficult to measure: large slit width is necessary to obtain sufficient light from a detonation but reduces our spectral resoluation; linearity of the spectrum (wavelength per film position) is questionable because of film dimensional stability, scanner stability and rigidity, etc. Calibration also seems to be a source of some error.

2. Matching of measured wavelengths with tabulated lines is further complicated by the large (but possibly incomplete, particularly in the case of molecular spectra) number of possible matches. Detonation conditions are considerably different from those in typical spectroscopic sources (arc, discharge, flame). Intensities are imprecise and nonstandard in the literature, and our measured intensities suffer from several problems. As usual, impurities are present and are not always easy to identify and often mimic expected species. Finally, the practical aspects of matching spectral lines is complicated by the fact that computerized databases are not generally and freely available. Books (e.g. Harrison (1969), Zaidel et al. (1970), and Pearse and Gaydon (1963)) are of limited availability and are extremely slow and tedious to use.

3. Intensity information is practically useless for temperature and population analyses for technical reasons outlined below.

4 Technical Problems

1. Film sensitivity: T-Max 400 is cheap and easy to handle and gives good constant sensitivity through the visible wavelengths, but has reduced response to IR radiation. A spectral sensitivity graph for T-Max 400 film provided by Kodak shows a decrease above 600 nm and a sharp cutoff around 650 nm. The graph does not extend below 400 nm but a Kodak representative stated that all films are sensitive to UV and the sensitivity graph could be expected to be flat below 400 nm. High speed IR film is available and gives improved response to IR, with some sacrifice in visible. The spectral sensitivity graph provided by Kodak shows a significant dip around 500 nm and higher levels in the UV than the IR. It is significantly more costly and difficult to handle. It is available in 24 frame rolls, must be developed by Graphic Arts Facilities, and should be refrigerated. Finally, regardless of film type, negative density is not directly proportional to incident radiation intensity.

2. Quantitative scanning: Besides stability and scaling issues, scanning negatives presents formidable problems for quantitative intensity measurement. Scanning raw negatives is at present preferable over intermediate printing because: 1) it eliminates further opportunities for variation, and 2) maximum spatial resolution (without enlargement) is obtained. Enlargement is practically impossible for continuous film strips. The primary difficulty with negative scanning is that conventional scanners measure reflected light, not transmitted light. Using the film strip in this mode results in the scanner measuring light that has been reflected by a white surface and transmitted through the film twice. With a perfectly reflective (mirrored) surface instead of white, scanned density could be interpreted as the square of the film density. Also, the transmitted-reflected light may appear with a ghost image caused by light reflected off the film front surface and thus reduce apparent resolution. Preferable, however, would be to use a backlit scanner. Note that the spectrum images and profiles shown below exhibit far less information than the original negatives.

3. Impurities: Impurities are a notorious problem in spectroscopy, and no less in detonations. Soot from hydrocarbon combustion is a major constituent, resulting in C_2 emission even in non-hydrocarbon shots and possibly contributing to significant continuum radiation. Metals from tube materials presumably also contribute, with copper from the exploding wire expected (though not always found) and sodium found but not expected. Finally, impurities in the gases are to be expected in different types and quantities depending on the gases used.

5 Recommendations

1. Perform detonations at conditions similar to those in flames and compare the two results.
2. Improve the calibration system by including polynomial or spline least squares fits and perhaps reject bad calibration lines. The calibration system should take an indefinite number of points, depending on whether it is for the purpose of collecting precise data or quick reference.
3. To check hypothetical but questionable identifications:
    - If an impurity is suspected, the line strength should increase with higher concentration and decrease if the impurity is removed. For example, if Ar impurity is suspected in one of the feed gases, intentionally adding Ar should strengthen the line while switching to gases known to be free of Ar should erase the line.
    - To check if a particular species is responsible for a line, look for other lines expected from that species.
    - Trace impurities should only show up as lines that are normally strong for that species.
4. Identification of spectral lines would be greatly enhanced by the acquisition of a computerized database of known lines. This will be most easily achieved for atomic spectra (possible for example the NIST Spectroscopic Properties of Atoms and Atomic Ions Database available from the Astro library as three PC disks under QC454.A8.M344.1992). In lieu of a raw database available for complete manipulation, a WWW site has been located that provides a search engine interface to the data on a published CD, at http://cfa-www.harvard.edu/amp/data/kur23/sekur.html.
5. Acquire and use a scanner designed for continuous film strips. Possible lead: Nikon LS-10/LS-10E Coolscan or LS-20 Coolscan II. For more information, check out www.nikonusa.com/products/electimage/bg/filmscan or call (516) 547-4355 or (800) 526-4566.
6. Further literature search should be made for additional detonation spectroscopy investigations and related work. The references listed in this document can serve as a starting point for citation index searches.
7. Attention should be paid to the spectrometer instructions for alignment. In particular, the reverse alignment procedure of shining light at the film holder position and aligning with the beam projected through the slit can be very helpful in acquiring more intensity. “White” light is most useful for this since the exact position of the source is less important, and a powerful source (stronger than a flashlight) may be necessary for extensive alignment. Also, the light incident on the spectrometer slit is vertically collimated by the inlet lens, if it is focussed at a point about 25-29 cm from the slit. This suggests that an arbitrary source should be focussed by two independent cylindrical lenses instead of a single spherical lens so it can be focussed horizontally on the slit but vertically at a point 25-29 cm from the slit.
8. Placement of three spectra on each film seems like a good maximum. A slit height of 5 mm and spacing between spectra of 2 mm are very satisfactory. Beware of backlash in the film racking gears.
9. A new calibration lamp should be acquired. Replacement bulbs for the old lamp seem to be difficult to obtain, and it is difficult to mount.
10. The film holder might benefit from some light sealing steps, as it currently requires care to prevent light leakage. The spectrometer instructions have some suggestions here, but replacement of some felt seals may be necessary. To prevent accidentally sliding the light shield behind the film instead of in front before removing the film holder, fold a piece of film around the end of the film holder.

6 Spectra and Profiles

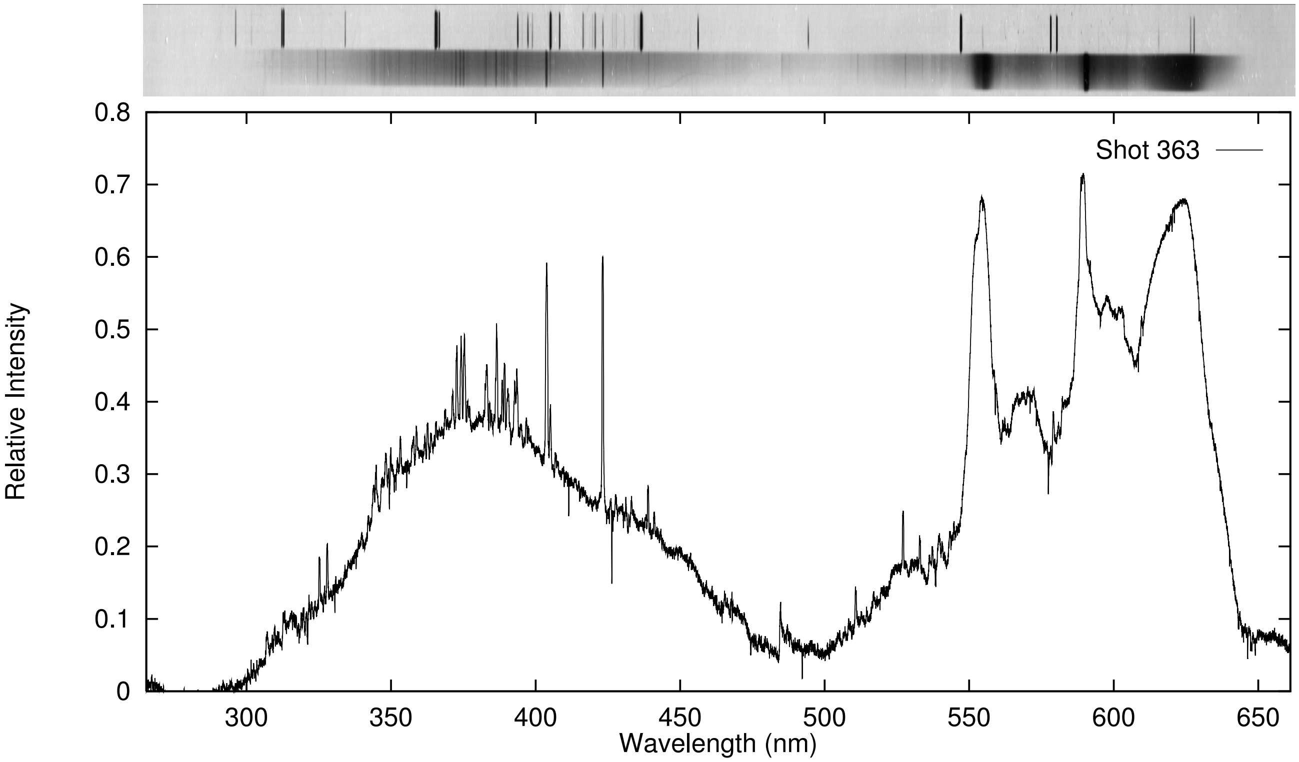

Figure 1: Shot 363 - $CH_3COCH_3+4O_2+3Ar$, 23 kPa

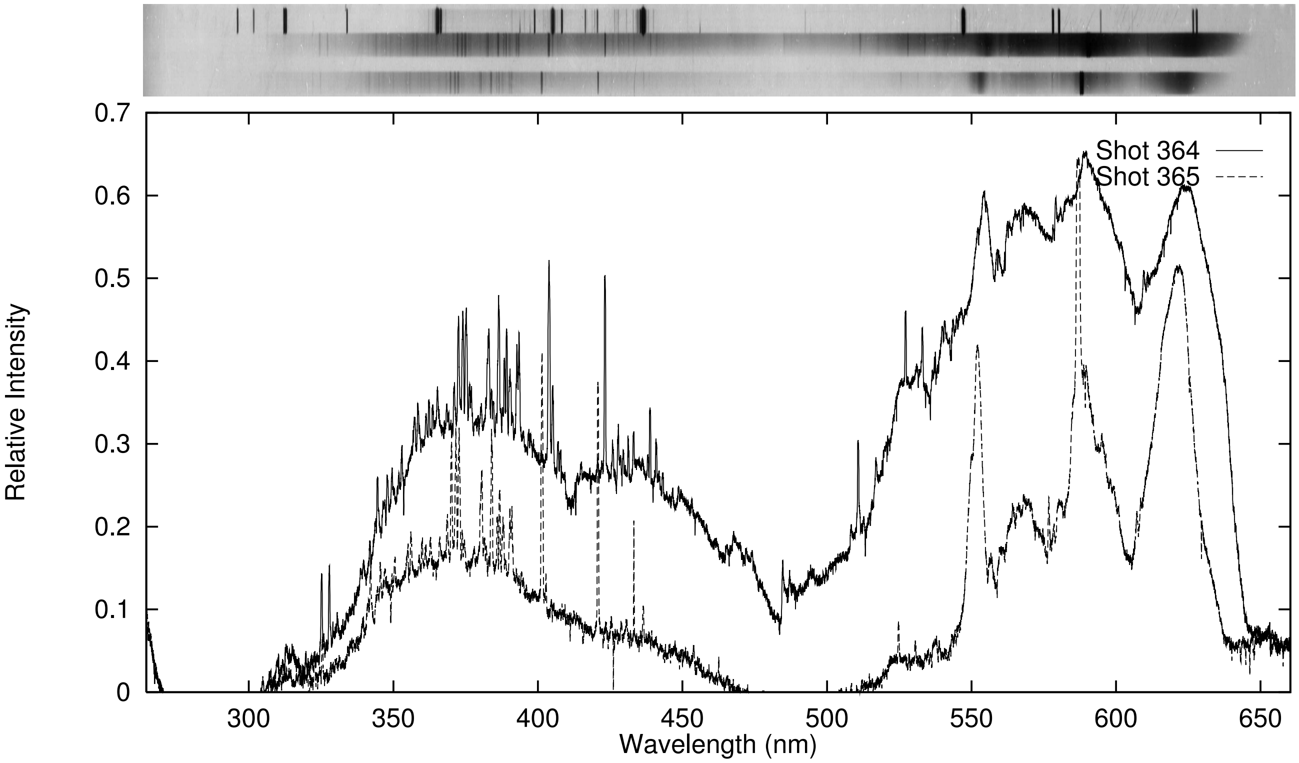

Figure 2: Shot 364 - $CH_3COCH_3+4O_2+4Ar$, 23 kPa; Shot 365 - $CH_3COCH_3+4O_2+5Ar$, 23 kPa

