Spectrochimica Acta Part B 144 (2018) 20–28

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Transition rate diagrams and excitation of titanium in a glow discharge in argon and neon

Zdeněk Weiss [a,*], Edward B.M. Steers [b,1], Juliet C. Pickering [c]

[a] Institute of Physics v.v.i., Czech Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czech Republic
[b] London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK
[c] Blackett Laboratory, Imperial College London, Prince Consort Road, London, SW7 2AZ, UK

ARTICLE INFO

Article history:
Received 31 December 2017
Received in revised form 27 February 2018
Accepted 7 March 2018
Available online 9 March 2018

Keywords:
Glow discharge
Emission spectroscopy
Titanium
Excitation
Ionization
Transition rate diagrams
Charge transfer
Argon
Neon

ABSTRACT

Emission spectra of titanium in a Grimm-type glow discharge in argon and neon were studied using the formalism of transition rate diagrams. Ti I spectra in argon and neon discharges are similar, without signs of selective excitation, and populations of Ti I levels exhibit a decreasing trend as function of energy, except for some scatter. A major excitation process of Ti II in argon discharge is charge transfer from argon ions to neutral titanium. In neon discharge, a strong selective excitation was observed of Ti II levels at ≈13.3–13.4 eV relative to the Ti I ground state. It was attributed to charge transfer from doubly charged titanium ions to neutral titanium, while the Ti^{++} ions are produced by charge transfer and ionization of neutral titanium by neon ions. Cascade excitation is important for Ti II levels up to an energy of ≈13 eV relative to the Ti I ground state, both in argon and neon discharges.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Excitation and ionization processes in glow discharge (GD) plasmas such as the Grimm-type glow discharge [1] are subject to continual attention by the spectroscopic community, because of their importance for analytical interpretation of experimental data in Glow Discharge Optical Emission Spectroscopy (GD-OES) [1–4]. The Grimm-type GD cell consist of a flat cathode (the sample) and a tubular anode placed perpendicularly to the sample, from which it is separated by a narrow gap. The plasma develops in the anode cavity and is viewed axially, from the side opposite to the sample (end-on observation). Unlike some other spectral sources, typical glow discharges are not in local thermodynamic equilibrium (LTE) conditions [5–6] and GD excitation and ionization cannot normally be described by equations based on an assumption that populations of ionized and excited species in the plasma have Saha- and Boltzmann distributions. An alternative approach consists in evaluating relative rates at which individual states of the atom or ion under study are populated and radiatively depopulated. For this purpose, the formalism of transition rate (TR) diagrams, probably the most thorough method of empirical description of glow discharge spectra currently available, was introduced recently by Z. Weiss and co-workers [7].

The relative intensity I_{ij} of an emission line associated with a radiative transition $i \rightarrow j$ between an upper level i and a lower level j of an atom or ion can be expressed as

$$I_{ij} = r_{i\rightarrow j} E_{ij} = r_{i\rightarrow j} \frac{hc}{\lambda_{ij}} \quad (1)$$

where λ_{ij} is the central wavelength of this transition, E_{ij} is the energy difference between the levels i and j, $r_{i\rightarrow j}$ is the rate of this transition, i.e., the number of quanta of wavelength λ_{ij} emitted per second. From Eq. (1), it follows that the rate $r_{i\rightarrow j}$ is proportional to the product $I_{ij}\lambda_{ij}$. Provided the variation of the relative sensitivity of the spectrometer with wavelength is known, transition rates associated with different emission lines can be evaluated from the observed spectrum, except for a common multiplicative constant. In this sense, the quantities referred to as transition rates are transition rates expressed in an arbitrary unit that, for the given spectra, is the same throughout this paper. Each level i is radiatively *depopulated* at a rate R_i^{depop} equal to the sum of the rates of all transitions associated with the lines of which i is the upper level and a level j is radiatively *populated* at a rate R_j^{pop} equal to the

* Corresponding author.
E-mail address: weissz@fzu.cz (Z. Weiss).
[1] Deceased February 2018.

https://doi.org/10.1016/j.sab.2018.03.003
0584-8547/© 2018 Elsevier B.V. All rights reserved.

sum of the rates of the radiative transitions populating this level, i.e., those transitions for which j is the lower level:

$$R_i^{depop} = \sum_{k<i} r_{i\to k} \quad ; \quad R_j^{pop} = \sum_{k>j} r_{k\to j} \tag{2}$$

A TR diagram consists of two plots with a common abscissa scale: in the top plot, radiative *depopulation* rates (R^{depop}) of individual levels are plotted as functions of the level energy, and similarly in the bottom plot for radiative *population* rates (R^{pop}), except that the ordinate scale in the bottom plot has values increasing downward. Energies of the levels are given relative to the ground state of the *atom* throughout this paper. If the lifetime of the upper state of an emission line is largely limited by radiative decay, then the rate of *collisional* excitation (R^{col}) of this state will be equal to the difference between the rate of its radiative de-excitation and the rate of its radiative excitation:

$$R_i^{col} = R_i^{depop} - R_i^{pop} \tag{3}$$

Hence, a peak in the top plot of a TR diagram, not balanced by a peak corresponding to the same levels in the bottom plot, indicates that a collisional process is in operation, which selectively populates levels having energies in the position of the peak. TR diagrams are thus especially suitable for investigating selective excitation processes, occurring with a high efficiency only in a narrow energy interval in the vicinity of a characteristic energy (see Section 3.2. below). This approach however depends on certain prerequisities: [1] the spectrum under study must be radiometrically calibrated, so that 'true' relative line intensities at different wavelengths are available, [2] the spectrum must be measured with a sufficient resolution to resolve adjacent lines well and [3] the wavelength region recorded must be as wide as possible, so that all important transitions are included. Also, [4] good reference information for the element under study is needed, to allow correct classification of the lines observed and the identification of the upper and the lower levels of the corresponding transitions.

