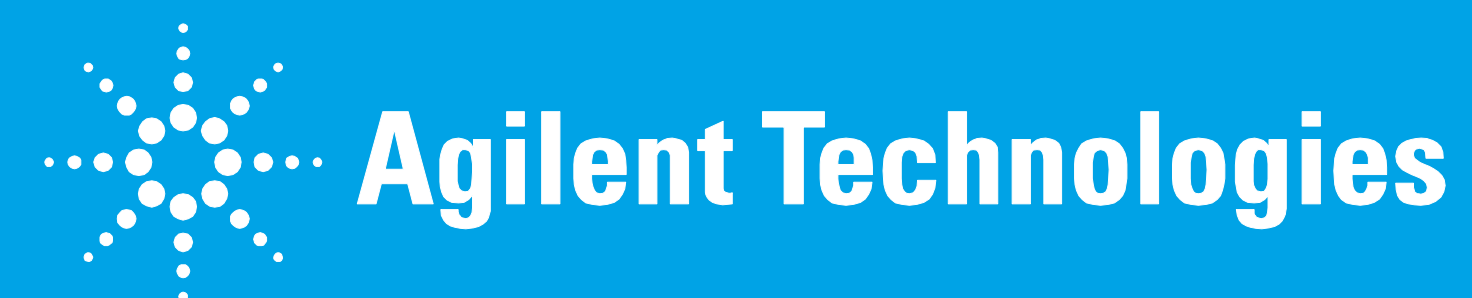# Fundamental Studies of a Nitrogen Microwave Plasma for Analytical Emission Spectroscopy

Nahid Chalyavi, Peter S. Doidge, Richard J.S. Morrison, Guthrie B. Partridge

Agilent Technologies

Introduction

In 2011, Agilent Technologies commercialized a microwave plasma atomic emission spectroscopy (MP-AES) instrument with the ability to form a magnetically excited high power atmospheric pressure plasma using N_2 support gas. While a nitrogen-based plasma has enormous operational cost benefits over an argon plasma, the physical properties of this plasma are less understood. In this work, fundamental aspects of the Agilent nitrogen plasma are characterized.

Experimental

Agilent 4200 MP-AES Instrument

Figure 1 shows the Agilent 4200 MP-AES spectrometer. Emissions from the vertically-oriented microwave plasma torch are viewed axially and directed by computer-controlled beam steering optics into a Czerny-Turner monochromator. The dispersed light is measured by a Hamamatsu CCD detector covering the spectral range from 180 nm to 780 nm.

