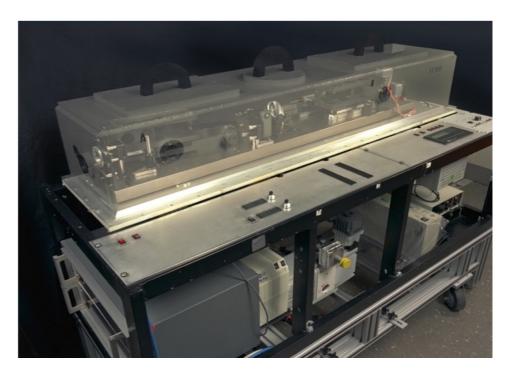
A New Approach to the Analysis of Experimental Atomic Spectra

Christian Clear, Jacob Ward, Gillian Nave

Dedicated to James E. Lawler, 1951 - 2023

29 years of Fourier transform spectroscopy at NIST



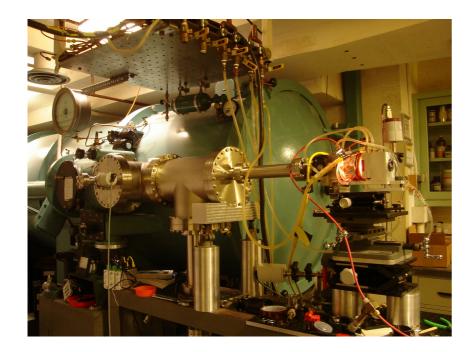


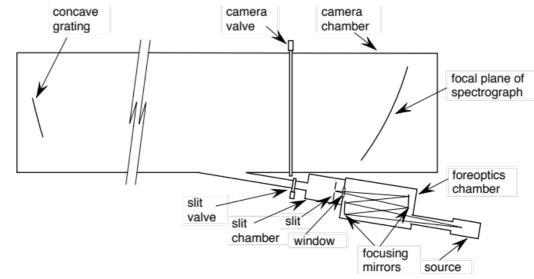
2-m FTS. Wavelength range 2200 Å – 5.5 μ m. Resolution 0.0025 cm⁻¹ (4 million at 1 μ m).

Brought to NIST in 1994 from Los Alamos National Laboratory by Craig Sansonetti and Joseph Reader Vacuum ultraviolet FTS. Wavelength range 1400 Å- 9000 Å. Resolution 0.025 cm⁻¹ (2 million at 2000 Å).

Brought to NIST in 1996 by Ulf Griesmann

Normal Incidence Spectrograph





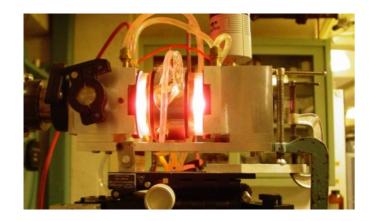
Normal incidence vacuum spectrograph.

Wavelength range: 300 Å - 5000 Å.

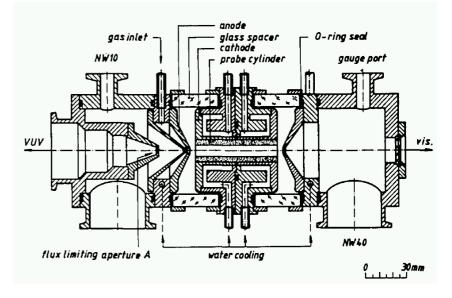
Resolving power: $\approx 150000 (1^{st} order)$ with photographic plates.

Also used with image plates at lower resolution

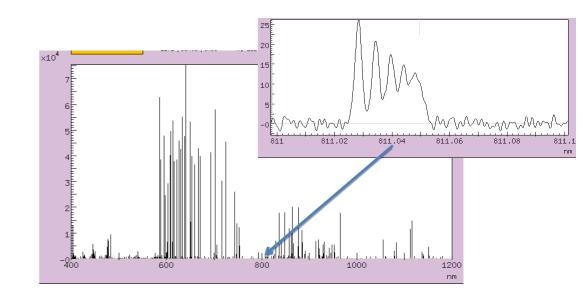
Hollow cathode lamps



High current (1-2 A) hollow cathode source.



