DETERMINATION OF TRANSITION PROBABILITIES FOR ARGON USING THOMSON SCATTERING ON AN INDUCTIVELY COUPLED PLASMA

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Abstract—The inductively coupled plasma is used as an emission source for determining transition probabilities of highly excited argon states. The population densities of these higher levels are assumed to be populated according to the Saha formula. To establish the Saha line we used the electron temperature from Thomson scattering together with the densities of three well-known levels by absolute line emission intensity measurements. In order to determine the transition probabilities the corresponding absolute line emission of 15 levels is measured using a two-dimensional optical multichannel analyser and is subsequently compared to the Saha line. The obtained transition probabilities have estimated maximum errors of less than 20% whereas the original specified inaccuracies are in most cases larger than 50%. Copyright © 1996 Elsevier Science Ltd

1. INTRODUCTION

While there are several advanced and accurate techniques to obtain information on plasma parameters, the simple method of measuring the intensity of emission lines\(^1,^2\) is still widely applied. The most simple method is the 2\(\Delta\) method which uses the relative intensity of two levels from which electron temperature \(T_e\) can be deduced. With absolute measurements of the intensities the value of the electron density \(n_e\) can be obtained as well.

These techniques are only successful if the levels in question are populated according to the Saha–Boltzmann law and if accurate values of the transition probability \(A\) are available. In most cases the transitions low in the atomic system are measured because of their high intensities and well-known \(A\)-values. However, especially the lower levels are very sensitive to deviations from equilibrium. Therefore, to determine the essential plasma parameters one should measure transitions high in the atomic system. Unfortunately, these higher levels have large inaccuracies in their \(A\)-value, often in the range of 25–50% or even higher. Moreover, since the \(A\)-values of higher states are generally low, the detection of radiation from the highly excited states is difficult.

In the past years, several efforts\(^3,^4\) have been made to measure and calculate transition probabilities with higher accuracies, often in order to obtain fundamental information on the atomic structure. Unfortunately, the most often treated transitions are situated in the lower part of the electronic system in which, as stated before, deviations from Saha equilibrium easily occur.

In this paper we present a method to obtain more accurate \(A\)-values for 15 highly excited levels in the argon system with an ionization potential \((I_p)\) smaller than 0.7 eV. The basis of the technique is to use the absolute densities of three relatively well-known highly excited states together with \(T_e\) obtained by Thomson scattering to construct the upper part of the atomic state distribution function \((\text{ASDF})\). With the assumption that these reference lines are in partial local Saha equilibrium (pLSE), we can predict the poorly known densities of other levels. Due to the advent of the two-dimensional CCD-array which can be placed in the focal plane of a spectrograph, we

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are able to measure with high accuracy simultaneously the emission of these lines and their background for various lateral positions. After Abel-inversion the local value of these emission coefficients can be obtained making a determination of the corresponding A-values possible.

2. EXPERIMENTAL SET-UP

The experiments are performed on an atmospheric 100 MHz inductively coupled argon plasma. The power of 1.2 kW input is coupled into the plasma with a coil of two windings. The argon flow through the quartz torch is about 13 l/min; the plasma radius is 9 mm. The measurements are obtained at 7 mm above the coil.

The two methods of measuring the plasma parameters are Thomson scattering (TS) and absolute line emission intensity (ALI) measurements. The first technique provides accurate electron temperatures and densities. It is based on the scattering of light from a pulsed Nd:YAG laser by the free electrons in the plasma, which is collected by a monochromator in combination with an intensified multichannel photodiode array. In this article we only use the Te-values obtained with this method. For more information on the set-up we refer to Ref. 7.

The absolute line emissions are measured using a 1 m monochromator with a two-dimensional CCD-array placed in the focal plane. The two dimensions of this optical multichannel analyser (OMA) offer the possibility to obtain in one single measurement spatially resolved information at 25 radial positions of an emission line with the adjacent continuum. The system is absolutely calibrated by a tungsten lamp. The data are Abel inverted to obtain local values of the emission coefficient. Note that Abel-inversion is required, but that it also introduces additional inaccuracy. Especially local information in the center of the plasma (r = 0 mm) is difficult to determine due to the presence of the hollow structure in the densities and temperatures. Therefore, we will use only the information obtained for r > 3.5 mm. For a detailed description of the set-up of measuring absolute line emission intensities (ALI) we refer to Ref. 2.

