The spectrum and term analysis of Nd III and hyperfine structure of energy levels in Co II

Introduction

Atomic spectral reference data are of paramount importance in observational astronomy. Data for fine structure energy levels and their associated transitions are key components in astrophysical plasma and radiative transfer models. Accuracies of ab initio theoretical calculations for these atomic data are limited, particularly for the open d- and f-shell heavy elements, where errors are at least a few percent and unsuitable for applications under moderate spectral resolving powers. Resolving powers of up to 100,000 have been achieved by the instruments on modern ground- and space-based telescopes, for example, on the Hubble Space Telescope, the Very Large Telescope (VLT), and the Extremely Large Telescope that is under construction. Astrophysical spectra observed by such instruments revealed an unprecedented number of unknown atomic spectral lines [1], see Figure 1 for example [2]. Furthermore, uncharacterisable spectral line distortion and broadening due to energy level hyperfine structure (HFS) and isotope shifts were revealed by the modern telescope spectrographs, these effects were previously thought to be negligible [3]. Unfortunately, the lack of reference atomic energy levels, transition wavelengths, and nuclear perturbation constants persists to this day. This problem is exacerbated by recent advances in gravitational wave astronomy and theories of nucleosynthesis, where neutron star merger spectra that are dominated by the heavy r-process elements could not be disentangled for detailed merger analyses [4, 5]. With newer electromagnetic and gravitational wave telescopes being planned and constructed, the demand for extensive and accurate atomic data is only set to increase. My thesis was dedicated to determining previously unknown reference spectral lines and hyperfine structure constants for species with the largest astrophysical interest, plus the innovations required to complete these tasks and evaluations on the prospects of solving the issue of astrophysical atomic data demands.

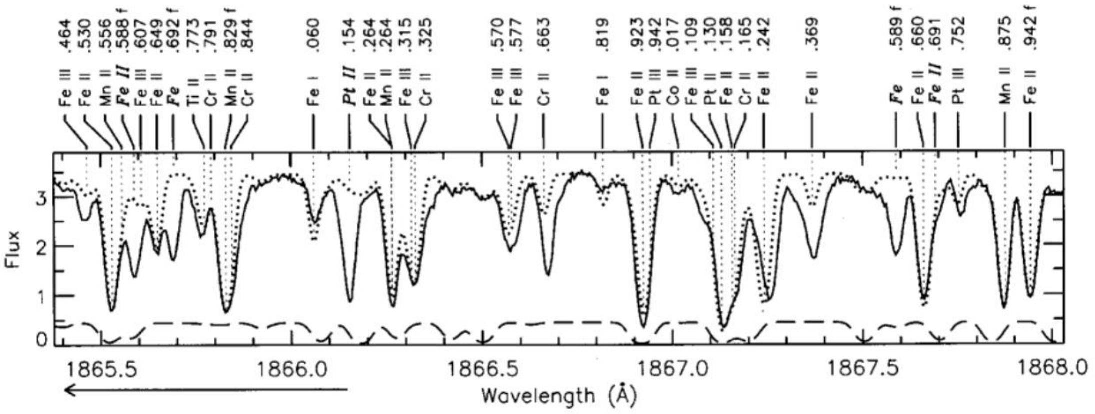


Figure 1: 0.25 nm section of a 125-269 nm UV spectrum (solid line) of the chemically peculiar binary star χ Lupi observed by the Goddard High Resolution Spectrograph on the Hubble Space Telescope [2]. Atomic data were used to model the stellar environment and absorption spectrum (dotted line). Evidently, several unknown absorption lines were missing from the model.

In the laboratory, I extensively investigated unknown energy levels and transition wavelengths of doubly ionised neodymium (Nd III, $Z = 60$) and HFS in the energy levels of singly ionised cobalt (Co II, $Z = 27$). Nd III belongs to the lanthanide group of elements ($56 < Z < 72$) that are of great interest in hot chemically peculiar stars (e.g. [6]) and neutron star merger kilonova investigations [4, 5]. The original investigation of Nd III energy levels was published in the 1960s [7], with only 29 energy levels deduced. This number increased to 40 four decades later using 70 classified transitions [8], which was still negligible compared to the tens of thousands of spectral lines we observe across the IR and UV for > 99% pure Nd plasmas. An example laboratory spectrum used for Nd III atomic structure analysis is shown in Figure 2, where blends are widespread and indistinguishable from line profile distortions from shifts between the seven naturally occurring isotopes of Nd. The immense number of lines requires restrictively challenging and time-consuming analysis, which typically takes ***years*** and is also a primary reason for the lack of atomic data for the heavy elements. Similarly, extensive hyperfine structure analysis for just one ion of an element also requires laborious but detailed analyses of most of its observed spectral lines. Hyperfine structure was investigated for only 28 energy levels of Co II [9, 10], in contrast, around 500 energy levels of Co II are known (e.g. [11]). As cobalt belongs to the high cosmic relative abundance iron group elements ($23 < Z < 29$), spectral lines of Co II are ubiquitous, access to accurate hyperfine structure constants for Co II is a requirement in modern high-resolution stellar spectroscopy.