Danzmann, Fischer, Kock, Kühne, Apl Opt. 27, 4947 (1988)





Commercial (10-20 mA) hollow cathode lamp

A typical spectrum of an irongroup element will contain several thousand lines

Sources for higher ionization stages





Penning discharge source. Suitable for singly-ionized and doubly-ionized spectra. Sliding spark source used to excite doubly-ionized through seven-times ionized spectra.

Rare Earth Elements (1996 - 2003): Measurements for Lighting Industry

- Metal halide lamps were the main sources used in commercial lighting, for street lights, stadiums, large commercial buildings, and more.
- Many had a poor color (e.g. sodium lamps, with a yellow color), and the ones with better color had poor efficiency.
- Both color and efficiency can be improved by adding rareearth elements – dysprosium, holmium. These have very complex spectra.
- Better wavelengths, energy levels, and transition probabilities required.



M. E. Wickliffe, J. E. Lawler, G. Nave,"Atomic transition probabilities for Dy I and Dy II," Journal of Quantitative Spectroscopy and Radiative Transfer 66, 363 (2000).

G. Nave, U. Griesmann, "New energy levels and classificiations of spectral lines from neutral and singly-ionized dysprosium (Dy I)," Physica Scripta 62, 463 (2000).

G. Nave, "Atomic transition rates for neutral holmium (Ho I)", J. Opt. Soc. Am. B 20, 2193 (2003).

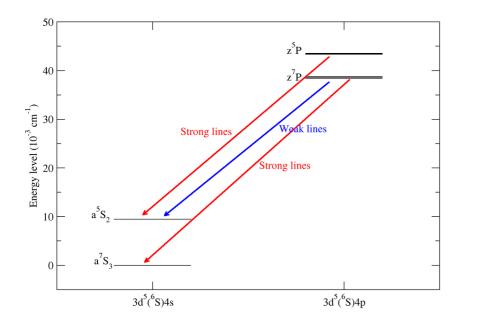
Measurements for astrophysics: Wavelengths and energy levels for Sc II-Ni II

| lon | Previous | Our work | |
|---------------------------------|----------|-------------------------------------|---|
| Fe II | 1978 | Completed | Nave & Johansson (2011) |
| Cr II | 1951 | Completed | Sansonetti & Nave (2014) |
| Mn II | 1964 | Completed | Liggins et al. (2021) |
| Ni II | 1970 | Publications in progress | Clear, ICL PhD Thesis (2022, 2023) |
| Sc II | 1980 | Publication in progress | Hala & Nave (2023) |
| Co II | 1998 | Spectra recorded, analysis begun | |
| VII | 1988 | Completed | Thorne et al. (2013) |
| Ti II | 1982 | Completed | Saloman (2012) |
| HFS (Mn II, Co II, Sc II) | | Completed | Townley-Smith et al. (2016), Lawler et al. (2016), Ding (2020), Hala (accepted) |

Complications

- Large number of lines and energy levels.
- Hyperfine or isotope structure
- Self Absorption / Self Reversal
- Mis-identified lines
- Blends
- Incorrect uncertainties
- Inaccurate calculations
- Problems in lines connected to levels

Connecting ground level in Mn II Liggins et al. 2021, ApJS 252:10



The intercombination lines connecting the quintet system to the septet system are weak.

Care is needed otherwise all of the quintet levels will be wrong!

In our highest current spectra, we have good SNR for the intercombination lines. But the LS-allowed strong lines are too strong to be usable!

Combining several different spectra and paying close attention to the wavelength calibration is necessary to get this right.