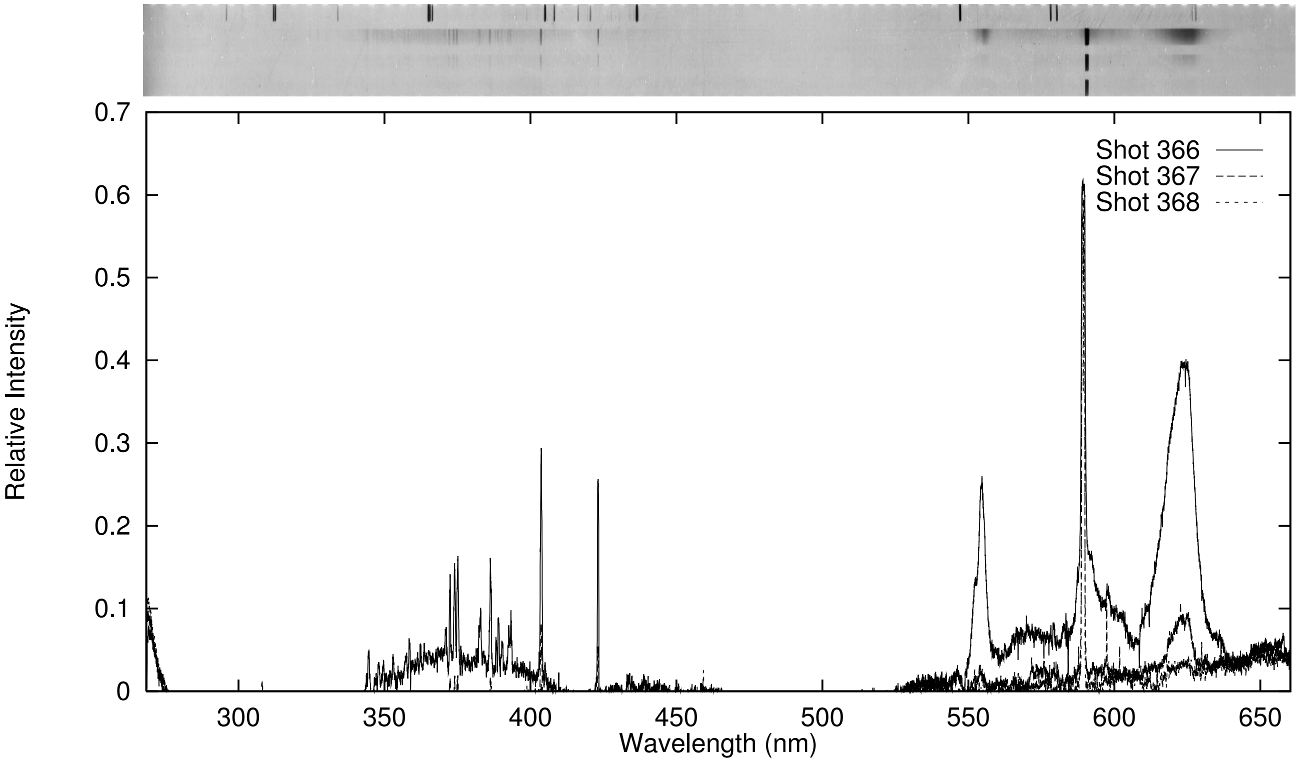

Figure 3: Shot 366 - CH_3COCH_3+$4O_2$+7Ar, 23 kPa; Shot 367 - CH_3COCH_3+$4O_2$+9Ar, 23 kPa

