Oscillator Strength Measurements in Lanthanides and Transition Metals Using Laser-Induced Breakdown Spectroscopy

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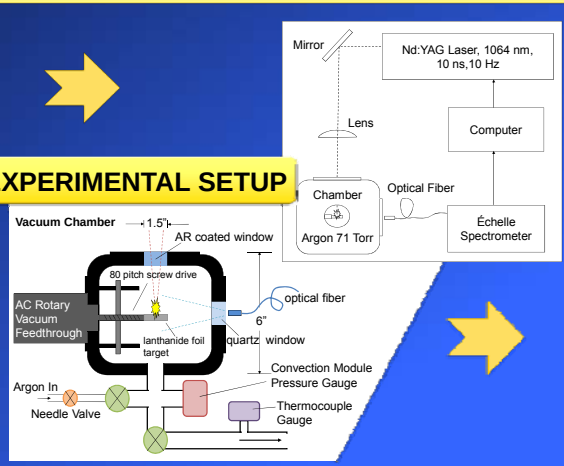
INTRODUCTION

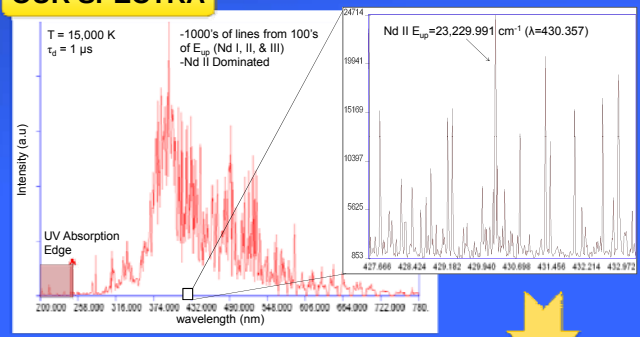
Nucleosynthesis is the process whereby nuclides heavier than that of hydrogen are generated in celestial bodies. Lanthanides and other heavy metals are found in chemically peculiar (C.P.) stars and these elements are of significant importance to astrophysicists studying galactic elemental abundances, stellar age predictions, as well as stellar opacity. A significant hindrance to astrophysicists in this area of research is poor accuracy of atomic data leading to imprecise calculations of age determinations and abundances in CP stars; thus, more accurate atomic data is required by astrophysicists.

We have completed a study on measurements of oscillator strengths in Nd, Gd, Sm, Pr, Cu, and Fe by using laser-induced breakdown spectroscopy (LIBS). LIBS has been employed for its ability to excite many upper energy levels from multiple ionizations in one laser-induced plasma giving tremendous amounts of data near instantaneously.

EXPERIMENTAL SETUP



OUR SPECTRA



"PATHOLOGICAL" PEAKS

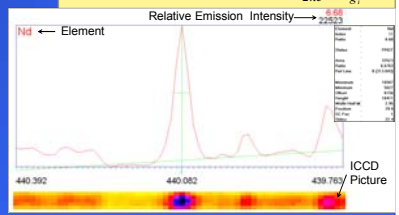
The spectra contain "pathological" peaks where lines from different upper energy levels overlap and are unresolved. This results in shouldered or blended lines which our program was unable to fit. If possible the peaks can be manually fit or are recorded as unmeasurable. A shoulder is pictured on the left and a blend is pictured on the right (looking at the two largest peaks).

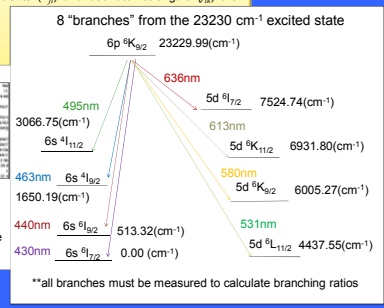
As well, weak branches (below 1%) (typically at wavelengths above 600 nm) were frequently unobserved or measured as noise. In the case of strong blended lines or weak missing lines, previously measured values were used .

RELATIVE INTENSITIES & BRANCHING RATIOS

Relative intensities are calculated from background-subtracted integrated areas under the curve by our spectrometer software, ESAWIN. Branching ratios (β_{ki}) are calculated from the relative intensities (I_{ki}) as shown below. With known lifetimes (τ_k), Einstein A coefficients (A_{ki}) and oscillator strengths (f_{ik}) are obtained.