Spectra recorded using NIST FT spectrometers

| Spectra | Purpose |
|---|--|
| | |
| Lanthanides: Ce, Tb, Dy, Ho | Atomic data for lighting (WI, TP, En, HFS) astrophysics. |
| Iron group elements: Sc-Cu, mainly I-II, some III | Atomic data for astrophysics (WI, TP, En, HFS), Wavelength standards |
| Noble gases: He-Xe | Atomic data, wavelength and intensity calibration of spectra |
| Others: F,Na,Al,Si,K,Ge,Ag,Pt | Many of these for wavelength calibration varying to atomic clocks (Ag) to astronomical spectra (Pt) |
| Actinides: Th, U | Wavelength calibration of spectrographs on ground- based telescopes |
| Molecules: I ₂ , S ₂ , HCN, CO, C ₂ H ₂ , | Wavelength calibration of astronomical spectrographs in visible (I_2) & IR (HCN,CO,C ₂ H ₂); atmospheric chemistry (S ₂). |
| Others | Laser-frequency comb for calibration of IR astronomical spectrograph; Fiber Fabry-Perot for calibration of visible astronomical spectrograph |

Use of archival spectra for Cr II transition probabilities

| Table | 1. | Table | of | Spectra |
|-------|----|-------|----|---------|
|-------|----|-------|----|---------|

| ID | Date | Wavelength | Wavenumber | Coadds | Resolution | Gas | Pressure | Current | Detector | Calibration | Comments |
|----|-------------------|-------------|----------------------|--------|----------------------|---------------------|----------|---------|----------|-----------------|-----------------------|
| | | Range | | | | | | | | Lamp | |
| | | (nm) | (\mathbf{cm}^{-1}) | | (cm^{-1}) | | (Pa) | (A) | | | |
| 1 | 2000 Oct 27 #1 | 183 to 317 | 31500 to 54600 | 64 | 0.08 | Ar | 80 | 0.7 | R7154 | $D_2 \# BQ0057$ | $_{ m HCL}a$ |
| 2 | 2000 Oct 27 $\#3$ | 183 to 317 | 31500 to 54600 | 64 | 0.08 | Ar | 85 | 1.5 | R7154 | $D_2 \# BQ0057$ | $_{ m HCL}a$ |
| 3 | 2000 Nov 06 $\#1$ | 249 to 400 | 25000 to 40100 | 64 | 0.033 | Ar | 85 | 0.7 | R106UH | $D_2 \# BR0065$ | $_{ m HCL}a$ $_{11}b$ |
| 4 | 2000 Nov 06 $#3$ | 183 to 320 | 31200 to 54600 | 128 | 0.09 | Ar | 85 | 1.5 | R7154 | $D_2 \# BR0065$ | $_{ m HCL}a$ |
| 5 | 2000 Nov 07 #1 | 183 to 317 | 31500 to 54600 | 128 | 0.06 | \mathbf{Ar} | 85 | 1.5 | R7154 | $D_2 \# BR0065$ | $_{ m HCL}a$ |
| 6 | 2000 Nov 07 $\#2$ | 183 to 317 | 31500 to 54600 | 64 | 0.06 | \mathbf{Ar} | 85 | 0.7 | R7154 | $D_2 \# BR0065$ | ${}_{ m HCL}a$ |
| 7 | 2000 Dec 08 $\#1$ | 183 to 322 | 31000 to 54600 | 128 | 0.15 | Ne | 0.4 | 1.4 | R7154 | None | Penning 17^{b} |
| 8 | 2011 Jun 10 $\#7$ | 285 to 1207 | 8280 to 35000 | 107 | 0.02 | Ne | 400 | 2 | diode | W lamp IR456 | $_{ m HCL}a$ $_{18}b$ |
| 9 | 2016 Apr 24 #5 | 190 to 704 | 14200 to 52500 | 259 | 0.1 | Ne | _C | 0.02 | R106UH & | $D_2 \# V0236$ | HCL |
| | | | | | | | | | R636-10 | & W $\#$ IR456 | |