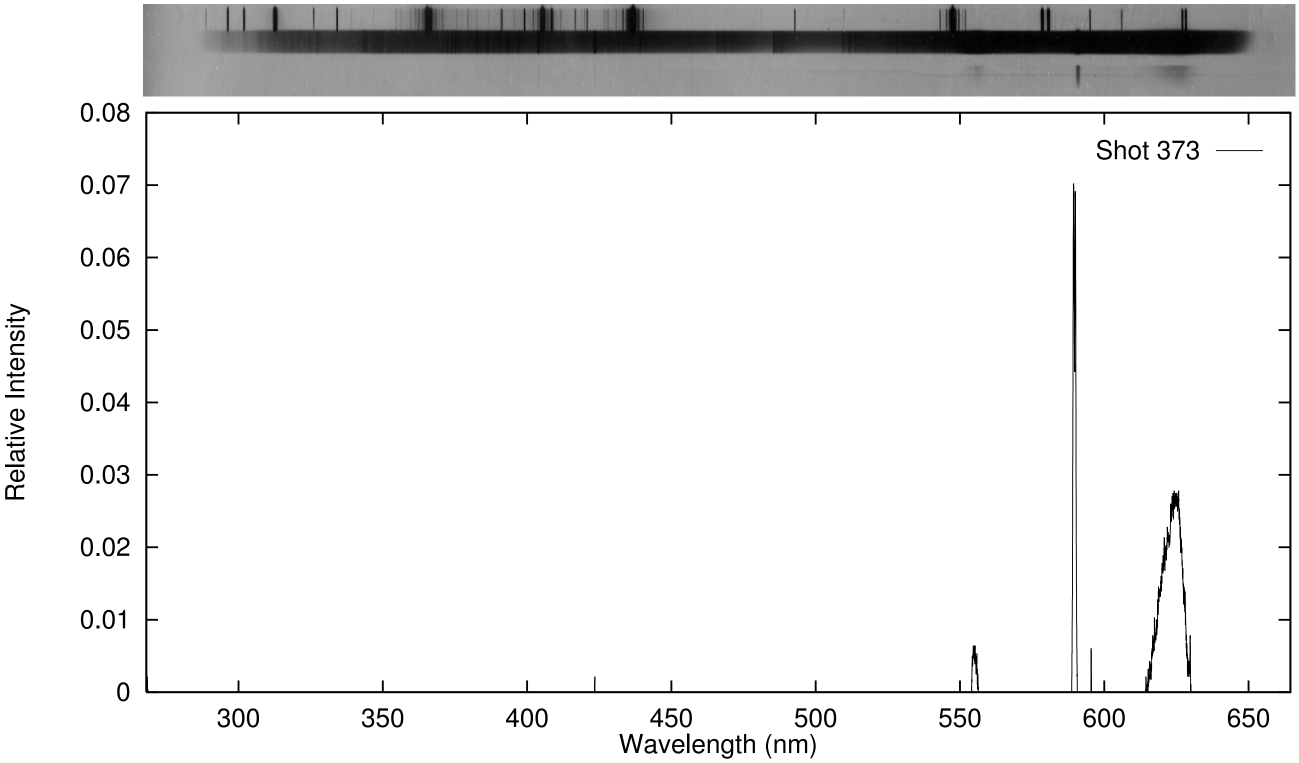

Figure 4: Shot 373 - $2H_2$+O_2, 101 kPa

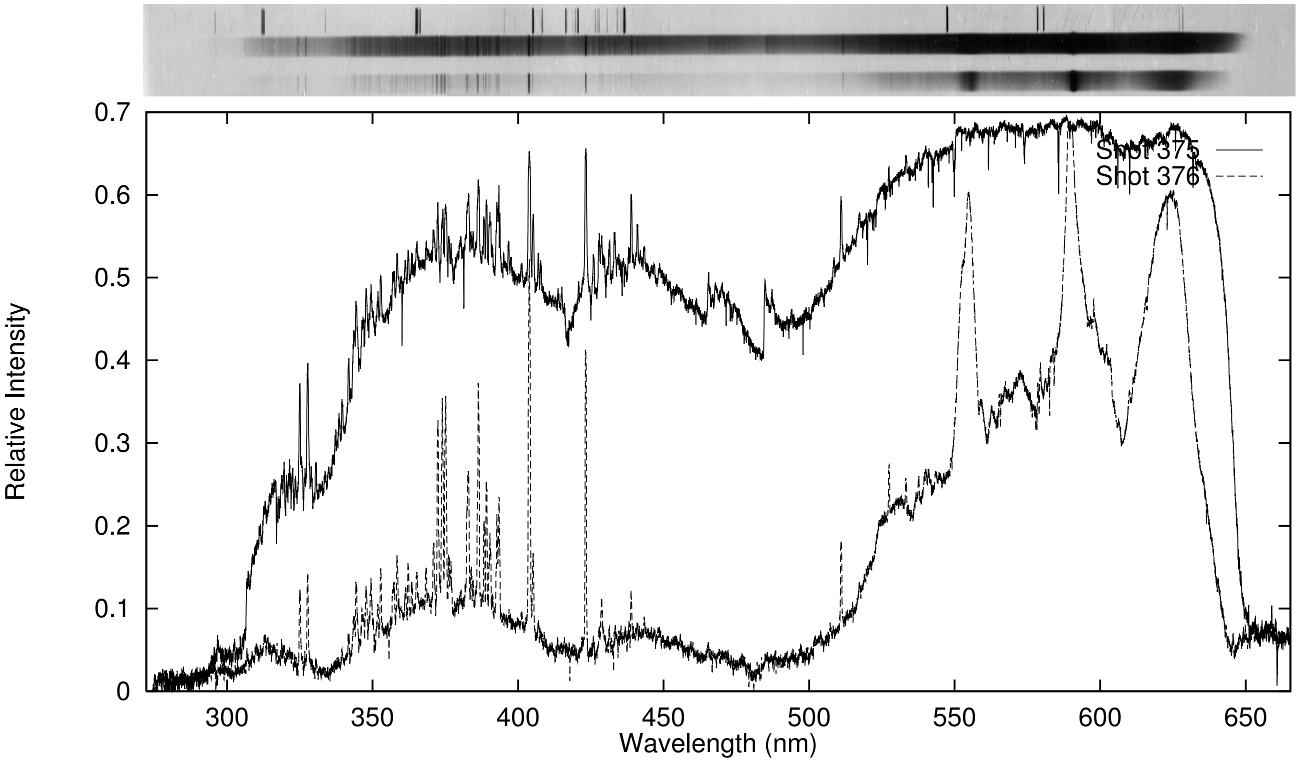

Figure 5: Shot 375 - $2H_2+O_2+2Ar$, 101 kPa; Shot 376 - $2H_2+O_2+4Ar$, 101 kPa

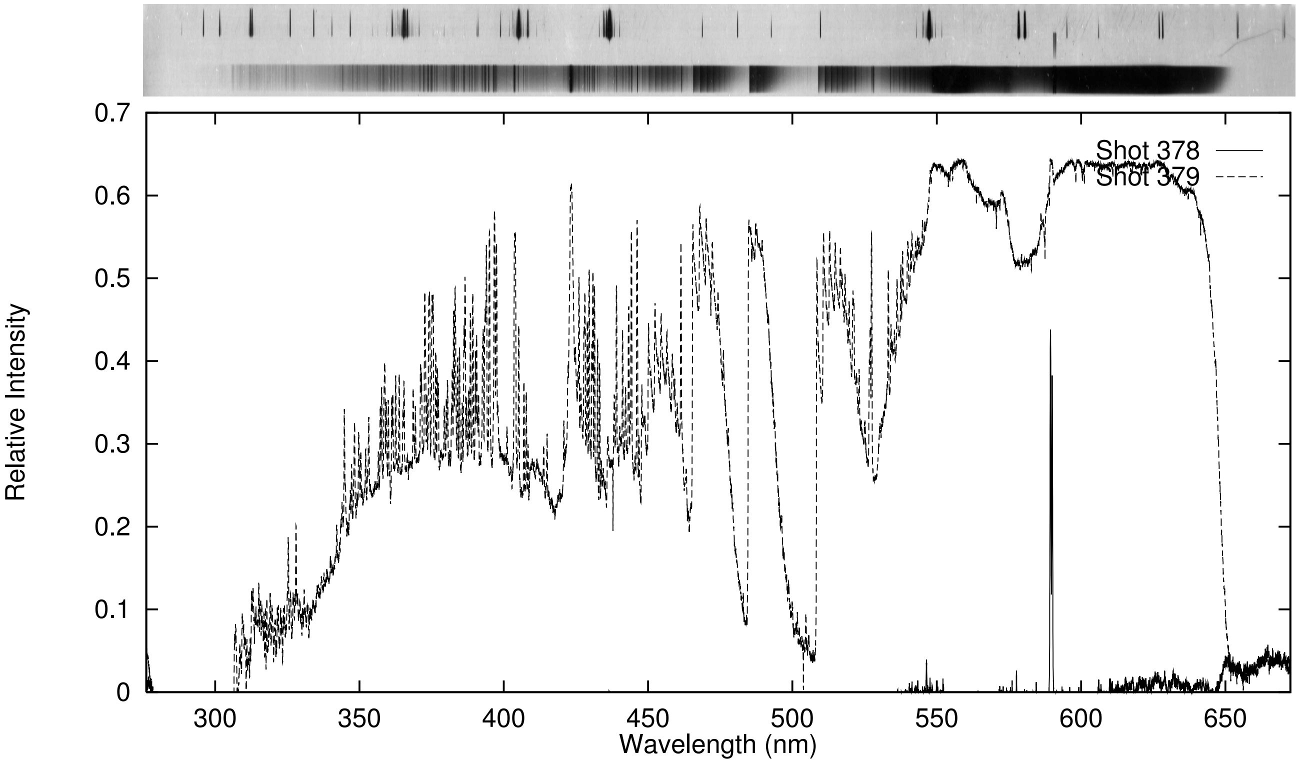

Figure 6: Shot 378 - $2H_2+O_2+8.78Ar$, 101 kPa; Shot 379 - $0.74C_2H_2+O_2$, 9.1 kPa

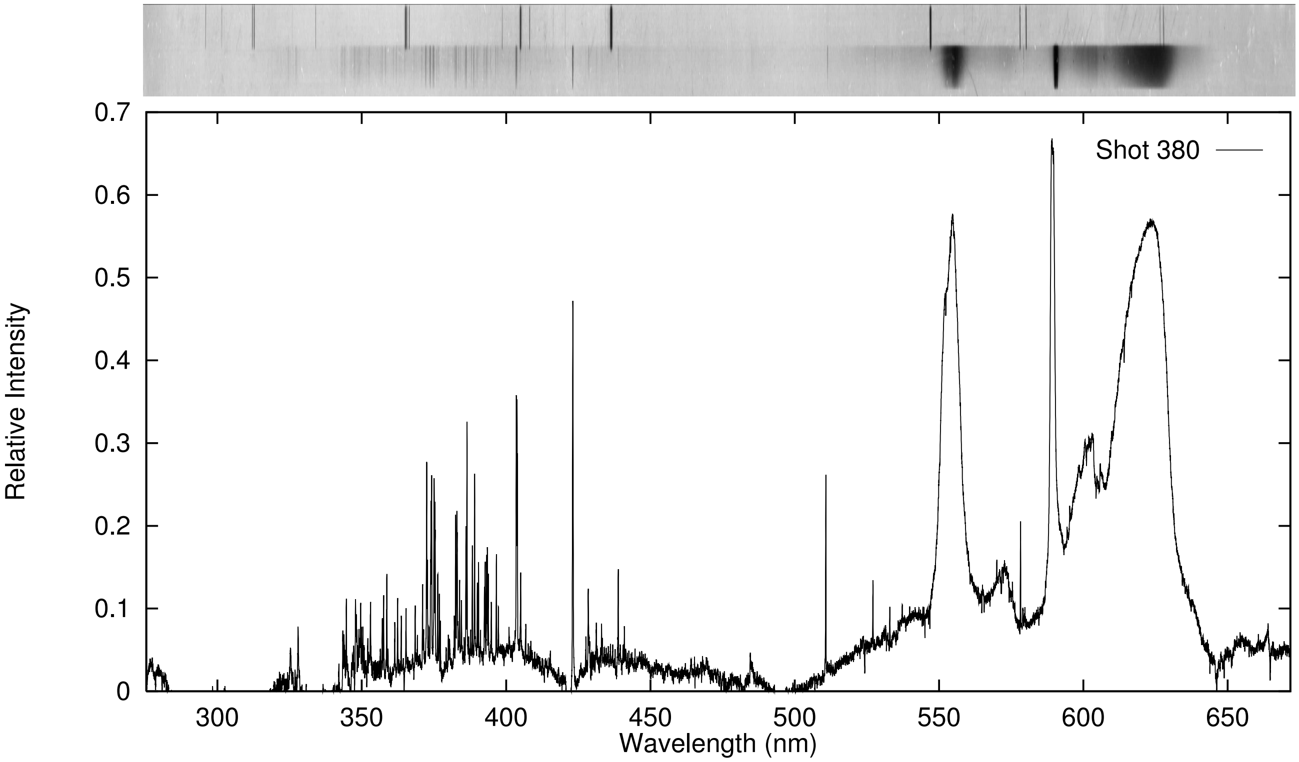

Figure 7: Shot 380 - $2H_2+O_2$, 101 kPa, No driver

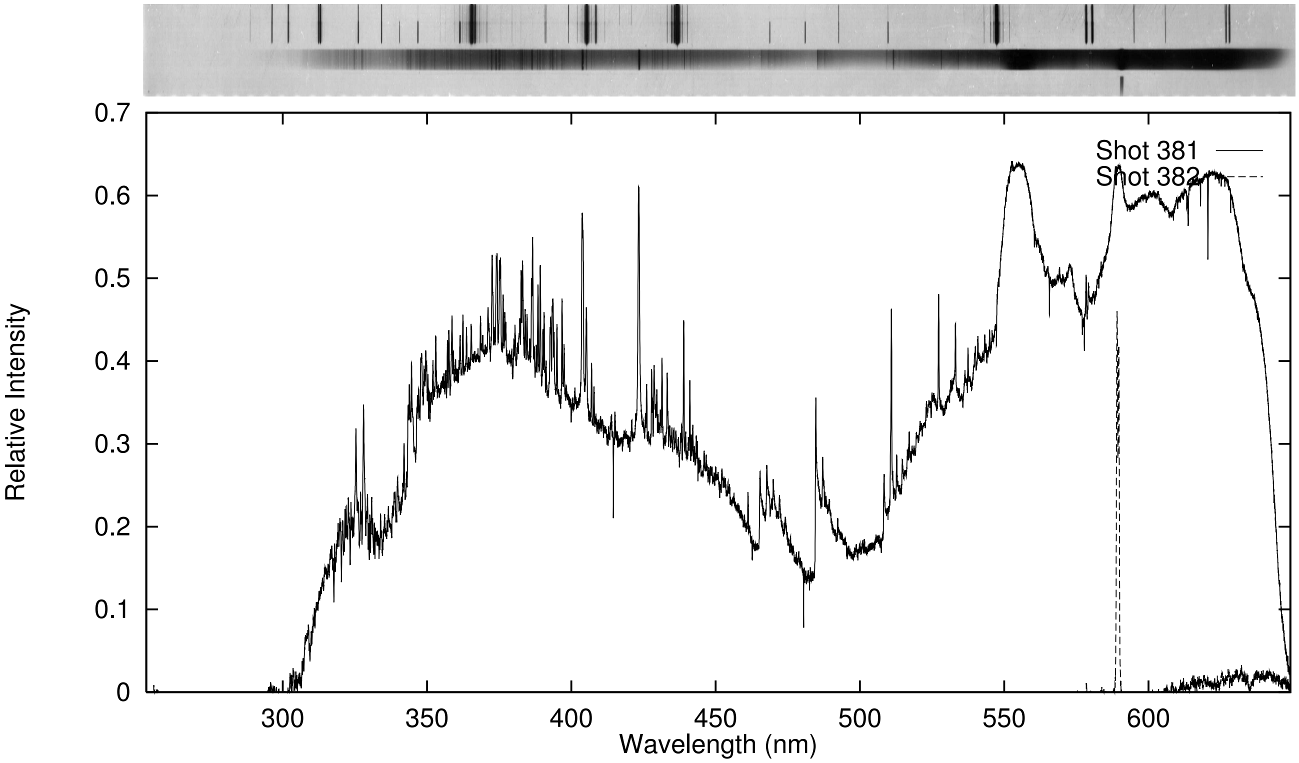

Figure 8: Shot 381 - $2H_2+O_2$, 101 kPa, No driver; Shot 382 - $2H_2+O_2+10Ar$, 101 kPa

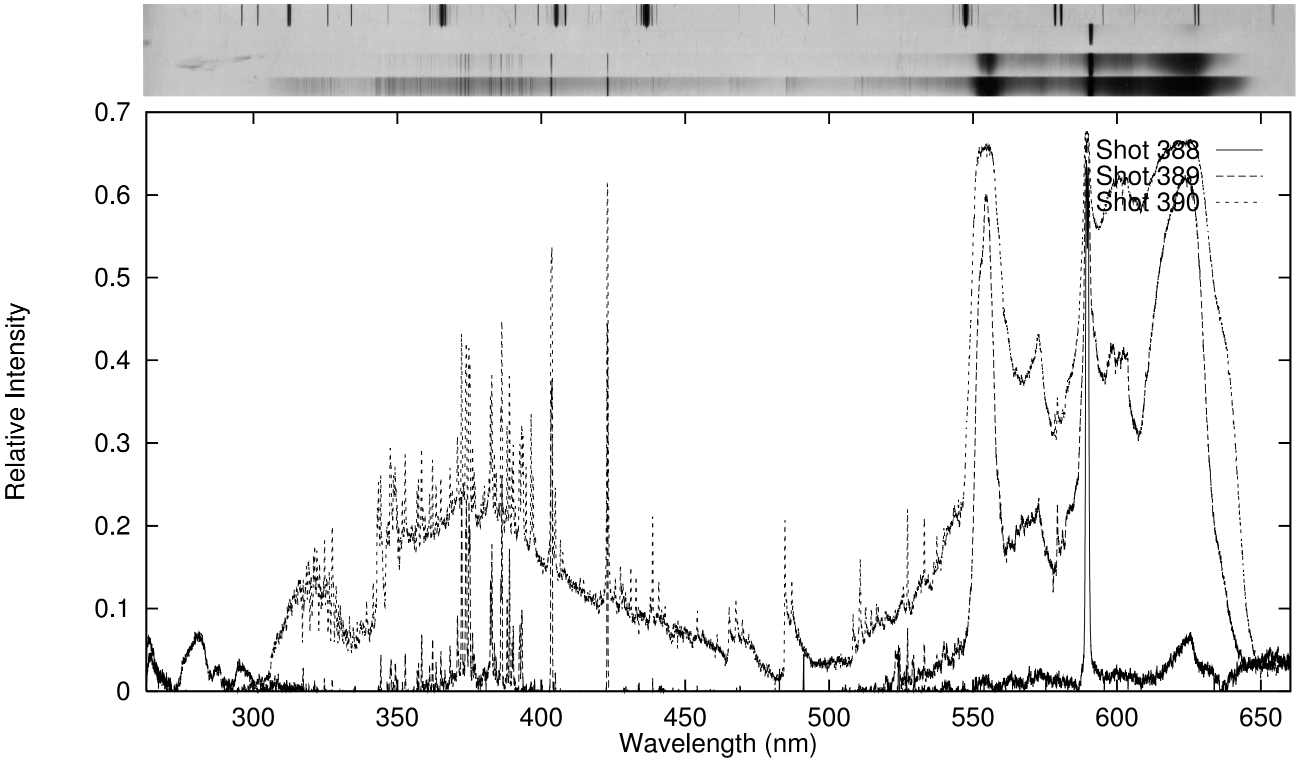

Figure 9: Shot 388 - $2H_2$+O_2+6Ar, 101 kPa; Shot 389 - $2H_2$+O_2+3Ar, 101 kPa; Shot 390 - $2H_2$+O_2+Ar, 101 kPa