3. METHOD OF DETERMINING TRANSITION PROBABILITIES

The transition probability A for a certain transition is an atomic constant, depending on the specific atomic structure only. Therefore, it is independent of the plasma conditions as long as fields in the plasma are not so high that the atomic structure is distorted. In the presented method, partial Local Saha Equilibrium (pLSE) is assumed for the levels with ionization energy Ie < 0.7 eV. In this case, the density \( n_p \) of state p per statistical weight \( g_p \) \( (\eta_p = n_p/g_p) \) is predicted by Saha's law:

\[
\eta_p = \frac{n_i n_e}{2g_p (2\pi m k_B T_e)^{3/2} e^{-E_i/(k_B T_e)}},
\]

(1)

where \( n_i \) and \( g_e \) are the density and statistical weight of the argon ion ground state and \( h, m, k_B \) and \( k_B \) have their usual meaning. So with this equation the level density per statistical weight \( \eta_p \) can be calculated easily for known plasma conditions, i.e. \( T_e \) and \( n_e \) under the assumption that \( n_i = n_i \).

On the other hand, the density of a state \( p \) can be obtained by measuring the emission coefficient \( j_{pq} \):

\[
j_{pq} = \frac{n(p) A_{pq} h \nu}{4\pi},
\]

(2)

of a transition from level \( p \) to level \( q \) emitting a photon \( h \nu \). For an optically open transition this emission coefficient can be obtained with ALI after Abel-inversion. Since the error margins in \( A \) as given in literature are much larger than those in the measured intensity \( j_{pq} \), a more accurate value for the transition probability can be obtained if an independent determination of the relevant level densities is available.

The method we follow is to construct the atomic state distribution function (ASDF) of highly excited states using a \( T_e \) value from Thomson scattering experiments together with a set of level densities obtained by ALI. Three emission lines are selected for this purpose as reference lines. These have a relatively low uncertainty in the transition probabilities of 25% and are situated high in the electronic system where the presence of pLSE may be assumed. The reference transitions
are 7s–4p, 6d–4p, and 5d’–4p with corresponding wavelengths of 588.9, 516.2, and 518.8 nm. To illustrate the method we present in Fig. 1 the upper part of the ASDF (ln η as a function of I_p) for r = 6 mm as obtained by ALI measurements of 15 levels. In this ASDF construction the A-values of Ref. 10 are used. The reference emission lines are indicated by crosses.

With the T_e value from Thomson scattering and the level densities η_p per statistical weight of the reference lines we determine the level density η_∞ at I_p = 0 using

\[
\ln \left( \frac{\eta_p}{\eta_\infty} \right) = \frac{1}{k_B T_e} I_p. \tag{3}
\]

Now η_∞ and the slope are known we have the Saha line as indicated by the full line in the figure. Note that the inaccuracy in the slope of this line is due to both the uncertainty of 5% in T_e from Thomson scattering and the combined effect of the errors in the absolute density based on the three reference lines. As indicated by the dotted lines, this leads to an uncertainty in the Saha predicted density for η_∞ of 17% which is still mainly due to the inaccuracies in A, but lower than 25% because of the use of three reference lines.

The absolute emission intensities j_p of transitions can now be used to determine the corresponding A-values by combining Eqs. (2) and (3):

\[
A_{pq} = \frac{4 \pi j_{pq} c}{h v g_q \eta_\infty} e^{-\left(\frac{\Delta E_{pq}}{k_B T_e}\right)}. \tag{4}
\]

This formula can be applied with T_e, η_∞ and j_p from experiments for all the different transitions. As can be seen from equation (4), the errors in A-values originate mainly from inaccuracies in η_∞ and j_p. This will be discussed in Sec. 4.