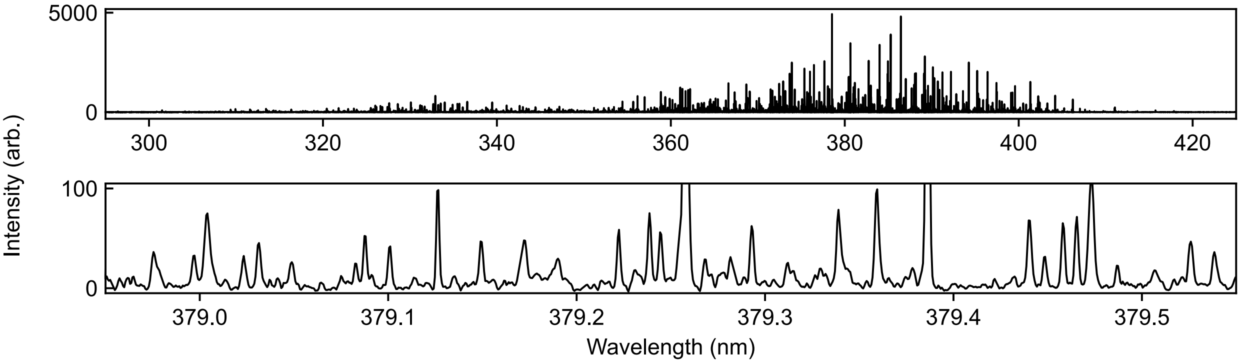


Figure 2: Example section of an observed high-resolution emission spectrum of neodymium (*Z* = 60) in the ultraviolet, at plasma temperatures of a few 1000 K. The lower plot shows an expanded section covering a mere range of 0.5 nm. The spectral resolution is limited by the Doppler width and about 8500 transitions were identified in this spectrum.

One of the most widely used experimental methods for such investigations is Fourier transform (FT) spectroscopy of metal discharges (e.g. Figure 2). Since the rapid advancements in high-resolution FT spectroscopy in the 1980s, it has taken more than 30 years to extensively investigate the open 3d-shell iron-group elements that were of high interest in astrophysical spectroscopy. As interests in lanthanide atomic data have grown, expanding the focus to include these much more complex open 4f-shell elements will require adaptations and improvements in current methodologies. For the Co II HFS investigations of my thesis, these are more challenging compared to those carried out for Co I [12], because the crucial spectral lines are deeper in the UV (i.e. stronger electric potential due to the removed electron, hence larger gaps between energy levels), causing larger Doppler broadening and HFS component transitions are less well-resolved. Furthermore, unlike for HFS investigations on Co I and many other species, highly accurate laser spectroscopy measurements for Co II HFS constants were not available, which also raised the minimum uncertainties that posed challenges in parameter constraints during the analysis. Therefore, to achieve my thesis objectives, I really needed to push existing methodologies beyond their limits.

Nd III energy level analysis

The atomic structure analysis of Nd III was the most challenging objective of my thesis. It had been attempted previously a few times [7, 8], but progress was slow due to lack of quality data to study the incredibly complex spectra of the neutral Nd and its ions. Specifically, the previously available spectra had limited spectral resolution, spectral range, and plasma variety. To explain these requirements, consider a spectrum less ideal than the one shown in Figure 2; a lower instrumental resolution would cause observed lines to blend together, increasing transition wavelength uncertainties; a narrower spectral range would cause fewer lines of an energy level to be observed, lowering the chances of observing resolved lines that could constrain its energy value; a lack of plasma variety would mean that changes in relative spectral line intensities between plasmas of different temperatures (e.g. level populations and Doppler widths) could not be used to identify lines.