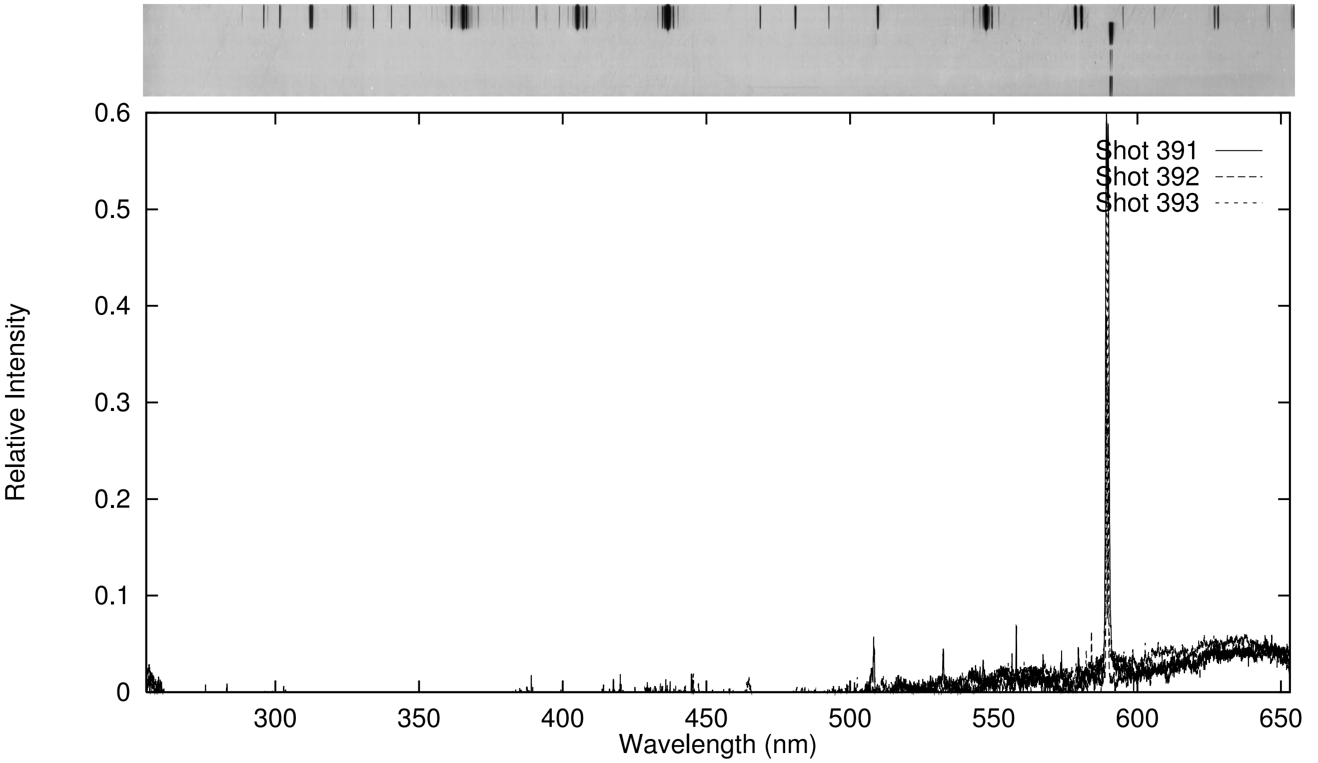

Figure 10: Shot 391 - $2H_2$+O_2+7Ar, 101 kPa; Shot 392 - $2H_2$+O_2+9Ar, 101 kPa; Shot 393 - H_2+$2O_2$, 101 kPa

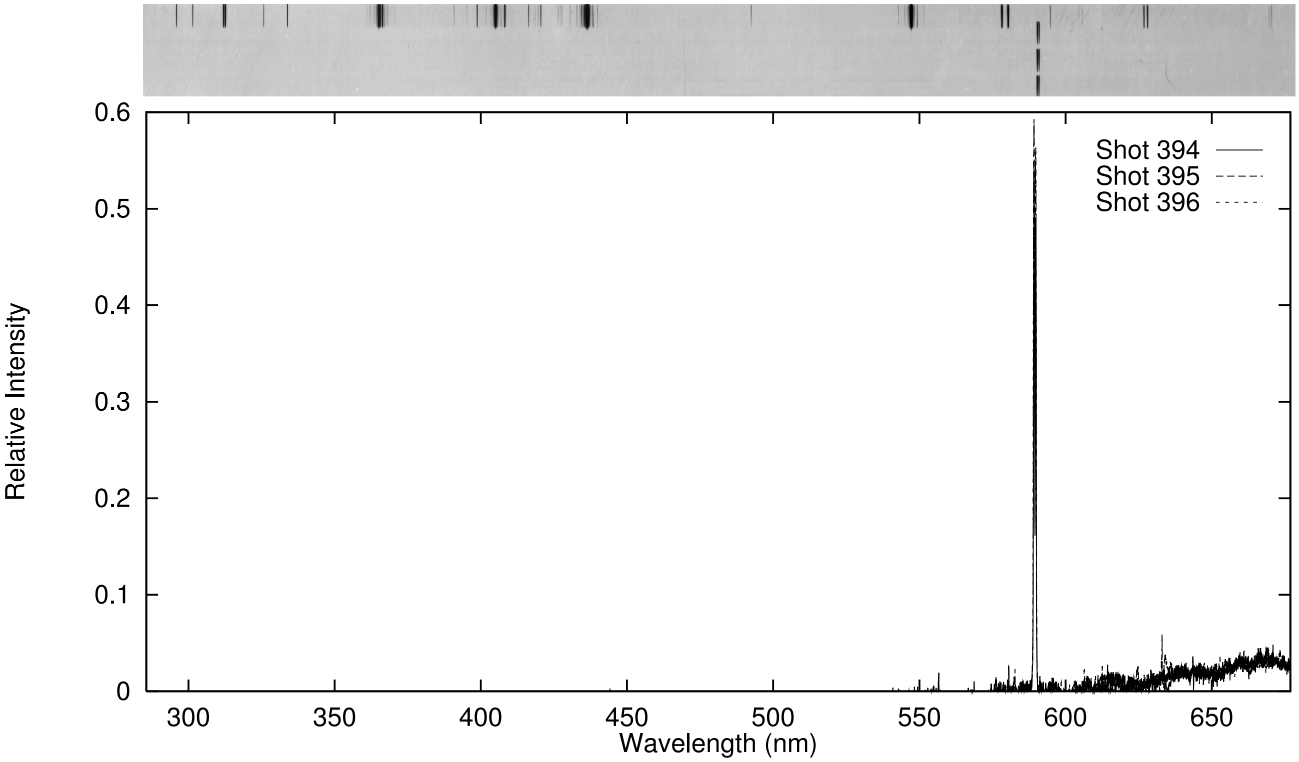

Figure 11: Shot 394 - H_2+2O_2, 101 kPa; Shot 395 - H_2+2O_2, 101 kPa; Shot 396 - H_2+2O_2, 101 kPa