Figure 1. The Agilent 4200 MP-AES

Thompson Scattering (TS) Experimental Setup

TS measurements were made using a Q-switched Nd-YAG laser operating at 532 nm. A half waveplate is used to rotate the (linear) polarization of the laser beam such that the angular distribution of the Thomson scattered light is maximized along the direction of the light collection optics. Scattered light is collected 90 degrees from the direction of laser propagation and refocused onto the input slit of a triple grating spectrometer (TGS) as seen in figure 2 below.
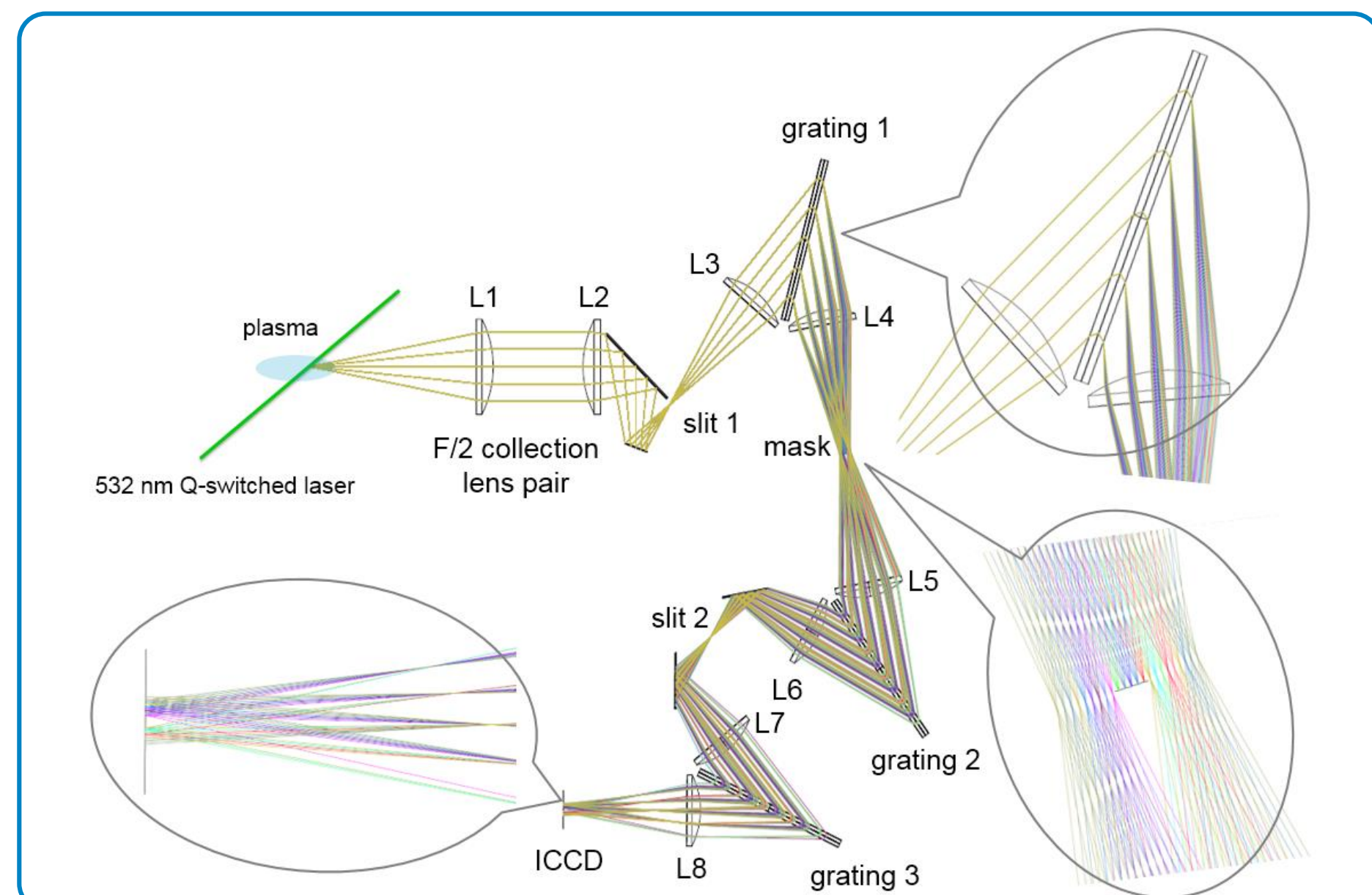