 a HCL: High current hollow cathode lamp

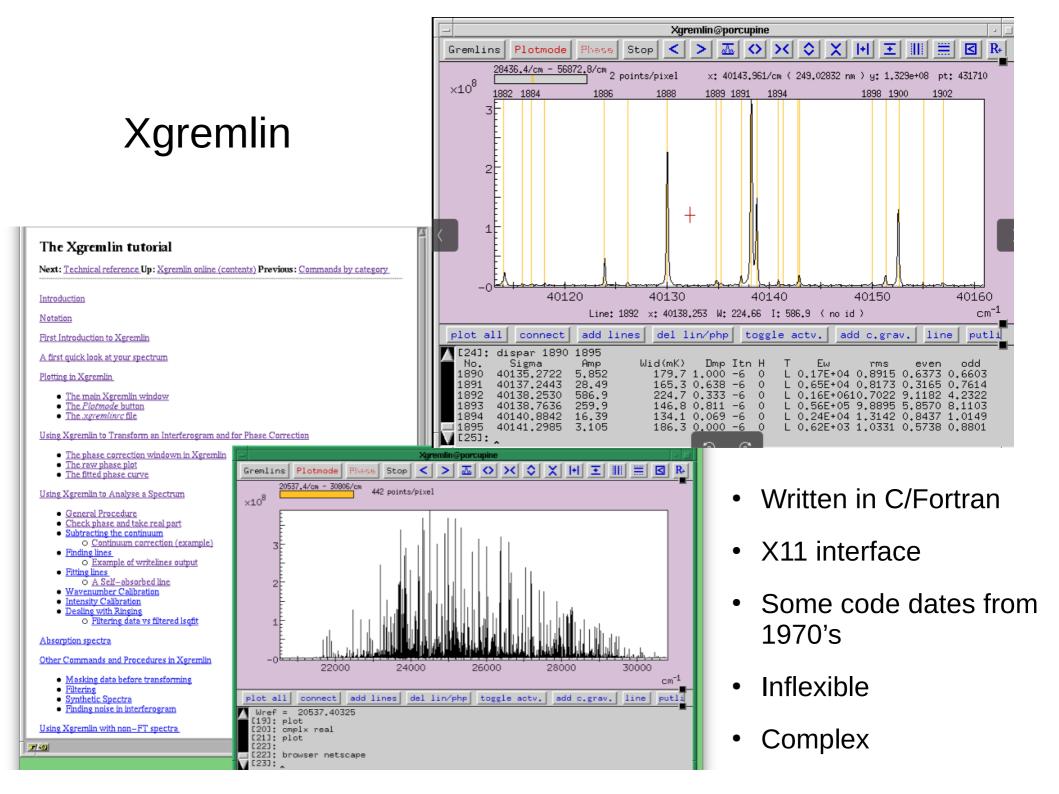
 b Number of spectrum in Table 2 of Lawler et al. (2017b)

 c Spectrum 9 was of a commercial Cr/Ne hollow cathode lamp and the gas pressure is unknown.

Spectra 1-7: Recorded in 2000 for TP work but never analyzed Spectrum 7: Radiometric calibration file was damaged Spectrum 8: Recorded for wavelengts/energy level work Spectrum 9: Low current lamp recorded to validate calibration of other files

Analysis challenges

- Too few people for analysis.
- Analysis of complex spectra (tens of thousands of lines, several hundred energy levels) has a steep learning curve and takes a long time to learn.
- Reliance on short-term students (both PhD and summer students).
- No continuity.
- Steep learning curve for current software.
- Different conventions for coding and matching atomic parameters (experiment and theory).



Analysis software

- Old code written in languages rarely taught (C, Fortran), but preserves key knowledge from experts. Many written for computers with small amounts of memory.
- Interfaces are platform specific (X11, Windows), and often not portable.
- Solution is every new person (student, intern) writes their own 'wrapper' specific to their platform and needs, that is often not easily understood by others and takes time out of a short summer project.
- Software does not preserve the analysis history of data, so the next student/intern cannot understand what has been done.

Solutions

- Data needs to be accompanied by code
- Version history of data and its processing needs to be conserved and easily accessible
- Needs to be common interface that is platform-independent and easily understood by new people
- Structure that is flexible enough that new analysis programs can easily be added to existing software

Heirarchical Data Format

- HF5 format consists of two structures:
 - Datasets (analogy a data file)
 - Groups (analogy a directory)

- Data are accompanied by metadata.
- More than one version of an analysis can be kept, so history of file processing can be preserved and easily accessed.