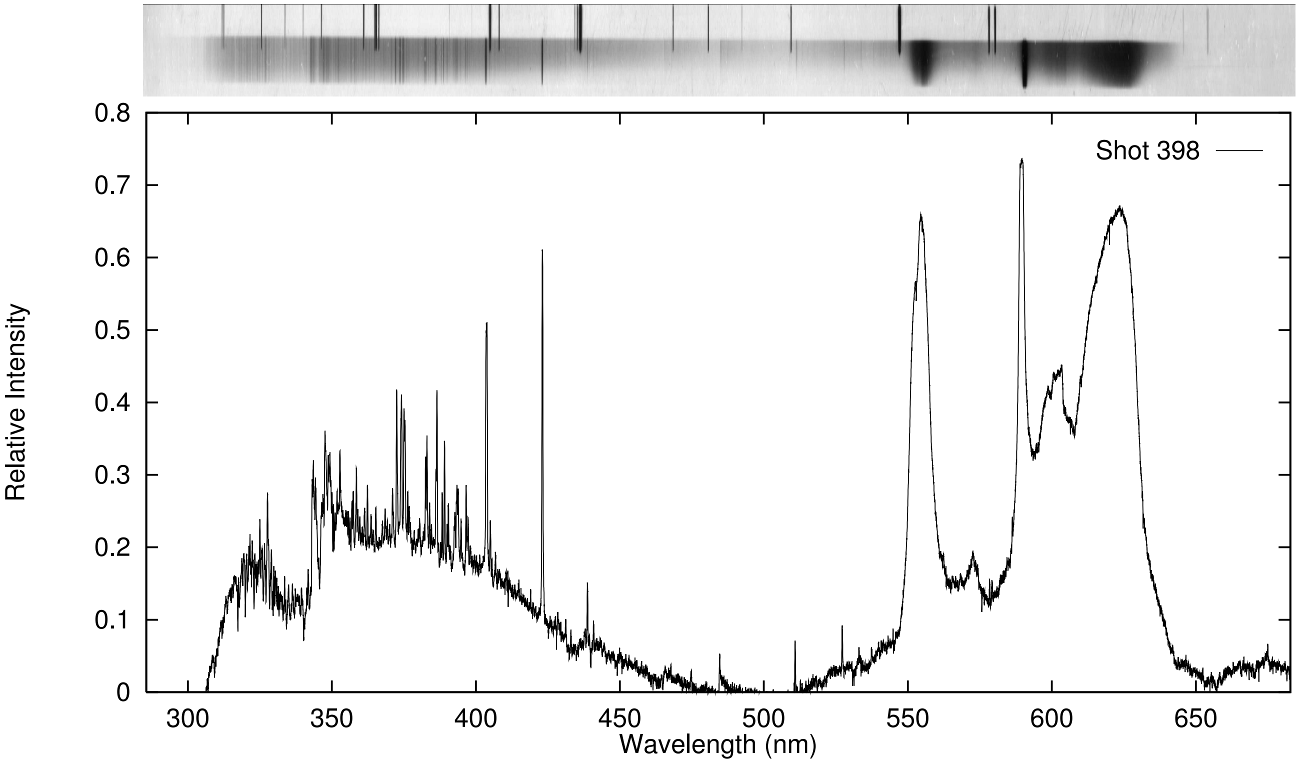

Figure 12: Shot 398 - $2H_2+O_2$, 101 kPa

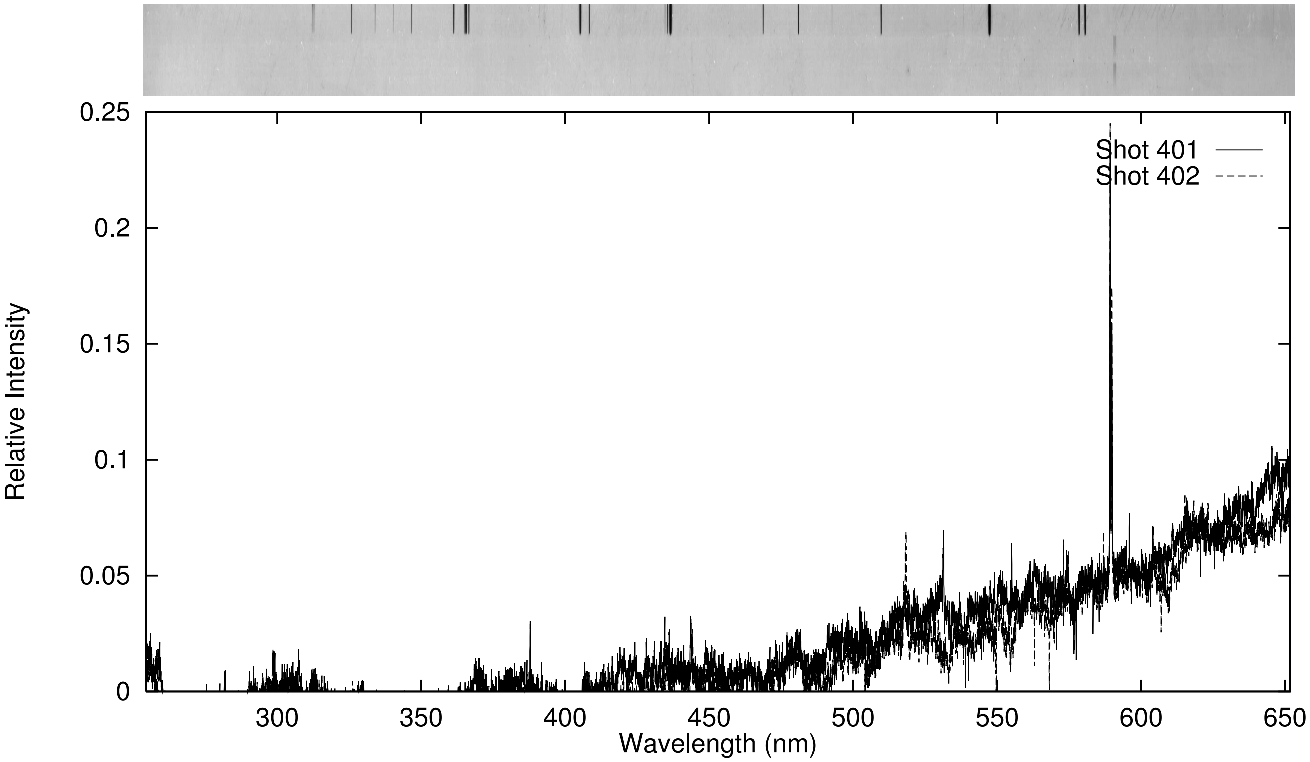

Figure 13: Shot 401 - $0.08H_2+N_2O$, 71 kPa; Shot 402 - $0.07H_2+N_2O$, 71 kPa

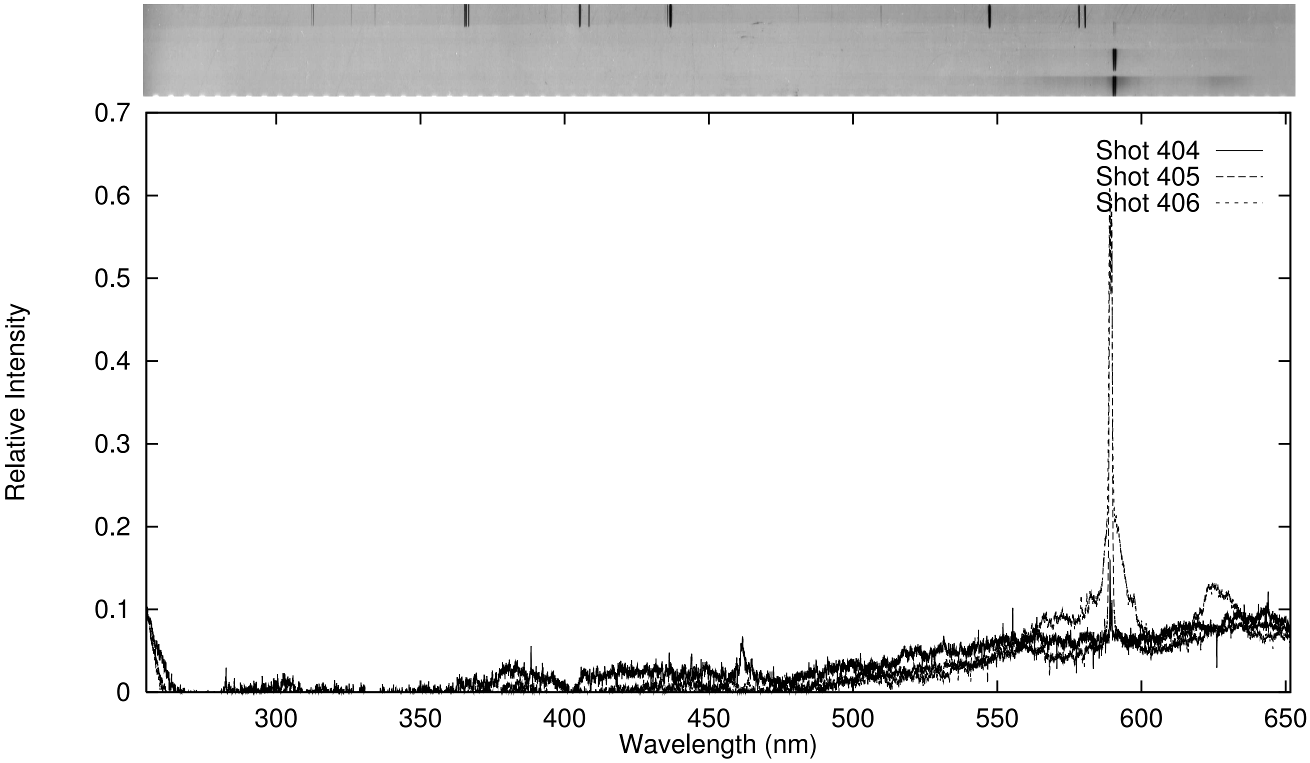

Figure 14: Shot 404 - $0.15H_2+N_2O$, 71 kPa; Shot 405 - $0.1C_6H_6+0.9H_2+1.2O_2+4.512N_2$, 101 kPa; Shot 406 - $C_6H_6+7.5O_2+28.2N_2$, 101 kPa

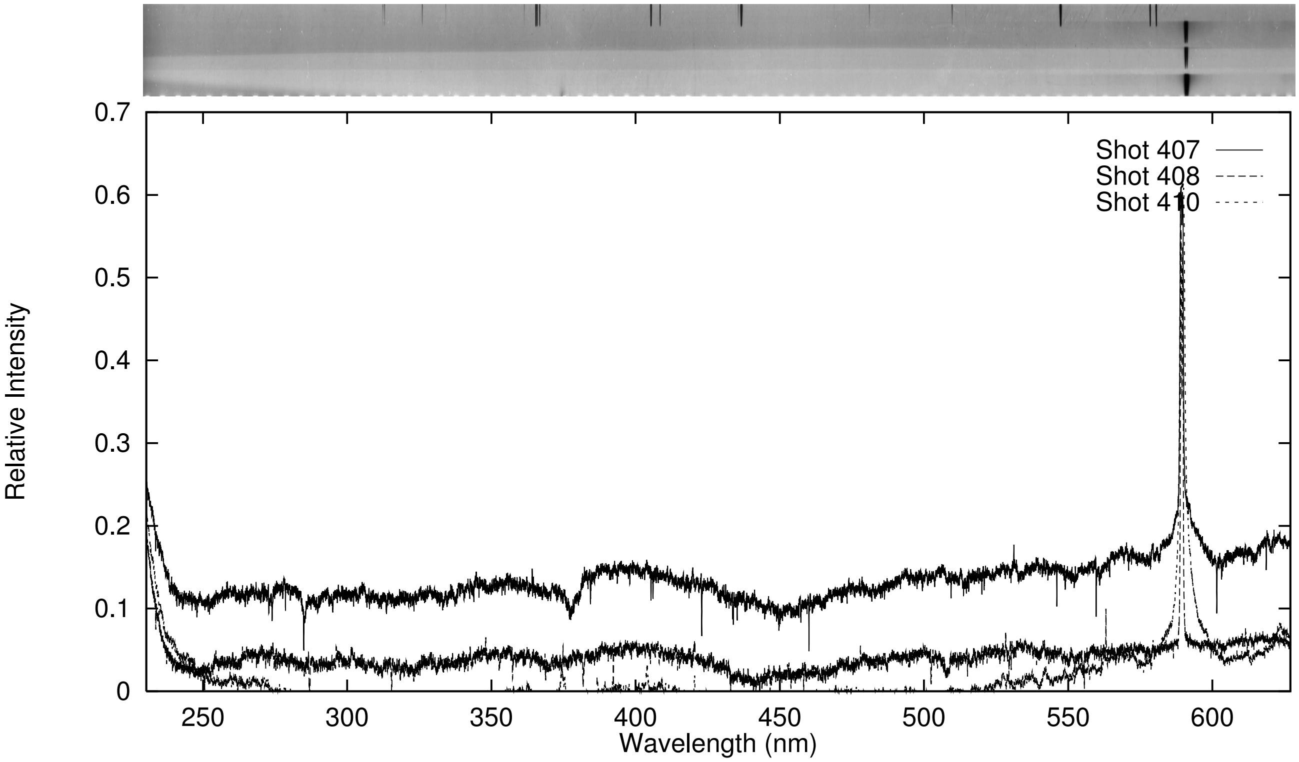

Figure 15: Shot 407 - $0.4C_6H_6+0.6H_2+3.3O_2+12.4N_2$, 101 kPa; Shot 408 - $0.2C_6H_6+0.8H_2+1.9O_2+7.14N_2$, 101 kPa; Shot 410 - $0.6C_6H_6+0.4H_2+4.7O_2+17.7N_2$, 101 kPa

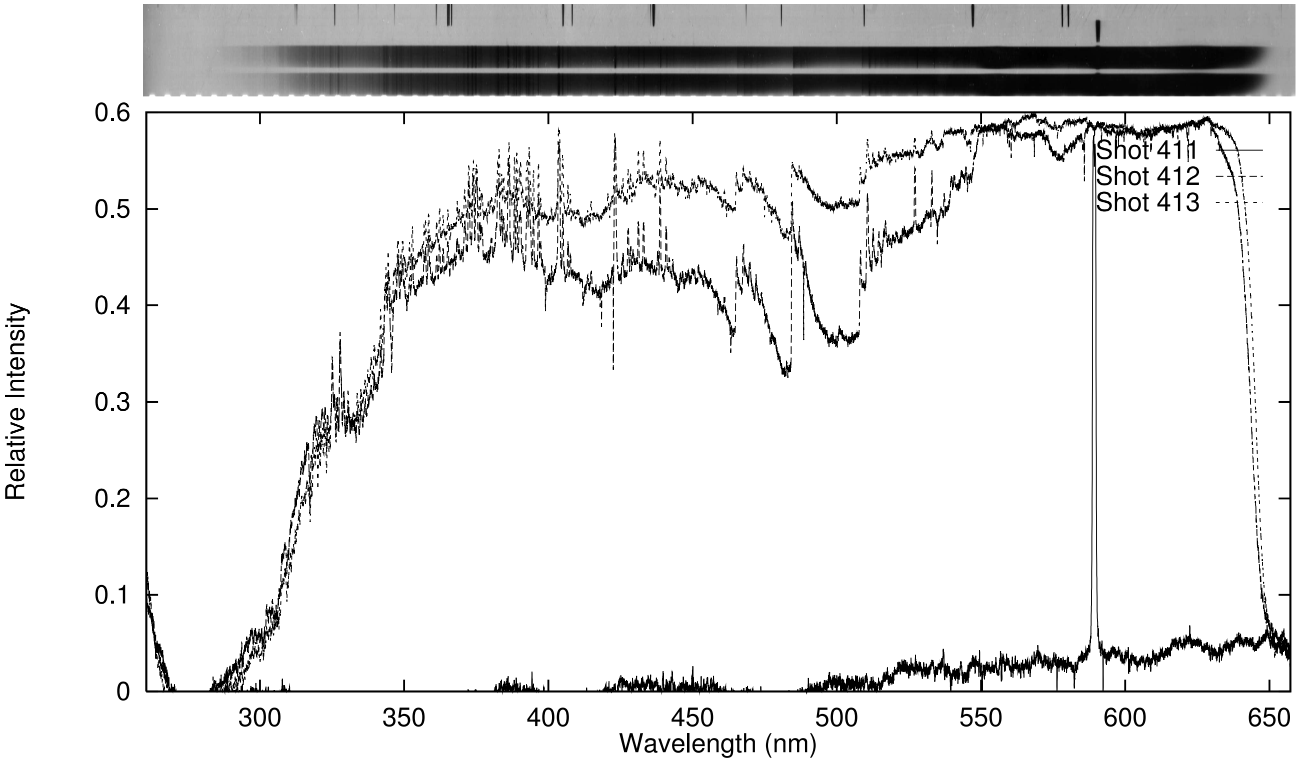

Figure 16: Shot 411 - $H_2+0.5O_2+1.88N_2$, 101 kPa; Shot 412 - $2H_2+O_2$, 101 kPa; Shot 413 - $2H_2+O_2$, 101 kPa