The high spectral resolution and wide spectral range of FT spectrometers were ideal in acquiring spectra for my Nd III energy level analysis. Since the strongest transitions between configurations of Nd III lie in the visible to vacuum-UV range [13], the Imperial College visible-VUV FT spectrometer [14] was suitable for the task, which I used to record Nd spectra within the region 11,500–54,000 cm^{-1} (870–185 nm, e.g. Figure 2). To fulfil the requirement for plasma variety, spectra of Nd were produced using water-cooled custom hollow cathode (lower temperature) and Penning discharge (higher temperature) lamps by sputtering 99.5% pure Nd cathodes with Ar gas. These are shown in Figure 3, running with currents and pressures that maximised intensities of Nd III transitions. To the best of my knowledge, these set-ups were not documented in the literature and were hence subject to unknown risks and required a considerable number of preliminary investigations. Additionally, I contacted the scientists who had worked on the previous Nd III energy level analysis [8] and formed an international collaboration to supplement my spectra with their spectra. The key spectra from the collaboration include those from Nd-rich magnetic and non-magnetic stars recorded by the Ultraviolet Visual Echelle Spectrograph (UVES) at the VLT, grating spectra of hot Nd vacuum sliding sparks recorded at the National Institute of Standards and Technology in the US and at the Institute of Spectroscopy of the Russian Academy of Sciences, and some unconfirmed potential Nd III line identifications made by authors of the original Nd III energy level analysis [7]. The collaboration was exceptionally fruitful as the supplementary data, grating and stellar spectra, enabled far more progress with the energy level analysis of Nd III, compared to my analyses solely using the FT spectra I recorded. For example, in addition to the expansion of the available spectral range and plasma variety, the Zeeman splitting spectral lines of magnetic stars were crucial evidence for a few dozen Nd III line classifications, and the high current sparks and long exposure times for grating spectroscopy

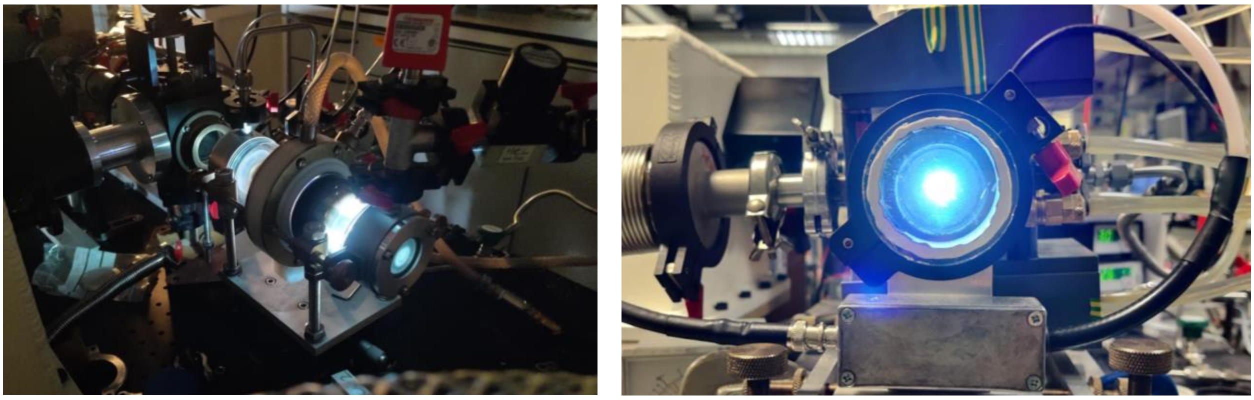


Figure 3: The custom water-cooled Nd-Ar hollow cathode discharge (left) and Nd-Ar Penning discharge (right) lamps from which my Nd FT spectra were recorded from.