Example HDF5 file structure

| | | | | | HDFView | w 3.1.4 | | | | | | | | | | - | □ × | |
|---|---------------|---|--|-----------------|--------------|----------|-----------|----------|-------------|----------|-------------|--|----------|--------|---------|--------|-----------|---|
| File Window Tools Help | Crl | II leve | ls at /Levels/ | [Cr_BF2.h5 in | /home/gillia | an/wo | rk/SAAS/g | github/S | AAS] | x | | | | | | | | |
| 🖻 🗂 < 🖪 🗓 | Table | Impor | rt/Export Data | | | | | | | | - | | | | | | | |
| Recent Files /home/gillian/work/SAAS/github/SAA | | | -, | | | | | | | | ✓ Clear Te | | | | | | t | |
| ✓ BCr_BF2.h5 | 0-base | d | | | | | | | | | | | | | | | | |
| \sim \cong Calculations | | | | | | | | | | | | | | | | | | 1 |
| 🖺 Calculations from Raassen & Uylings | Attribute Cre | 1 | | | | (| | | | | ام | | | | | | | |
| ∼ '■Levels | Number of a | - | _ | | | | | | | | ` | | | Add At | tribute | Delete | Attribute | |
| in Cr II levels | Nome | | J | desig | energy | key | | lifetime | parity | species | uncertainty | | Volue | :01(_) | | | | |
| ✓ ■ Previous Identifications | Name | | 2.5 d | | 0.0000 | d5a6 | S2 | - | 1 | Cr II | 0.0007 | | Value[5 | 0]() | | | | |
| Cr II identifications from Sansonetti & Nav | | | | | 11961.7464 | 5D4s_a | | | | Cr II | 0.0005 | | TABLE | | | | | |
| ✓ ■ Spectra | FIELD_0_FI | | | | 12032.5447 | 5D4s_a | | | | Cr II | 0.0005 | | _ | | | | | |
| ~ | FIELD_0_N | | | | 12147.7713 | 5D4s_a | | | | Cr II | 0.0005 | | J | | | | | |
| ✓ intensity calibrated linelists | FIELD_1_FI | | | 5D4s_a6D3 | | 5D4s_a | | | | Cr II | 0.0005 | | | | | | | |
| Cr110600.001.wintcorr | FIELD_1_N | - | | | 12496.4565 | 5D4s_a | | | | Cr II | 0.0005 | | desig | | | | | |
| ~ spectrum | FIELD_2_FI | | | | 19528.2293 | 5D4s_a | | | | Cr II | 0.0005 | | | | | | | |
| spectrum | FIELD_2_N | - | | | 19631.2058 | 5D4s_a | | | | Cr II | 0.0005 | | energy | | | | | |
| > Cr110700.001 | FIELD_3_FI | - | | | 19797.8594 | 5D4s_a | | | | Cr II | 0.0005 | | | | | | | |
| ∼ 📹 Target levels | FIELD_3_N | | | | 20024.0117 | 5D4s_a | | | | Cr II | 0.0005 | | key | | | | | |
| ill z6F5 | FIELD_4_FI | | 2.5 d | | 20512.063 | | G2 | | | Cr II | 0.0005 | | | | | | | |
| | FIELD_4_N | 11 5 | 5.5 d | 15 <u>a</u> 4G5 | 20512.0959 | d5a4 | G5 | - | 1 | Cr II | 0.0007 | | lifetime | | | | | |
| | FIELD_5_FI | LL S | tring, | 1 = 1, | padding = H5 | I_SIK_NU | LLI | ±KM, cse | $t = H_{2}$ | L_CSET_A | SCII Scalar | | | | | | | |
| | | | | | padding = H5 | | | | | | | | parity | | | | | |
| | FIELD_6_FI | LL S | tring, | length = 1, j | padding = H5 | T_STR_NU | LLTE | ERM, cse | t = H57 | Γ_CSET_A | SCII Scalar | | | | | | | |
| | FIELD_6_N | AME S | tring, | length = 7, j | padding = H5 | T_STR_NU | ILLTE | ERM, cse | t = H51 | CSET_U | JTF8 Scalar | | species | | | | | |
| | FIELD_7_FI | LL S | tring, | length = 1, j | padding = H5 | T_STR_NU | LLTE | ERM, cse | t = H57 | Γ_CSET_A | SCII Scalar | | | | | | | |
| | FIELD_7_N | D_7_NAME String, length = 11, padding = H5T_STR_NULLTERM, cset = H5T_CSET_UTF8 Scalar | | | | | | | | | | | uncerta | inty | | | | |
| | NROWS | 64-bit integer Scalar | | | | | | | | | - | | | | | | | |
| TITLE | | | E String, length = 58, padding = H5T STR NULLTERM, cset = H5T CSET UTF8 Scalar | | | | | | | | | /Users/gnave/OneDrive - NIST/SAAS/githul | | | | | | I |
| VERSION | | | tring, | length = 3, 1 | padding = H5 | T STR NU | LLTE | ERM, cse | t = H51 | Г CSET U | JTF8 Scalar | | 2.7 | | | | | |
| | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | |

Very preliminary UI for BFs

| Branch | | | | | | | | | | | | | | | - 0 |
|--|--------------------|---------|-------------------|--------------|-------------------------------|--------------|--|---------------|--------------------------------------|----------------------|--------------------------------|----------------|--|---------------------|------------------|
| le Edit View Help esignation Energy (cm- | 1) Energy Unc. (cm | -1) J | Lifetime (ns) Lif | et 6 | 5.043435.00F | 200 <u>1</u> | | | | | | | Cr110700.001_r | | C 11070 |
| IF4p_24G5 65709.4418 | 0.0011 | | 4.42 0.0 | | Cr042416.005 | <u>_</u> | 1e9 Cr102700.001_r | 1e9 C | r102700.003_r | 1e9 Cr1 | 10600.001_r | 10 | 10 | 1 5- | e9 Cr11070 |
| IF4p_p4G4 65383.9035 | 0.0011 | 4.5 | 4.91 0.0 | 5 60 | 1 1 | | 4- | 5 - | | 2.0 - | | 1.0 - | | | |
| IF4p_24G3 65256.8513 | 0.0011 | 3.5 | 4.84 0.0 | 40 | | | 3 - | 4 - | | 1997 | | 0.8 - | | 4- | |
| IF4p_34G2 65156.4895 | 0.0011 | 2.5 | 4.73 0.0 | 97.1 | | | 2 - | 3- | | 1.5 - | | 0.6 - | | 3 - | |
| 1F4p_z2F3 68759.7991 | 0.0012 | 3.5 | 0.0 0.0 | 20 | | | | 2- | | 1.0 - | | 0.4 - | | 2 - | |
| IF4p_z2F2 68583.3148 | 0.0012 | 2.5 | 0.0 0.0 | | | | 1- | 1- 1 | | 0.5 - 1 | | 0.2 - 1 | | 1- | |
| IF4p_22D2 67387.0906 | 0.0012 | 2.5 | 3.1 0.0 | 0 | handho | m | on how have | 0.1 | - In | 0.0 - WW | w horny | N 0.0 | hand have | 0- | Lum |
| IF4p_z2D1 67379.295 | 0.0012 | 1.5 | 3.1 0.0 | 5 | | | | · · | |] [| | | | | |
| F4p_y4F4 67448.5405 | 0.0012 | 4.5 | 2.9 0.0 | 5 5 | 1 | | 168 | 2.5 | | 1 168 | 1.04 | 16 | 8 | 2.5 | le8 |
| F4p_y4F3 67393.4495 | 0.0012 | 1.5 | 2.9 0.0 | | M | | 0.0 | 0.0 | M | 0 | - Mr | 0 | M | 0.0 - | 1 |
| 8F4p_y4F2 67012.0754 | 0.0011 | 2.5 | 3.7 0.0 | -5 | | | 2.5 | 2.5 | . Y | | n j | -5- | Y | 2.5 | |
| 8F4p_y4F1 67070.4394 | 0.0012 | 1.5 | 3.9 0.0 | 5 | 36224 36225 Wavenumber (cn | | 36224 36225 36226 Wavenumber (cm-1) | | 5224 36225 36226 avenumber (cm-1) | | 4 36225 36220 number (cm-1) | 5 | 36224 36225 36226 Wavenumber (cm-1) | | 36224 Wavenur |
| IF4p_y2G4 70107.6226 | 0.0012 | 4.5 | 0.0 0.0 | 36276 | i. 1241 cm-1 | | the second secon | | | | | | | | |
| IF4p_y2G3 69903.4828 | 0.0012 | 3.5 | 0.0 0.0 | | | | | | | | | | | | |
| 8F4p_x4D3 67875.3689 | 0.0012 | 3.5 | 0.0 0.0 | 5 | Cr042416.005 | ŗ | | | | le8 Cr1 | 10600.001_r | 16 | 9 Cr110700.001_r | 1 | e8 Cr110 |