The aim of this paper is to present TR diagrams of Ti I and Ti II in a Grimm-type GD source in argon and neon and thus contribute to the existing knowledge of the excitation and ionization processes involved. Emission spectra of titanium have been studied extensively in the past in various contexts relevant to this paper [8–17]. Results reported in those papers will be mentioned further in the text and related to the findings reported here.

2. Experimental details

An excellent tool for studies like this is the vacuum high resolution VUV-VIS Fourier Transform (FT) spectrometer at the Blackett Laboratory, Imperial College London [18]. This instrument was used to collect spectral data presented here, in conjunction with a free-standing Grimm-type glow discharge source. Emission spectra reported here were measured using high purity titanium as cathode (Ti-1-23, Vacuumschmelze Hanau, Germany, with 99.91% Ti and traces of iron (0.05%) and some other elements). The Grimm-type source was operated at 'standard' conditions in argon and neon (dc discharge with a 4 mm-internal diameter anode in the constant voltage-constant current mode at 700 V, 20 mA, stabilized by adjusting the pressure of the working gas). Experimental setup and details of the FTS measurements can be found in our earlier papers, e.g. Ref. [9–11]. Radiometric calibration of the FTS spectra was performed using standard lamps, a tungsten-halogen lamp and a deuterium lamp, with known radiation characteristics, and by the branching ratio method [6]. The spectra span over the wavelength range of 160 nm to ≈630 nm, in three separate partially overlapping spectral regions. All the results presented below concern transition rates, themselves depending on line intensities. It is appropriate to mention here the experimental errors involved. There are two major sources of errors: [1] systematic errors caused by an imperfect radiometric calibration of the spectra and [2] error arising from the SNR (signal-to-noise ratio) of the observed spectral line, typically 1/SNR [18]. An estimated relative uncertainty of the radiometric calibration throughout the whole wavelength range is ≈10–20% for the measurements reported here. But only a minority of the lines involved in the determination of the TR-s come from the ends of the wavelength range, so, the overall systematic uncertainty related to the radiometric calibration will be lower: few percent (estimated). All the considerations in Section 3 (Results and discussion) concern large differences in the transition rates, typically by an order of magnitude or bigger, i.e., greatly exceeding the estimated experimental uncertainties. In particular, for the highest transition rates, error bars in the TR diagrams presented below will be comparable with the size of the symbols of individual points. The uncertainties may become significantly larger for low transition rates (weak lines), which, however, does not affect the conclusions.

Table 1
Identification and classification of observed lines in the emission spectra of this work.

	Number of lines	
Discharge type	Ti-Ar	Ti-Ne
All lines in the spectrum	1446	1388
of which: supposedly Ti	1062	1147
supposedly Ar or Ne	384	241
Identified as: Ti I	322	383
Identified as: Ti II	643	596
Identified as: Ti III	7	15
Ti unidentified	28	133
Ti blended[a]	62	20

[a] At resol. = 1 pm; Ti-Ar and Ti-Ne blends are also included.

All lines with the SNR > 10 were considered. Intensity-calibrated linelists from the three spectral regions were merged together and lines of argon or neon were filtered out using Ar- and Ne linelists from our earlier work on the spectral catalogue [19]. Those had been generated in the past as coincidences in the linelists originating from experiments with the same working gas but with different pure elements as cathodes. Lines in the resulting 'Ti-only' linelists were then classified according to the NIST database [20]. Our experimental 'Ti-only' linelist (1217 lines) was compared with the list of 4063 Ti lines listed in the NIST database (Ti I from 203 to 630 nm, Ti II and Ti III from 160 to 630 nm). The comparison between the measured wavelengths and those listed by NIST was performed by a computer program, at a tolerance of 0.8 pm. In addition a few coincidences were found, in which the difference between the measured and the listed wavelength is from 0.8 pm to ≈1.2 pm. The NIST reference list for Ti I and Ti II is based on a recent compilation by E.B. Saloman [21]. The primary source of information on the Ti I spectrum in the NIST database were the papers by Forsberg [22] and Litzén [23]. The Ti II linelist of NIST is based on papers by Gianfrani et al. [24], Huldt et al. [25] and Pickering et al [17]. The NIST listing of Ti III lines comes from Shirai et al [26]. Some lines not listed in the NIST database were identified based on the PLASUS [27] database and the tables by Striganov and Sventinskii [28]. An overview of these operations, showing the number of lines of each kind is in Table 1.

There were still 155 supposedly Ti lines remaining, which ought to be classified. These 'residual' lines were not included in the calculations of the TR diagrams, and will likely include transitions involving experimentally unknown energy levels. In argon discharge, the total radiative depopulation rate which they represent is 6.85×10^3, in neon it is 3.41×10^4 (see footnote[2]). These are small fractions of the total observed gross radiative depopulation rates (e.g. 1.53×10^7 for Ti II in argon discharge and 9.26×10^6 for Ti II in neon discharge). The strongest unidentified lines, supposedly Ti, occurring in the Ti-Ne and the Ti-Ar discharges, are listed in Table 2. The columns with the heading 'TR-s' contain relative

[2] Transition rates are expressed in the same units that are used in the ordinate scaling of the TR diagrams and throughout the whole paper.

Download English Version:

https://daneshyari.com/en/article/7673836

Download Persian Version:

https://daneshyari.com/article/7673836

Daneshyari.com