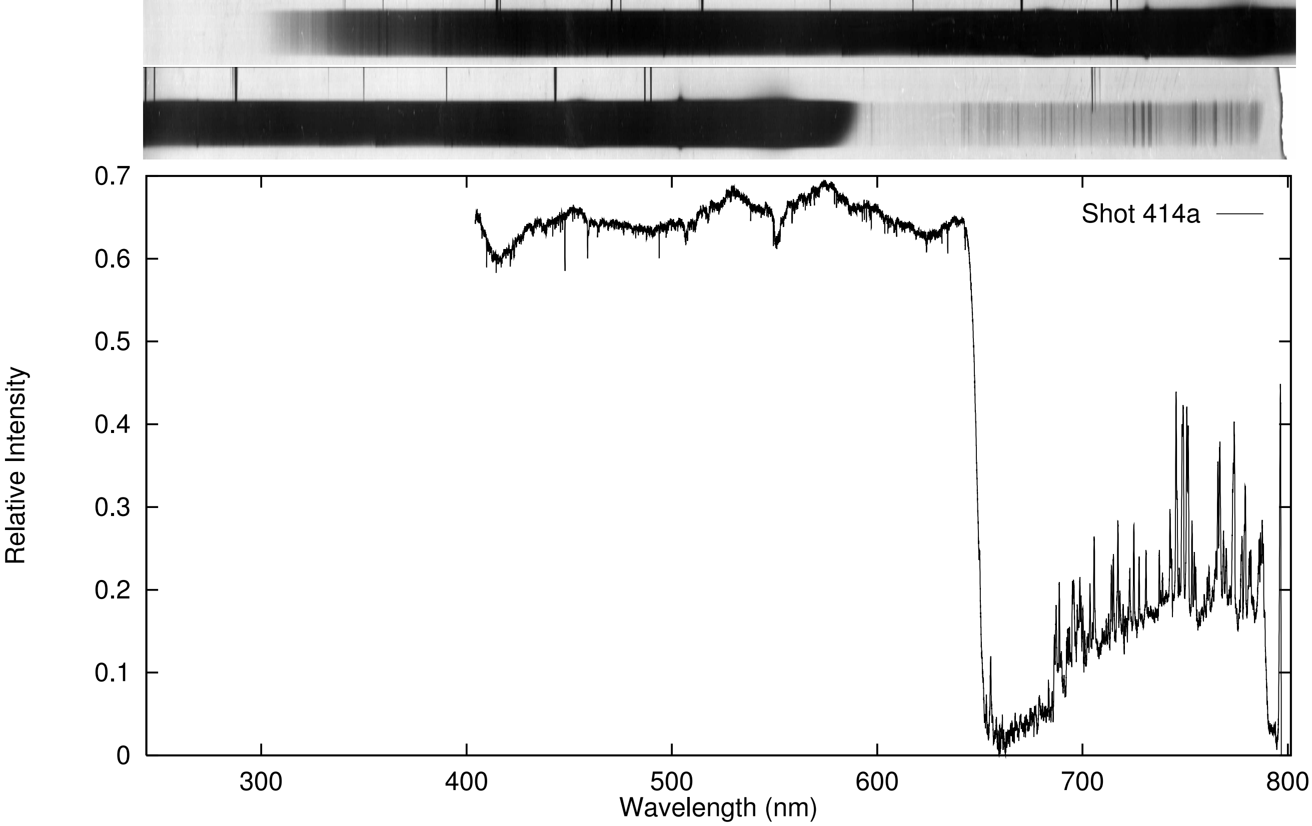

Figure 17: Shot 414 - $2H_2+O_2$, 101 kPa

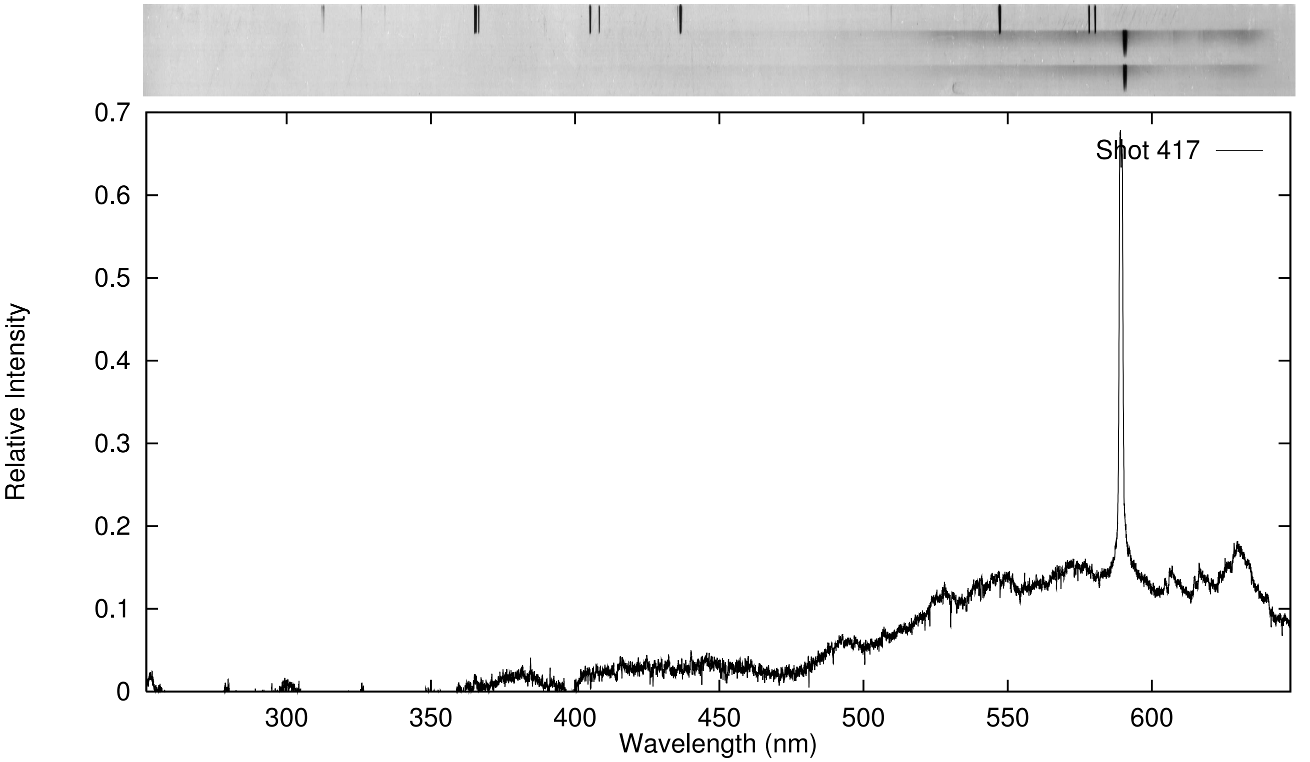

Figure 18: Shot 417 - $0.124H_2+N_2O$, 71 kPa; Shot 418 - $0.25H_2+N_2O$, 71 kPa

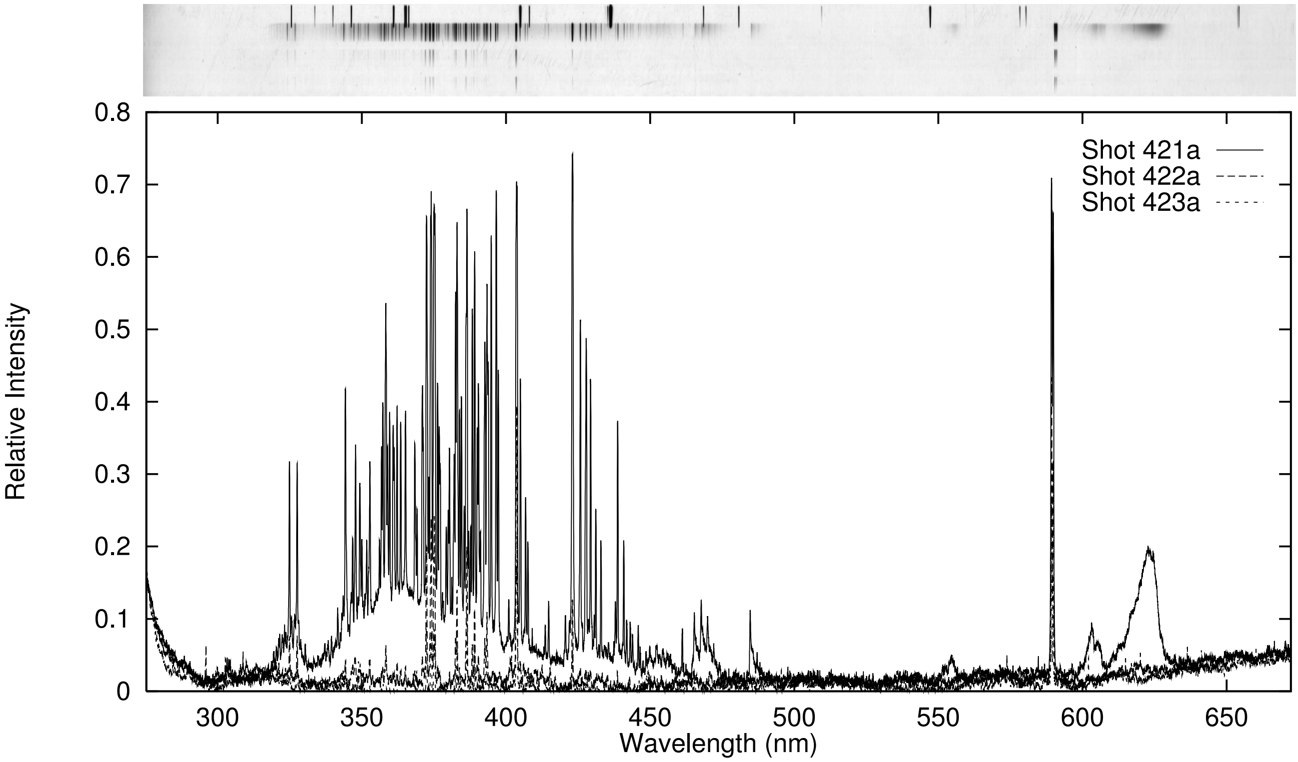

Figure 19: Shot 421 - 2.72C_2H_2+O_2, 5.85 kPa, IR Film; Shot 422 - 2H_2+O_2, 20 kPa, IR Film; Shot 423 - 2H_2+O_2, 20 kPa, IR Film