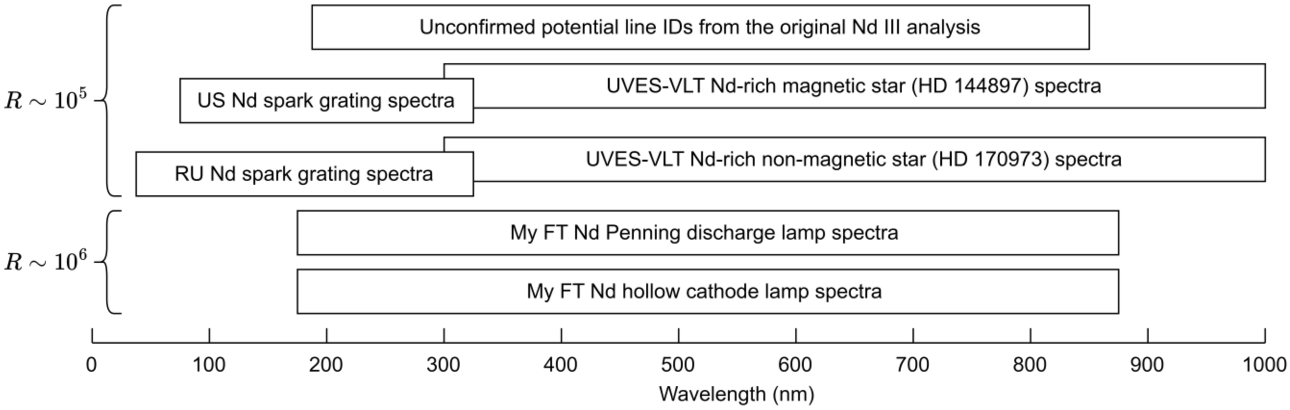


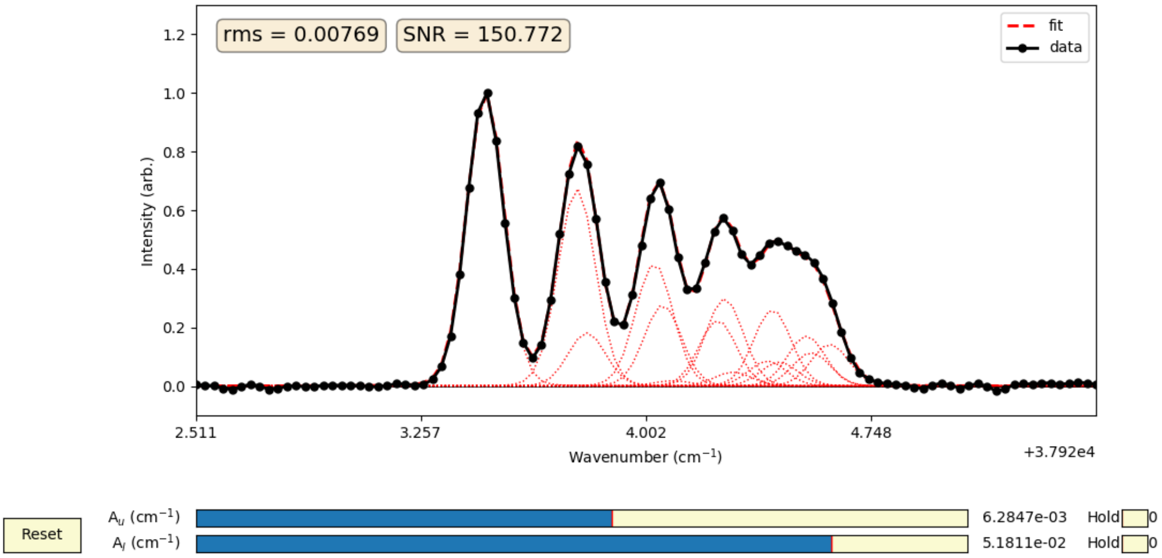
Figure 4: Extent of all spectral data used for the Nd III energy level analysis [15]; spectral resolving powers are indicated on the left.

produced weaker Nd III lines that were not observable by FT spectroscopy. The extent of the experimental data used is illustrated in Figure 4, all previous progress on the atomic structure of Nd III had been made using the spectra with resolving powers of around 100,000, my FT spectra at ten times the resolving power was expected to offer dramatic improvements in our knowledge of the energy level and spectrum of Nd III.

After extracting approximately 20,000 transition wavelengths and relative intensities from my FT spectra through line profile fitting using my computer programs, wavelengths were calibrated onto the absolute scale set by the Cs standard (e.g. [16]) using Ar II lines [17], and relative intensities were calibrated using tungsten and deuterium continuum lamps recorded along with the Nd spectra. Then, the new Nd III energy level analysis began. This involved matching coincidental level energy separations and relative intensity patterns predicted by theory, where energy levels were found one at a time by filtering out spurious matches based on theoretical and experimental uncertainties. The analysis required extreme attention-to-detail and corroboration of observations between all spectra of Figure 4, as well as with the atomic structure and transition probability calculations for Nd III that are highly demanding, as extensive semi-empirical parameterisations were made in obtaining meaningful interpretations of the experimental spectra. In total, 985 transitions and 264 energy level of Nd III were classified [15, 18], which is about an order of magnitude improvement in the extent of previously published data (only 70 transitions and 40 levels). The new level energies and transition wavelengths are accurate to a few parts in 10^8, fully meeting the accuracy requirements for astrophysical spectra with resolving powers up to 100,000. The newly identified levels also spanned seven different electronic configurations, enabled a revision of the Nd III ionisation energy at twice the accuracy of the previously published value, more reliable semi-empirical transition probability calculations that are crucial in analysing Nd III stellar absorption lines, and experimental transition probability measurements to be carried out for Nd III [18].