Figure 2. Triple grating spectrometer

Results and Discussion

Plasma Composition

Nitrogen plasma composition can be calculated using Chemical Equilibrium with Applications (CEA) code, which is based on the principle that chemical equilibrium corresponds to a minimum value of the Gibbs Free Energy, as shown in Figure 3.
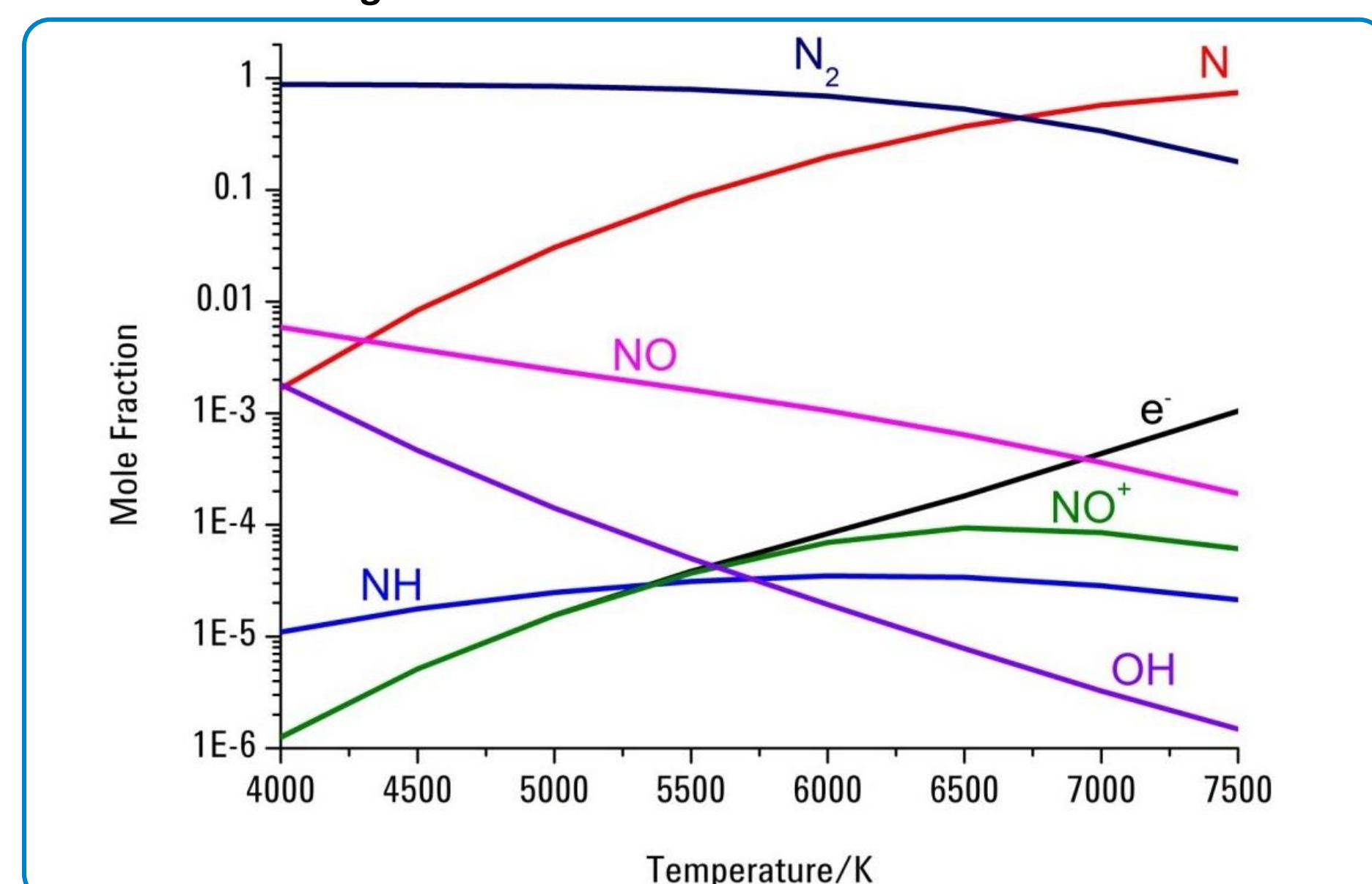

Figure 3. Simulated plasma composition as a function of temperature when introducing N_2, aqueous aerosol and water vapor at the mole fractions 0.9565, 0.0301, and 0.0134, respectively.

At 5000 K the equilibrium calculation predicts electron density of ~ 2×10^{19} e⁻/m³ .