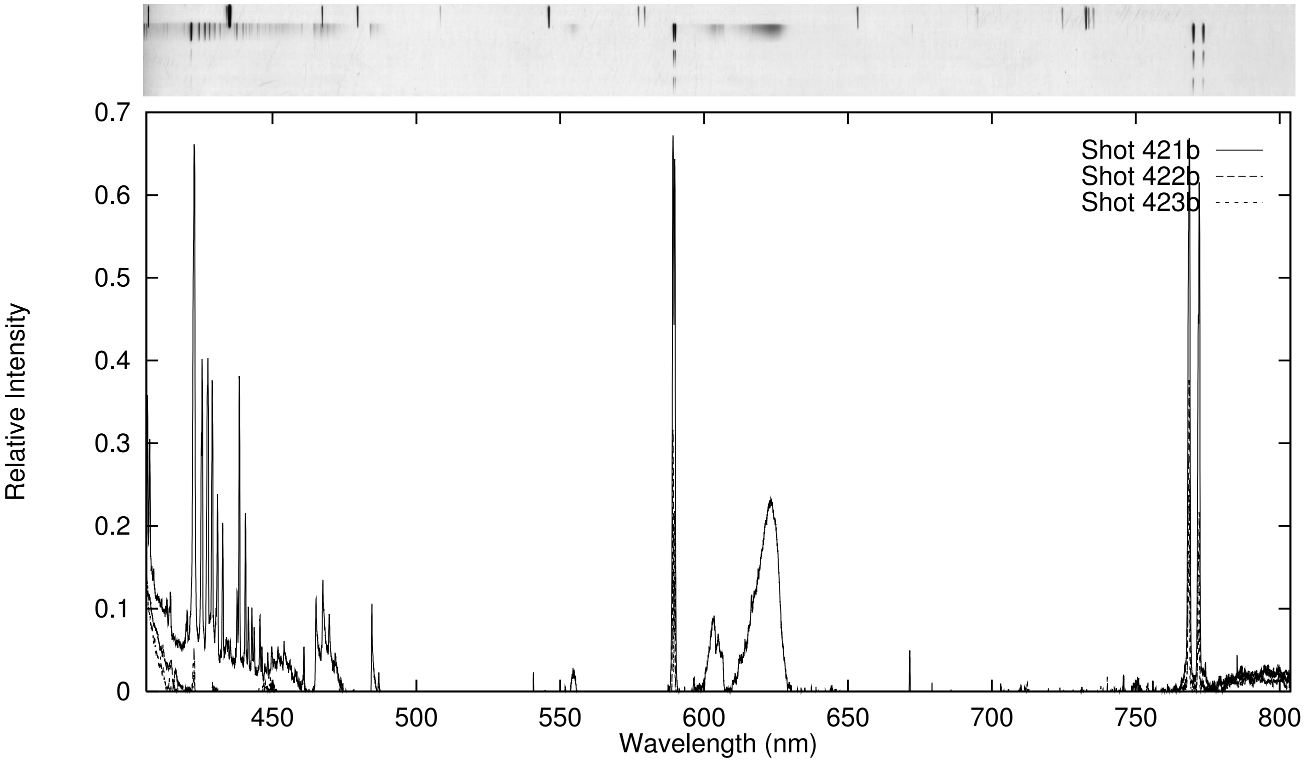

Figure 20: Shot 421 - 2.72C_2H_2+O_2, 5.85 kPa, IR Film; Shot 422 - 2H_2+O_2, 20 kPa, IR Film; Shot 423 - 2H_2+O_2, 20 kPa, IR Film

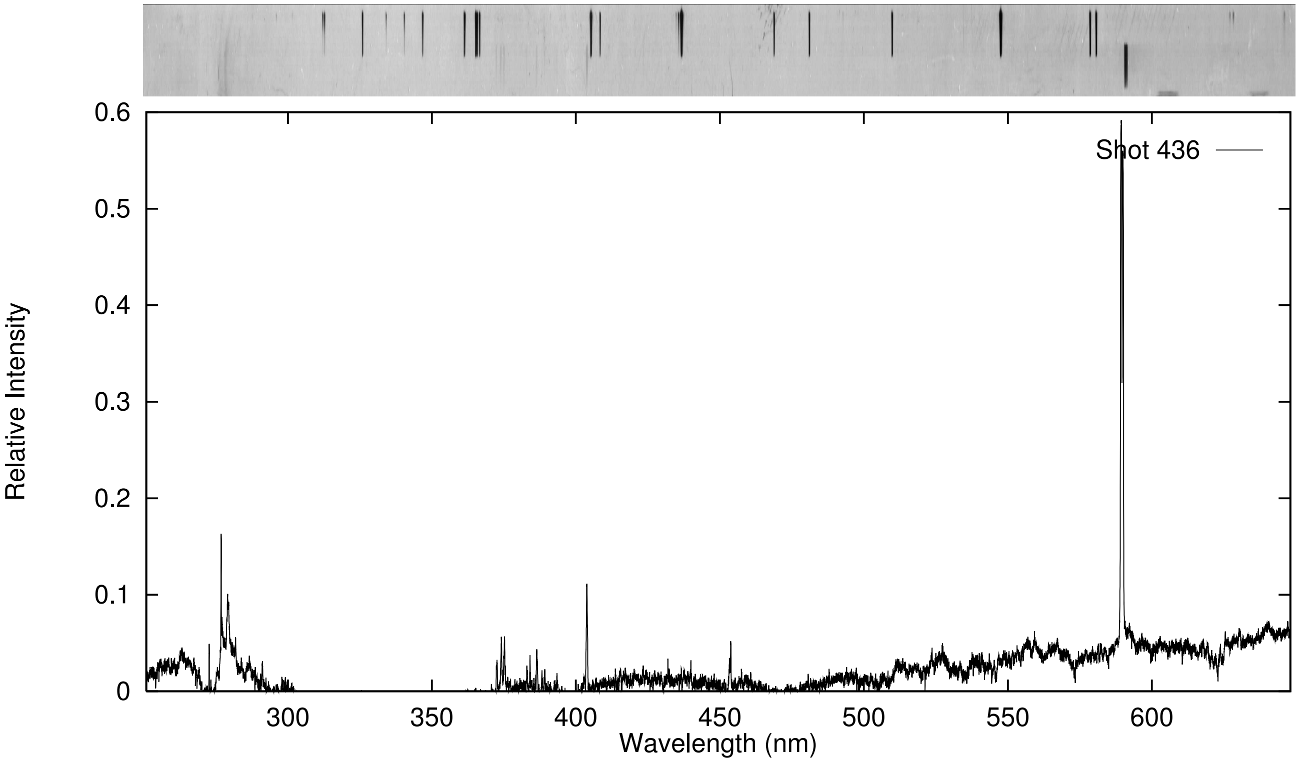

Figure 21: Shot 436 - $2H_2$+O_2, 20 kPa

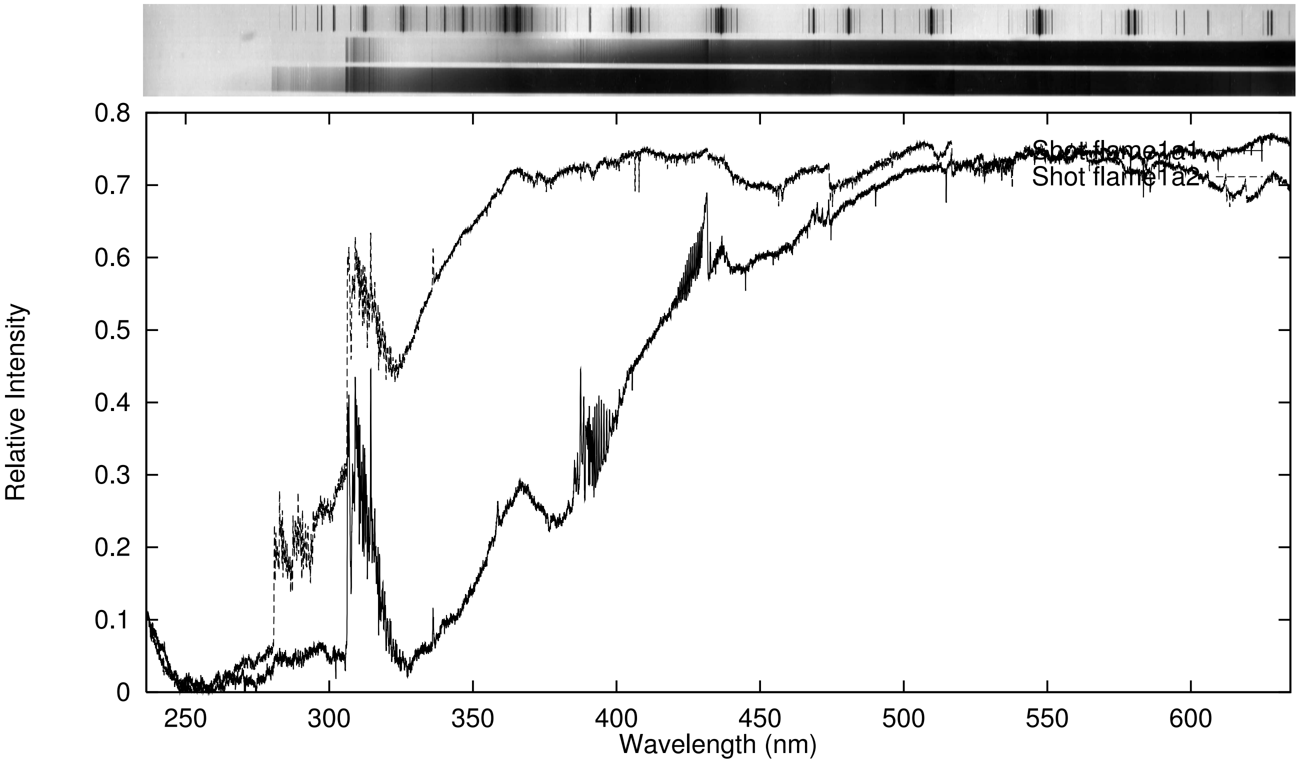

Figure 22: Flame 1a1 - C_2H_2+O_2 Flame, 100 kPa; Flame 1a2 - C_2H_2+Air Diffusion Flame, 100 kPa

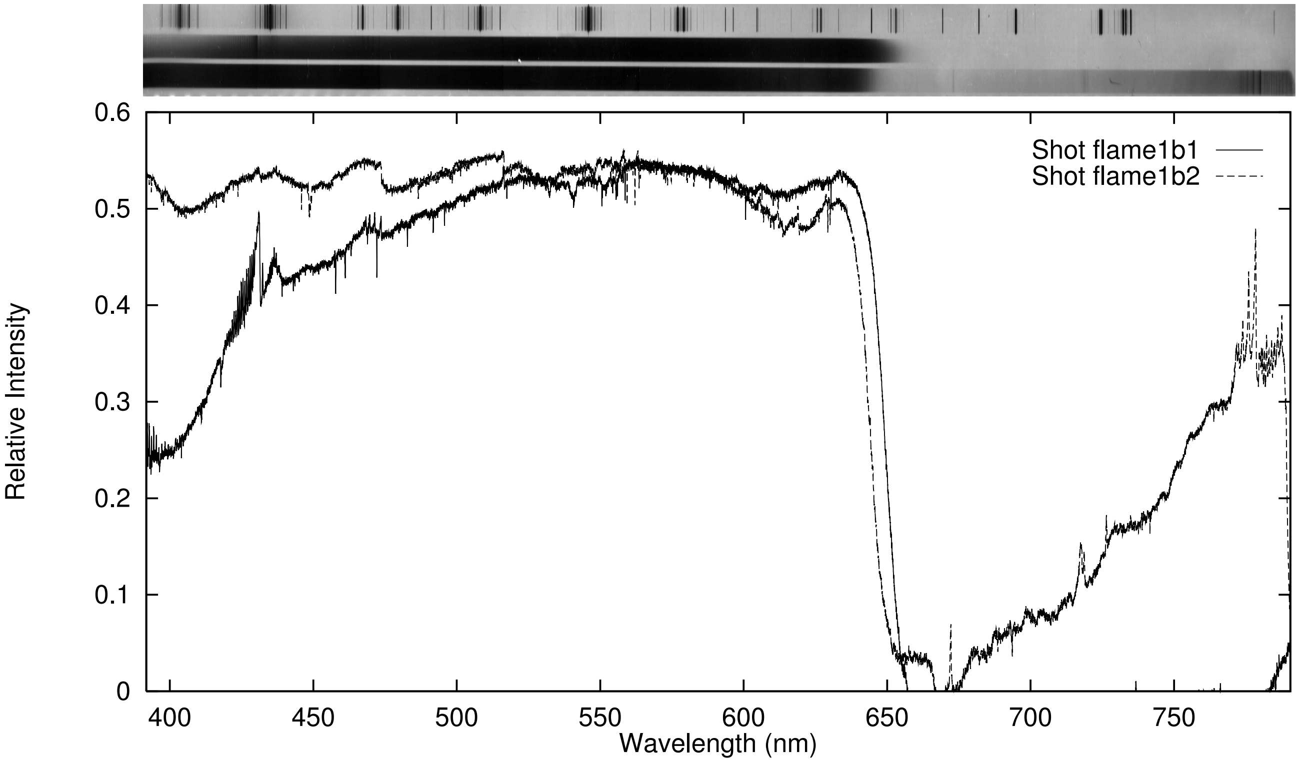

Figure 23: Flame 1b1 - $C_2H_2+O_2$ Flame, 100 kPa; Flame 1a2 - C_2H_2+Air Diffusion Flame, 100 kPa

7 Spectral line identification

Thus far, exhaustive and conclusive identification of spectral lines in all shots, nor even all mixtures for which spectra have been taken, have not been performed. For the purposes of this document, one spectrum has been extensively examined and others have been surveyed for interesting and distinct lines.