Co II HFS investigation

My other objective was to extensively determine magnetic dipole hyperfine interaction (*A*) constants for as many known Co II energy levels as possible. The widely accepted method is to empirically extract the HFS constants through non-linear least-squares fitting of model line profiles to each observed transition of each energy level. This required the use of all FT spectra from the Co II energy level analysis [11] covering the region 3000–70,422 cm^{-1} (3333–142 nm). However, model line profile parameter initialisation for observed line profile fitting was not straightforward and subject to ambiguity due to the lack of high precision laser measurements, the limited knowledge of Co II HFS constants, and the large quantities of under-resolved hyperfine component transitions in the UV. My solution to this problem was by creating an efficient way of acquiring initial line profile fitting parameters before carrying out the fitting and to find a set of *A* constants that could be reliably determined as reference values. For example, starting with the few line profiles with better resolved HFS component transitions with fitting parameters that are easy to 'guess', once the *A* constants for these lines are determined, they could then be used as fixed parameters in other transitions of their associated energy levels. I created the *hfs_fit* program [19] to apply my proposed methodologies. An example HFS analysis of a Co II spectral line is shown in Figure 5. This spectral line was one of the few better resolved lines to be investigated first, its *A* constants and HFS component line width were then used as references and fixed for fitting line profiles with no resolved components, which in fact comprised of most of the Co II lines analysed.



A_u (cm^{-1}) 6.2847e-03 Hold 0

A_l (cm^{-1}) 5.1811e-02 Hold 0

Figure 5: Main parts of the graphical user interface of *hfs_fit* during the HFS analysis of a Co II transition. The observed fine structure transition line profile (circles connected by the solid line) is fitted by the sum (dashed line behind the solid line) of the HFS component transitions (traced by the dotted lines). Positions of the HFS component lines are determined by A_u and A_l constants of the upper and lower energy levels, respectively, which are adjustable using the sliders with instant visual feedback on the fit for the user.

By carefully considering parameter constraints in the line profile fitting of over 700 Co II spectral lines that showed significant HFS, *A* constants were determined for 292 known energy levels of Co II [20]. This was more than an order of magnitude increase in the number of previously known *A* constants for Co II and covered most known energy levels of Co II, especially those with electron densities closer to the nucleus that produce significant HFS line broadening in stellar spectra. To the best of my knowledge, this was the highest number of HFS *A* constants ever to be determined in one project for a particular species. Astronomers have already applied this data for nucleosynthesis investigations [21], and my results have been verified experimentally [22, 23] and theoretically [24] by more recent publications.

Key conclusions

My thesis has demonstrated capabilities of modern laboratory spectroscopy in fulfilling astronomical demands for empirical reference atomic energy levels, transition wavelengths, and hyperfine structure splitting constants for species with the most complex atomic structure. While FT spectroscopy remains one of the best methods for these tasks, significant spectral data supplementation through international collaborations, new experimental set-ups for plasma and spectrum production, and more efficient analysis software had to be introduced in achieving my objectives. As the focus of laboratory atomic spectroscopy for astrophysics now includes the lanthanide elements, my methods and results for Nd III will set a standard for the inevitable future spectrum analyses of all other low-ionisation stage lanthanide species. From my Co II HFS analysis, I also demonstrated how a large fraction of HFS *A* constants of a species could be determined without accurate laser reference measurements and without many observed line profiles with resolved HFS components.

The order-of-magnitude improvements in the extent of the known energy level and transitions of Nd III and of the known HFS constants of Co II will enable significantly more reliable applications of these two species in astrophysical spectroscopy, as my results were also confirmed and reviewed by other scientists around the world. For example, Nd III absorption lines in hot chemically peculiar stars can now be used for magnetic field measurements and abundance determinations, Co II absorption lines in all stars can now be modelled including HFS effects, which can eliminate existing Co II abundance uncertainties by up to a few 0.1 dex. For spectral investigations of neutron star mergers, the current extent of experimental spectral data of Nd III is expected to be insufficient, because many high-lying configurations near the ionisation energy remain unknown. However, the large quantities of Nd III energy levels that I determined will constrain and improve theoretical atomic structure models, which will supplement my experimental data and significantly reduce uncertainties in kilonova spectral synthesis. Lastly, I anticipate that future investigations into other astrophysically important heavy atomic species will build upon and enhance my methodologies and findings, leading to further advancements in the field. The key strategies would include high spectral resolutions, wide spectral ranges, variety of plasma spectrum sources, and accurate semi-empirical atomic structure calculations, incorporating these strategies would of course be an international effort.

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