![Fig. 1. State population density as a function of the ionization energy I_p of level p. The full line is the level population predicted by Saha based on T_e by Thomson scattering and η_∞ by three level densities as obtained by emission experiments, indicated by crosses. The outer dotted lines indicate the inaccuracy interval. The measurements are carried out on an inductively coupled plasma with an input power of 1.2 kW at a radius of 6 mm from the center and at 7 mm above the load coil.](image-url)
4. RESULTS AND DISCUSSION

The method of determining transition probabilities as presented in the previous section is applied on 15 transitions in the argon system close to the ionization limit. The procedure is repeated for nine different radial positions between 3.8 and 3.7 mm resulting in nine $A$-values for each transition. By averaging these values systematic deviations due to errors in the shape of the radial profile are almost completely removed. The results with estimated inaccuracies of 20% are presented in Table 1 and are compared with the original values for the transition probabilities taken from Wiese et al.\textsuperscript{10} Most of these values have inaccuracies of 50% or even larger, so that a significant improvement of the $A$-values is achieved. Note that all the obtained $A$-values are within the uncertainties of those given in Ref. 10.

The origins of the inaccuracies can be divided in two parts: first, those related to the determination of the Saha line which predicts the density of the levels and second the inaccuracies associated with the measurement of the various $j_w$-values. Note that the instability of the plasma can also be a source of error, however, these are taken into account in the measured parameters $n_e$ and $T_e$.

Concerning the Saha line, we have the errors in the Thomson scattering determined $T_e$-value which is 5%.\textsuperscript{1} More important is the inaccuracy induced by the uncertainty of the $A$-values of the three reference lines (25%) which together give rise to an uncertainty of 14% in the $n_e$ determination. The error of 9% in the $j_w$-value required for the three reference points is also present, but will be reduced to 3% by the treatment of the nine radial positions. The Saha line together with the uncertainty margin is depicted in Fig. 1 by respectively the full and dotted lines. Concluding, we may state that an inaccuracy of the three reference lines is the most important error source in the determination of the Saha line.

In principle, the $n_e$ from Thomson scattering experiments could be used for calculating $\eta_{\infty}$. However, since the inaccuracy in $n_e$ is 15%, this will cause an uncertainty in the density $\eta_{\infty}$ of about 30% due to the $n_e^2$-dependency. Nevertheless, Thomson scattering and the reference points by AL1 are in agreement for the value of $\eta_{\infty}$ within 10%. Lowering the inaccuracy in the Saha line can be best achieved by determining more accurate values of $n_e$ with Thomson scattering (< 6%) to obtain an accurate value of $\eta_{\infty}$ or improving the used method by reducing the errors in the intensity measurements by treating more than three levels to increase the accuracy of $\eta_{\infty}$. The last option is difficult to implement since most of the $A$-values high in the electron system have large inaccuracies.

In the second place we have the inaccuracies associated with the emission coefficient $j_w$. As stated before this is better than 9%. This inaccuracy has several contributions. The use of the CCD array as a detector enables measurements with a small inaccuracy of less than 1%, including dark current and read-out noise. The absolute calibration of the set-up using a tungsten ribbon lamp together with the variations in plasma intensities introduces an error of 4%. Finally, Abel inversion can influence the radial profile. However, for positions larger than $r \sim 3.5 \text{ mm}$ this inaccuracy is less

<table>
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<th>$\lambda$ (nm)</th>
<th>$j_0$ (eV)</th>
<th>$E_p$ (cm$^{-1}$)</th>
<th>$A^{\text{old}}$ (10$^5$ s$^{-1}$)</th>
<th>$\Delta A/A^{\text{old}}$ (%)</th>
<th>$A^{\text{new}}$ (10$^5$ s$^{-1}$)</th>
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than 5%. All these inaccuracies together make the emission intensity measurements of $j_p$ accurate within 9%. Combining the errors in the Saha line construction (17%) and the $j_p$ determination (9%) and averaging the nine, for the different radial positions obtained, $A$-values lead to a total inaccuracy in the transition probabilities of less than 20%.

Figure 2 shows the result of the ASDF construction using the new $A$-values for three different plasma positions. It is found that the corrected transition probabilities are indeed independent from plasma conditions. Comparing these results with the uncorrected level densities of Fig. 1, shows that the decrease in scatter is striking. For the different positions the obtained level densities are, within the accuracy, on one line. In general, all the scatter is created by the inaccuracies in the determination of the $j_p$ for the radial position in question (CCD-read out and Abel-inversion).

5. CONCLUSIONS

The inductively coupled plasma can be used as a source for determining transition probabilities for transitions high in the argon system, because of the presence of partial local Saha equilibrium for highly excited states in parts on this plasma. A combination of absolute line emission measurements with Thomson scattering experiments allows improving the accuracy in the transition probability of often about 50% down to 20%.

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REFERENCES