Results and Discussion

Spectral Background Model

Although the nitrogen plasma background emission is complex, the structure is entirely predictable and can be accurately modelled (as shown in Figure 4).
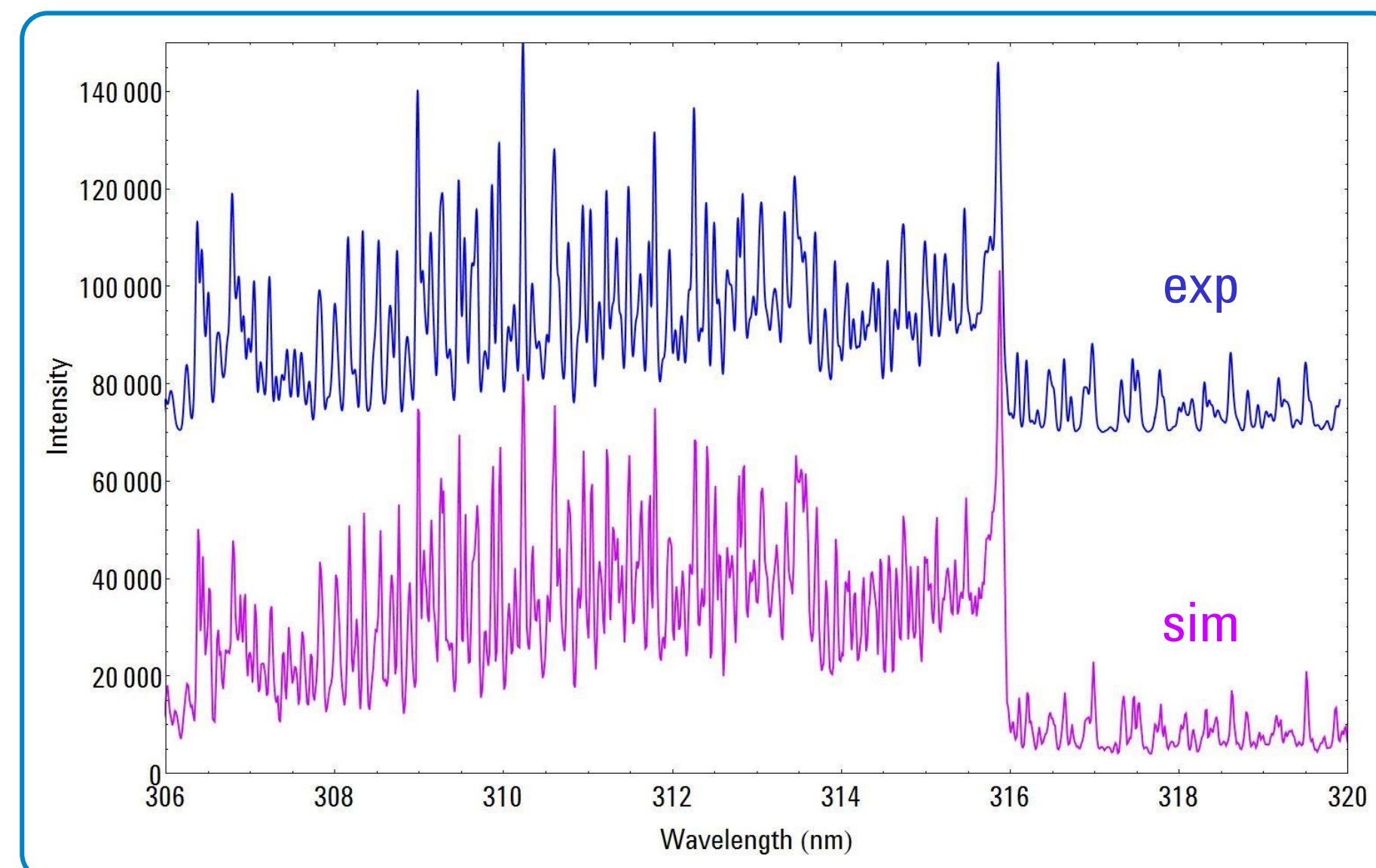

Figure 4. Comparison of an experimental and simulated emission spectrum in a spectral region containing contributions from OH* and N_2*. The simulated spectrum was generated using Specair program, assuming rotational temperature of 5000 K for OH A-X (0,0) and N_2 C-B (1,0) bands.

In the "auto" background correction mode in the MP Expert software, models of the plasma background emission are constructed from replicate readings of blanks, blank-subtracted standards, and any suspected interferent species. This computational approach yields high quality results even when it becomes difficult to recognize the presence of an analyte peak in an emission spectrum.