| 8F4p_x4D2 67867.7867 | 0.0012 | 2.5 | 0.0 0.0 | 5 | ٨ | | | | | | | 00 | | 4- | 0.001 |
| 8F4p_x4D1 67870.2106 | 0.0012 | 1.5 | 0.0 0.0 | 4 | | | | | | 2 - | | .00 - | | 2 - | . Ma |
| Cr042416.005_r Cr061011.007_c Cr102700.001_r Cr102700.003_r Cr100600.001_r Cr100500.001_r Cr100700.001_r | Wavenumber Max | Wavenum | nber Min | 2 0 -2 | Mm M | M | | | | | W YWM | .50250025 | myhm | 0 - -2 - -4 - | MMM |
| Cr120800.001_r cr110600.003_r | | | | 0 -1 | | | | | | 1e8 0- -1 | 1/111 | 5 0 - | * | 0 -2 | .e8 |
| | | | | | Upper Level Lines All Lines | Lower | Ritz Obs. | Cr042416.00 | 5 r Cr042416.005 r Cr04 | 12416.005 + C+102700 | 001 + Cr102700.001 | r Cr102700.001 | r Cr102700.003 r Cr102700 | 003 r Cr1023 | /00.003 r.Cr |
| | | | | | nsity log(gf) Lower Level | Energy (cm | -1) Wavenumber (cm-1) Wavenumber (cm | n-1) eq_width | snr i | ine_used eq_wid | th snr | line_used | eq_width snr | line | used |
| | | | | 28 | -1.0463 3G4s_b4G4 | | 33774.5132 33774.5100 | 0.0 | 8.84429 True | | nan | nan | nan nan | nan | 0.0 |
| | | | | 20 | -1.1835 3G4s_b4G3 | | 33872.3591 33872.3570 | 0.0 | 5.891013 True | nan | nan | nan | nan nan | nan | 0.0 |
| | | | | nan | -2.5597 3G4s_b4G2 | | 33975.4687 nan | nan | nan nan | nan | nan | nan | nan nan | nan | nar |
| | | | | nan | -4.7986 d5b4F2 | 32854.9399 | 34538.5096 nan | nan | nan nan | nan | nan | nan | nan nan | nan | nar |
| | | | | 23 | -1.3179 d5b4F4 | 32854.2497 | 34539.1998 34539.2250 | nan | nan nan | nan | nan | nan | nan nan | nan | nar |
| | | | | 100 | -0.4327 d5b4F3 | 32836.6527 | 34556.7968 34556.7981 | 0.0 | 26.054098 True | nan | nan | nan | nan nan | nan | 0.0 |

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Potential methods

- Wavelength/Intensity calibration of spectra
- Optimization of energy levels using LOPT
- Energy level searches
- Measurement of branching fractions and transition probabilities
- Hyperfine/Isotope structure analysis
- ???

Conclusions

We have too few people in atomic spectroscopy to maintain the field – we need new people, a more efficient way of training them, and better tools to archive, distribute, and analyze our data.

Combination of a 'storage container' like hdf5 with better userfriendly software offers promise for increasing our efficiency.

This is a multi-year project and cannot be achieved with a few people working on their own.

Come and join our team!