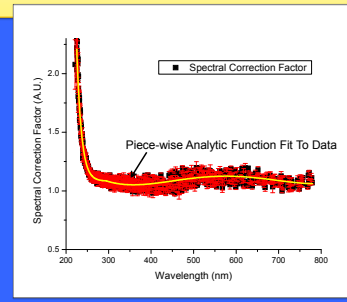
$$\beta_{ki} = \frac{A_{ki}}{\sum_i A_{ki}} = \frac{I_{ki}}{\sum_i I_{ki}} = A_{ki}\tau_k \qquad \tau_k^{-1} = \sum_i A_{ki} \qquad f_{ik} = \frac{m_e c \varepsilon_o \lambda^2}{2\pi e^2} \cdot \frac{g_k}{g_i} \cdot A_{ki}$$





CALIBRATION

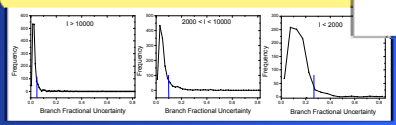
Our calibration procedure uses a fiber-coupled NIST traceable deuterium-tungsten calibration lamp. Lamp emission spectra are recorded by our spectrometer and compared with the spectra collected through our quartz window and optical fiber. The ratio gives a spectral calibration curve (*below*) that is used to calculate spectral correction factors at every wavelength. Our UV absorption edge is clearly seen making lines below 250 nm unmeasurable.

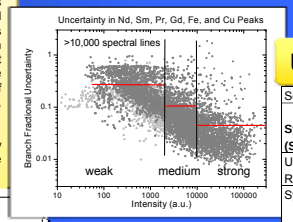


UNCERTAINTY ANALYSIS

Uncertainty in the spectral correction factor arose from uncertainty in the fit of the spectral calibration curve as well as from the scatter of day-to-day measurements. Statistical uncertainty was determined from 10 repeated measurements and was intensity dependent. Peaks with larger emission intensity exhibited the least scatter and possessed the least fractional uncertainty. Weak peaks possessed very large uncertainty (up to and exceeding 100%). Three categories of peaks were thus defined (shown at *right*) "strong", "medium", and "weak" each with a different uncertainty (as shown in table)

The statistical uncertainty (red line at *right*) for each category was determined by an upper limit where only $1/e^2$ of the measurements (blue line *below*) exceeded the uncertainty.

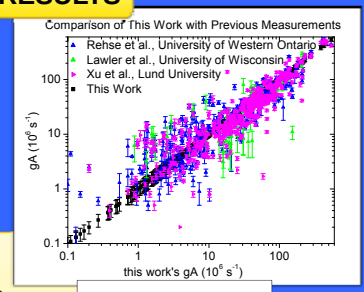




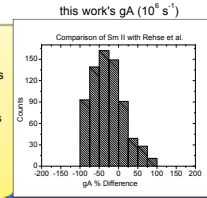
UNCERTAINTY BUDGET TABLE

Source of Uncertainty	Uncertainty (%) Peak Intensity (a.u.) Strong (>10000)	Moderate (2000-10000)	Weak (<2000)
Systematic Uncertainty (Spectral Correction Factor)			
Uncertainty in Fit to Data	3	3	3
Reproducibility in Spectral Calibration	4.4	4.4	4.4
Systematic Total (added in quadrature)	5.3	5.3	5.3
Statistical Uncertainty			
Branch Uncertainty from 10000 spectral lines	5	10	27
Total Uncertainty (added in quadrature)	**7.3**	**11.3**	**27.5**

RESULTS



Results obtained include:
- Pr II – 60 upper energy levels with 425 transitions
- Nd I – 74 upper energy levels with 83 transitions
- Nd II – 24 upper energy levels with 179 transitions
- Nd III – 1 upper energy level with 2 transitions
- Sm I – 45 upper energy levels with 75 transitions
- Sm II – Over 100 upper energy levels with over 500 transitions
- Sm III – 12 upper energy levels with 30 transitions
- Gd I – 90 upper energy levels with 179 transitions
- Gd II – Over 100 upper energy levels with over 600 transitions
- Gd III – 4 upper energy levels with 24 transitions
- Cu I – 70 upper energy levels with over 300 transitions
- Cu II – 28 upper energy levels with 150 transitions
- Fe I – Over 100 upper energy levels with over 700 transitions
- Fe II – Over 100 upper energy levels with over 700 transitions



FUTURE WORK

Future work will investigate laser-induced plasma parameters that could effect measured branching ratios such as argon pressure, observation delay time, and emission optics geometry. LIBS-LIF will be used to selectively populate specific upper energy levels, reducing or eliminating blends and weak lines. Neutrals and doubly-ionized species will also be further explored by changing the observation delay time and possibly utilizing dual-pulse LIBS since this work was optimized for singly-ionized species.

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