Electron Density and Temperatures from Thomson Scattering Experiments

For TS measurements of N_2 plasma, rotational Raman scattering is considered, as it overlaps with the same spectral region as the Thomson scattered photons (see Figure 5).
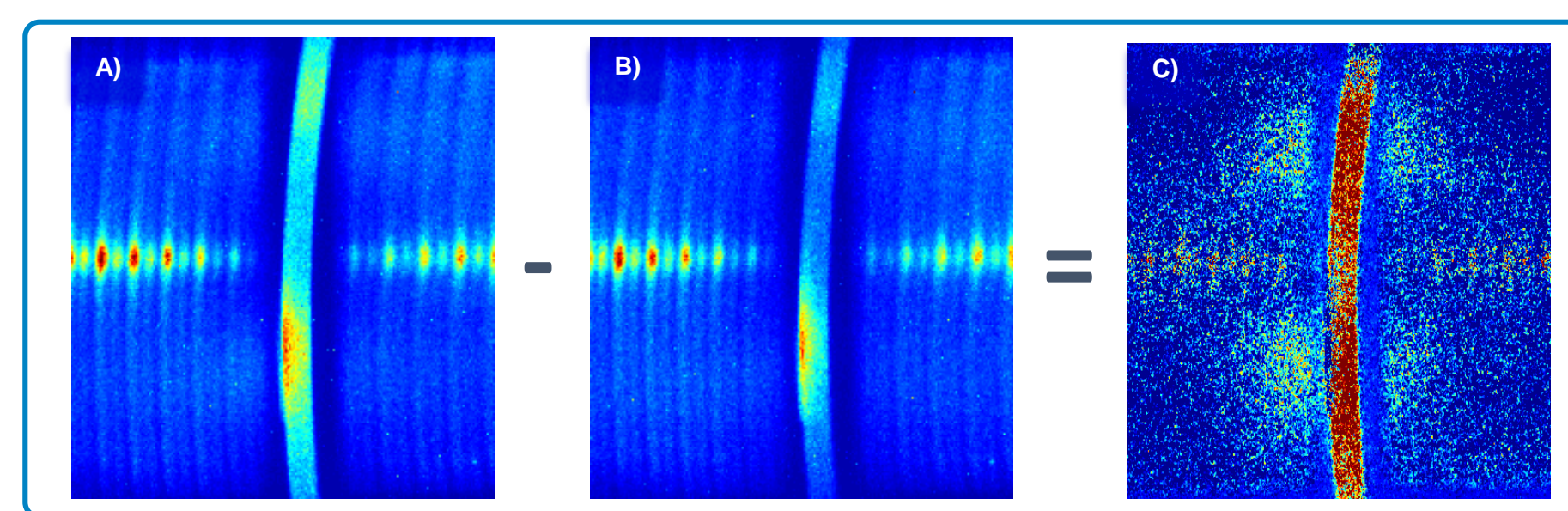

Figure 5. Removal of Raman signal by polarization control. A) Spectral image contains both Raman and TS signals. B) Polarization of collected light is rotated 90° so only Raman light passes through the spectrometer. C) Subtracted image C = A – c*B where c is a scaling factor.

The shape function of the observed TS spectral distribution is determined by the value of the scattering parameter,