7.1 Notation

Some shorthand notation is used to describe spectral lines:

R	Bandhead degraded to the red
V	Bandhead degraded to the violet
[]	Intensity from discharge (in atomic spectra)
F	Intensity from flames

7.2 Calibration

Naturally the precision with which spectral lines can be labeled and thus the accuracy with which they can be identified is limited by the precision and accuracy of the wavelength calibration. This fact is actually quite important because there are some difficulties that make calibration tricky and because the number of tabulated lines that must be considered as matches for observed lines can be drastically reduced if the wavelength uncertainty can be decreased. Currently, with care, wavelengths measured from our films can be stated with an uncertainty of around 0.3 nm. Note that this limitation derives from the calibration imprecision. The current limit on scan resolution is about 0.024 nm, spectral lines typically appear about 0.5 nm wide, and features as small as 0.05 nm can theoretically be discriminated. In contrast, tables of lines give wavelengths to at least 0.001 nm precision.

Calibration uncertainty arises from two effects: difficulty of unequivocally identifying some calibration lamp lines, and apparent variation in the wavelength-film position relationship. There are some very strong lines in the mercury-cadmium lamp that can be easily identified, but these are often overexposed and very broad, or consist of several closely spaced lines. Also, not all lines are equally useful, since farther spaced lines result in a more accurate calibration. In any case, use of isolated, narrow (not overexposed), distant lines is preferable. Calibration line identification is further complicated by the large number of weak lines that are tabulated and the possibility of the presence of impurities (typically electrode material or bulb gas). A plot of the lines used for calibration is given in Fig. 24, below. This difficulty can be overcome with careful examination of tabulated lines.

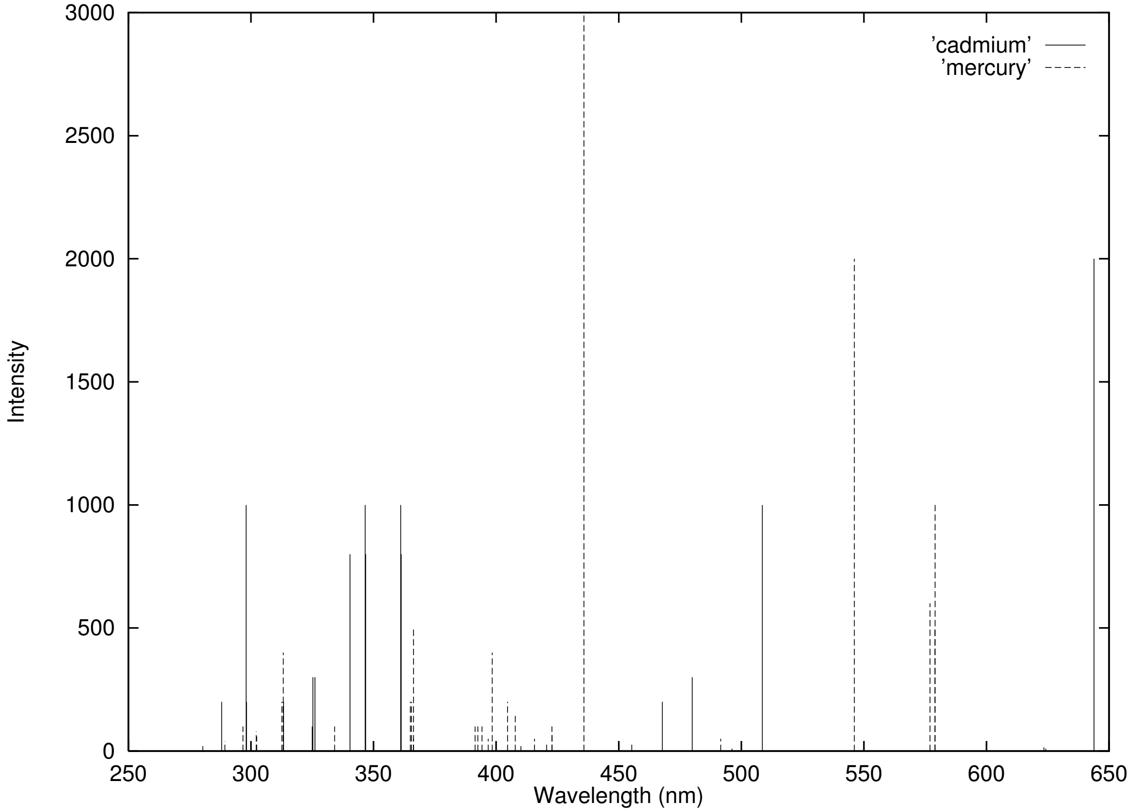

Figure 24: Mercury-Cadmium Calibration Lines

Checking the consistency of different calibration lines shows a variation between interpolated and expected wavelengths of up to 0.3 nm. This suggests that the relationship between line positions in the digitized spectra and wavelength is not strictly linear. To account for this is substantially more involved than the previous problem, but can be accomplished by using least squares fitting of a number of lines to a non-linear function such as a polynomial or spline.

7.3 Notes

- Shots 364 and 365 show relative motion.
- What is the hump typically visible in the data around 375 nm? It could be the continuous emission typical of CO-Air and propane-air flames, although it shows up in shots ostensibly containing no carbon. Can the magnitude of the hump be correlated with the sootiness of the tube?
- The peak(s) at 589 nm could also be C_2, except that they show up equally strongly in all shots, irregardless of carbon content. The C_2 emission here is probably present but masked by Na.
- Wien's Law:

  $$\lambda_{max} T = 2897.8\ \mu m \cdot K$$

  so black body radiation corresponding to the the CJ temperature would be around 800 nm and higher.
- Argon lines should be weak to nonexistent in the 300-600 nm range.
- Element data and molecular data are from different sources. Intensity data are normally imprecise, particularly when comparing different types of radiation sources, and especially between different references.

7.4 Shot 363

Table 1 gives some tentative identifications of lines found in acetone-oxygen-argon detonations, from shot 363.

Table 1: Shot 363 observed lines and tentative identifications

Measured λ	Candidate Species	Tabulated λ	Tabulated Intensity
306.3 R	OH	306.36 R	10
324.8	Ar	324.982	[25]
	CO	324.21 V	6
	CO_2	324.69 R	8
327.5	CO_2	326.46 R, 326.99 R	7, 7
	Ar	327.336	[5]
372.4	Ar	372.929	[200]
374.9 V	Ar	374.692, 375.050	[5], [5]
382.8	O_2	382.9 R	8
	C_2	382.56 V	6
	Ar II	383.043	[10]
386.3	Ar	386.426	[10]
388.9	CH	388.9 R	4
393.3	Ar	393.255	[25]
403.5	C_2	404.18 V	3
	CH	402.53 R	3F
404.8	CO_2	404.89 R	5
422.9	Ar	422.818, 422.989	[40], [10]
438.7	C_2	438.25 V, 437.14 V	2, 3
	CO	438.03 V	[7]
484.5	CO	483.53 V	[10]
510.7	C_2	509.77 V	2
532.8	CO	533.05 R	[5]
554.0	C_2	554.07 V	5
572.9 V	CN	573.02 R	5
588.7	Na	588.9953	9000
	C_2	587.8 Hi Press.	5
589.6	Na	589.5923	5000
	C_2	589.93 Hi Press.	10
603.2 V	CO	603.7 R	[8]
624 D	CO	624.4 R	[5]

Table 2 lists some lines expected in hydrocarbon detonations like shot 363, for comparison with Table 1.

7.5 Shot 379

Table 3 gives tentative identifications of lines observed in acetylene-oxygen detonations, from shot 379.

7.6 Shot 381

Table 4 gives tentative identifications of lines observed in hydrogen-oxygen detonations, from shot 381.

7.7 Oxy-Acetylene Welding Torch and Acetylene-Air Diffusion Flames

Table 5 gives tentative identifications of lines observed in acetylene-oxygen and acetylene-air flames.

References

Bradley, J. (1962). *Shock Waves in Chemistry and Physics.* New York: John Wiley & Sons Inc.

Table 2: Shot 363 expected lines

Species	Wavelength	Intensity
C_2 Swan	516.5 V	10F
	512.93 V	7F
	473.7 V	9F
	471.52 V	8F
	438.25 V	2F
	469.76 V	6F
High Pressure C_2	589.93 V	10
	587.8	5
	543.49 V	3
	468.02 V	10
	466.3	6
	436.88 V	5
CHO	329.92 R	10F
	373.05 R	5F
C	426.727	500
	426.702	350

Table 3: Shot 379 observed lines and identification

Measured λ	Candidate Species	Tabulated λ	Tabulated Intensity
465.0 R	CO	466.13 V	5
484.4 R	CO	482.35 R	8
508.0 R	CO	507.09 R	8

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Table 4: Shot 381 observed lines and identification

Measured λ	Candidate Species	Tabulated λ	Tabulated Intensity
324.9	CO_2	324.69 R	8
	CO	324.21 V	6
327.5	CO_2	326.99 R	7
	CO_2	326.46 R	7
	Cu	327.3962	3000
344.2	OH	342.81 R	4F
	Ar	344.258	[10]
	Cu	344.0507	10
	O	344.04	[20]
403.3	CH	402.53 R	3F
403.6	O_2	402.1 R	7F
	Ar	403.297	[20]
	Ar	403.383	[30]
438.5	C_2	438.25 V	2F
	CO	438.03 V	7
	C_2	437.14 V	3F
	Fe	438.3547	1000
440.6	CO	439.31 V	8
	NCO	440.36 V	10
	Fe	440.4752	1000
465.0 R	CuH	464.84 R	6
	Cu	464.9266	60
	O	464.9148	[300]
484.4 R	N_2	483.71 R	10
510.6	C_2	509.77 V	2F
	Fe	510.7452	100
	Fe	510.6441	25
	Cu	510.5541	500
532.8	CO	533.05 R	5
	N_2	532.69 V	5
	O	532.898	[100]
	O	532.959	[150]
	O	533.066	[500]
	Fe	532.805	400
	Fe	532.4182	400
553.8 D	C_2	554.07 V	5F
588.9	Na	588.9953	9000
	C_2	587.8 Hi Press.	5
589.5	Na	589.5923	5000
	C_2	589.93 Hi Press.	10

Table 5: Acetylene-Air diffusion flame lines and identification

Measured λ	Candidate Species	Tabulated λ	Tabulated Intensity
280.9 R	OH	281.13 R	8F
306.3 R	OH	306.36 R	10F
336.1	NH	336.0	10F
387.5	CH	387.13	6
	CN	387.14 V	8F
388.6	CH	388.90	5
431.5 V	CH	431.42 V	10f
473.9 V	C_2	473.71 V	9F
516.0 V	C_2	516.52 V	10F
550.0	C_2	550.19 V	3F
563.6	C_2	563.55 V	9F
612.0	C_2	612.21 V	3F
618.9	C_2	619.12 V	4V
672.5 V	CO	680.4 R	8
	CO	668.57 R	7
	N_2	678.86 V	6
718.2 V	H_2O	716.45 R	6F
	C_2 Hi Press.	708.32 V	4
778.9 V	NO	778.76 V	5
	N_2	778.0 R	10
	OH	775.58 R	10F