$$\alpha = (k\lambda_D)^{-1} = \frac{\lambda_L}{\sin\left(\frac{\theta}{2}\right)} \cdot \left(\frac{n_e e^2}{4\pi k_B T_e}\right)^{\frac{1}{2}}$$

Where k is the magnitude of the differential scattering vector $\boldsymbol{k}$ (the vector difference between the wave vectors of the incoming and scattered light), λ_D is the Debye length, λ_L is the laser wavelength, θ is the observation angle relative to the laser propagation direction, n_e is the electron density, e is the electron charge, k_B is the Boltzmann constant and T_e is the electron energy. Data fit to TS distribution is shown in Figure 6.
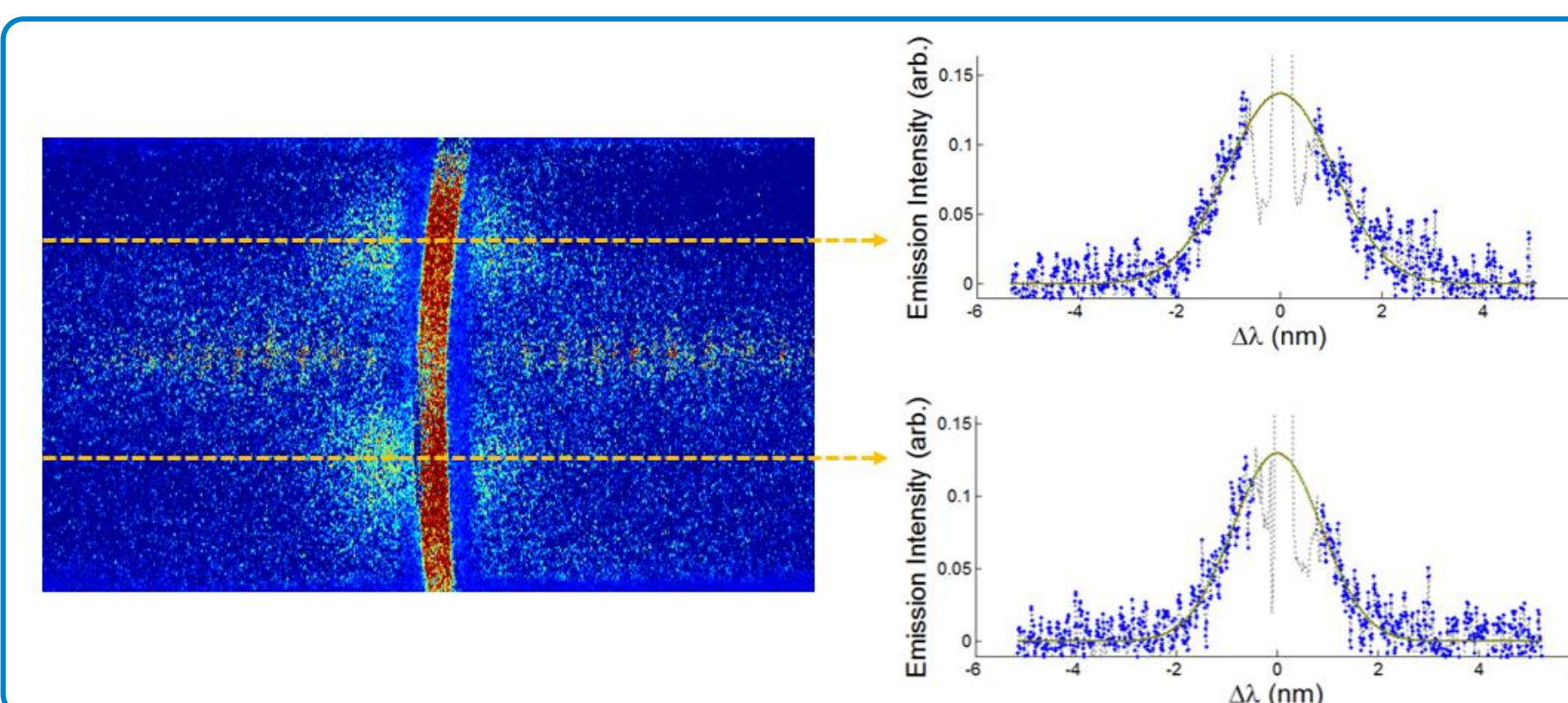

Figure 6. The spectral profiles at right correspond to integrated 190 um tall strips taken along the dashed arrows shown. Blue dots show the data used in fitting, while the dotted grey profiles show the excluded data at the central portion of the spectra where scattered light is attenuated by the triple grating mask.

From fits such as these across multiple datasets we measure peak n_e values in the range $1.3 \pm 0.3 \times 10^{19}$ e⁻/m³ with T_e values of 0.5 ± 0.05 eV.

Electronic Excitation and Rotational Temperatures

As shown in Figure 7, Boltzmann "slope" excitation temperatures were derived from measurements of lines of the spectra of Cr I, Fe I, Ti I, and Ti II and the values were between 5100 and 5400 K.

To derive a rotational temperature from the N_2^+ spectrum, the emission from the B-X transition was simulated using the PGOPHER software and the best match between simulation and experiment was found in the 4000-5000 K temperature range.
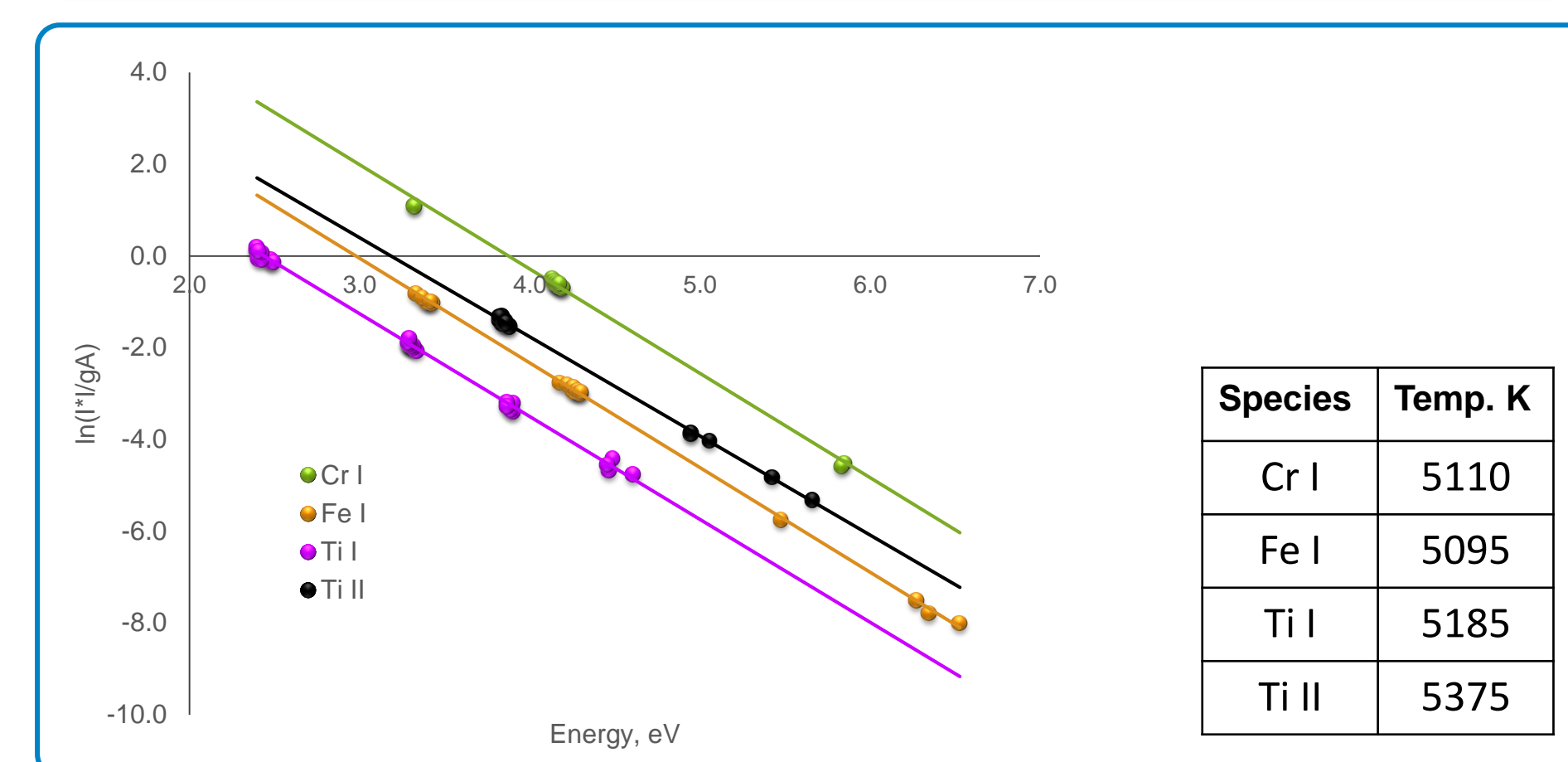
Results and Discussion

Figure 7. Boltzmann "slope" plots for Cr I, Fe I, Ti I, and Ti II.

Species	Temp. K
Cr I	5110
Fe I	5095
Ti I	5185
Ti II	5375

Ionic-to-atomic Line Intensity Ratios

Table 1 shows values of the calculated and measured Mg II/I intensity ratios (280.27, 285.21 nm). The excitation temperature was measured using the Fe I lines and electron density was calculated using the CEA model. These values were then substituted in the Saha-Boltzmann equation, with the assumption $T_e = T_{exc}$, to determine a ratio under the specified conditions.

Table 1. Comparison of experimental and calculated ionic-to-atomic Mg line ratios.

Nebulizer flow rate (L/min)	Exp. excitation temp. (K)	Calc. electron density (e⁻/m³)	Calc. Mg ratio	Exp. Mg ratio
0.50	5095	2.70E+19	0.55	0.62
0.60	4930	2.01E+19	0.39	0.49
0.70	4820	1.63E+19	0.30	0.37

The measured and calculated Mg ratios are in good agreement and are much lower than the value of ~ 8-14 which is found for the plasma in a commercial Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument (such as Agilent's 5110), for which higher temperatures and electron densities are typically observed. Robustness of the microwave plasma cannot, of course, be defined by Mg ratio values characteristic of the ICP.

Examining Proximity to Local Thermal Equilibrium (LTE)

If LTE can be assumed, microwave plasma emission spectra should be predictable. Using a large database of spectral lines and tabulated partition functions for atoms and ions, a generic code was developed to predict atomic emission spectra given just two input parameters, T and θ. Here, θ is an (assumed) ratio of the electron temperature T_e to the heavy particle temperature, T , i.e. $\theta = T_e/T$. As shown in Figure 8, a very good agreement is observed between experimental spectra of Mn and Co and the spectra simulated using $T = 4800$ K and $\theta = 1.06$.
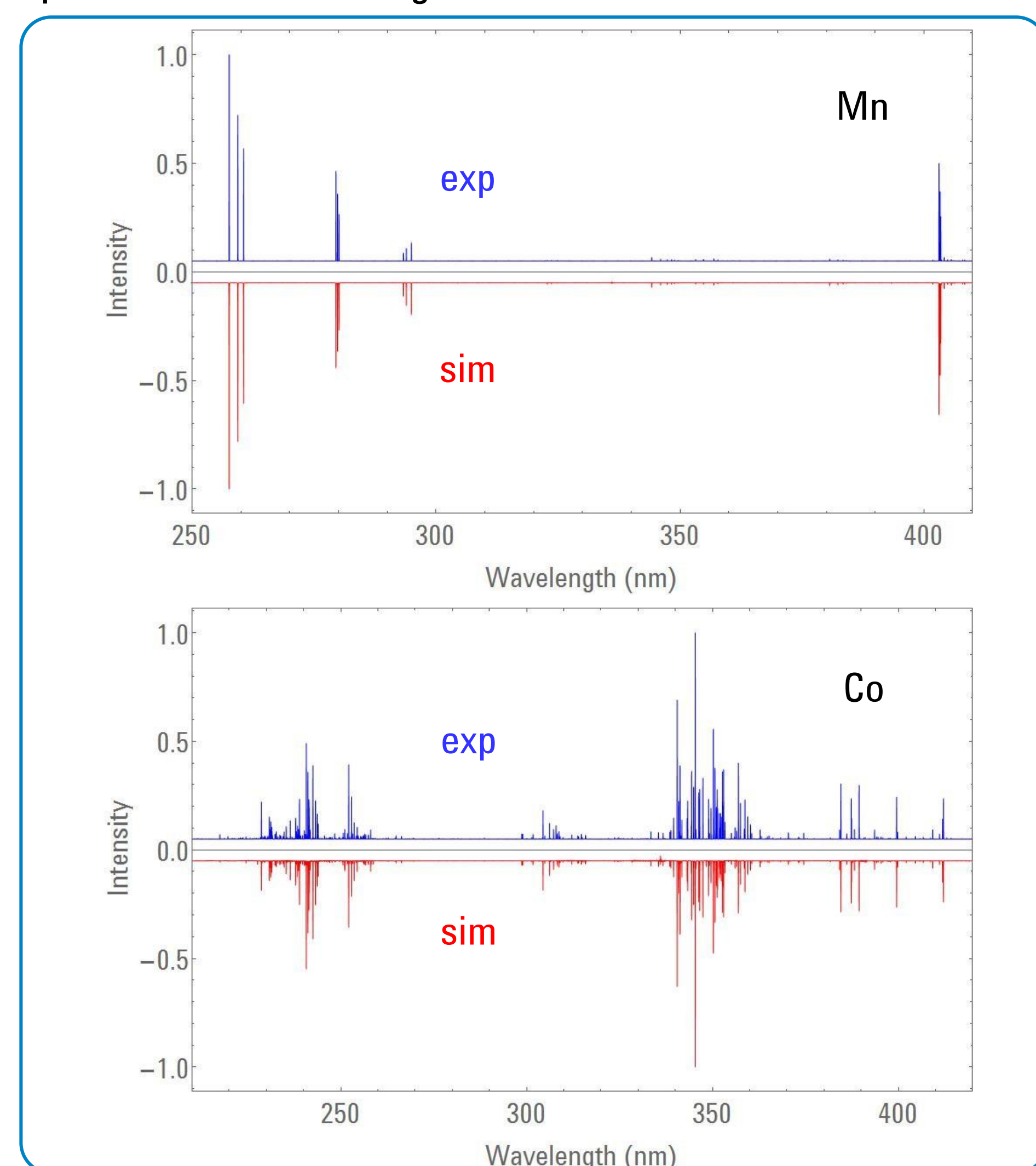

Figure 8. Comparison of synthetic emission spectra of Mn and Co (T=4800K, θ=1.06) with experimental spectra recorded on an Agilent 4200 MP-AES instrument. The fact that θ value is close to 1.0 justifies proximity to LTE.

Conclusions

• The Agilent 4200 MP-AES instrument generates an analytical plasma that appears to be fairly close to LTE conditions, with a plasma temperature near 5000K and an electron density of ~ 2×10^{19} e⁻/m³, under typical operating conditions. This conclusion is supported through direct TS measurement of the plasma electron density and temperature

• Close proximity to LTE also means that full scan analyte emission spectra recorded on 4200 MP-AES are predictable, and good agreement between modelled and measured spectra was obtained.