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Review

Transition rates and transition rate diagrams in atomic emission spectroscopy: A review

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

[a] LECO Instrumente Plzeň, s.r.o., Plaská 66, 323 00 Plzeň, 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

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ABSTRACT

In low pressure plasmas with low electron densities, such as glow discharges, radiative de-excitation is a major de-excitation process of most excited states. Their relative de-excitation rates can be determined by emission spectroscopy, making it possible to study excitation processes in these discharges. This is in contrast to denser plasmas, in which such considerations are usually based on relative populations of excited states and concepts related to thermodynamic equilibrium. In the approach using reaction rates rather than populations, a convenient tool is the recently introduced formalism of transition rate diagrams. This formalism is reviewed, its relevance to different plasmas is discussed and some recent results on glow discharge excitation of manganese, copper and iron ions are presented. The prospects for the use of this formalism for the comparison of rate constants and cross sections for charge transfer reactions with argon ions of elements of interest in analytical glow discharge spectroscopy are discussed.

Contents

1. Introduction

In atomic emission spectroscopy, the advent of modern spectrometers with CCD detectors and sophisticated data acquisition systems some years ago made it possible to collect spectra over wide continuous wavelength ranges, sort out effectively the resulting data and use them for analytical purposes. Most elements have rather complex emission spectra, depending strongly on the spectral source used and excitation conditions. The spectra differ *inter alia* by the appearance and relative intensities of different emission lines of the elements present. Interpretation of emission spectra in terms of the excitation processes involved and the plasma parameters controlling them is a complex task. The introduction of transition rate diagrams (TR diagrams) by Z. Weiss and co-workers in the past 2 years [1–3] was an attempt to create a tool that would provide a better insight into the excitation of different

* Corresponding author.
E-mail address: weissz@leco.cz (Z. Weiss).

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elements in a glow discharge, based on their emission spectra. This review is an introduction to TR diagrams and a summary of what has been done so far on this topic.

2. Excitation and de-excitation in laboratory plasmas

2.1. Transition rates and TR diagrams

The concept of TR diagrams [1–3] can be described as follows: The true relative intensity I_{ij} of an emission line[a] 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

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

where λ_{ij} is the wavelength of this line, E_{ij} is the energy difference betwen the levels i and j, $n_{i\rightarrow j}$ 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 $n_{i\rightarrow j}$ 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 spectrum, is the same throughout the whole 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 sum of the rates of the radiative transitions populating this level, i.e., those transitions for which j is the lower level:

$$R_i^{depop} = \sum_{k<i} n_{i\rightarrow k} \quad ; \quad R_j^{pop} = \sum_{k>j} n_{k\rightarrow j}. \quad (2)$$

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 in the bottom plot, the same is done with radiative *population* rates (R^{pop}), except that the ordinate scale in the bottom plot has values increasing downward (see Fig. 1). Energies of the levels are given relative to the ground state of the *atom* in Fig. 1 and 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 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^{col}):

$$R_i^{col} = R_i^{depop} - R_i^{pop}. \quad (3)$$

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. If there are high transition rates for a given level or group of levels in both plots (top and bottom), it is an indication of a cascade excitation/de-excitation sequence in which this level participates. In Fig. 1 is a TR diagram describing emission spectrum of manganese ions in an argon glow discharge [1]. The strongest multiplets observed in the Mn II spectrum are depicted by horizontal arrows connecting the upper term and the lower term of

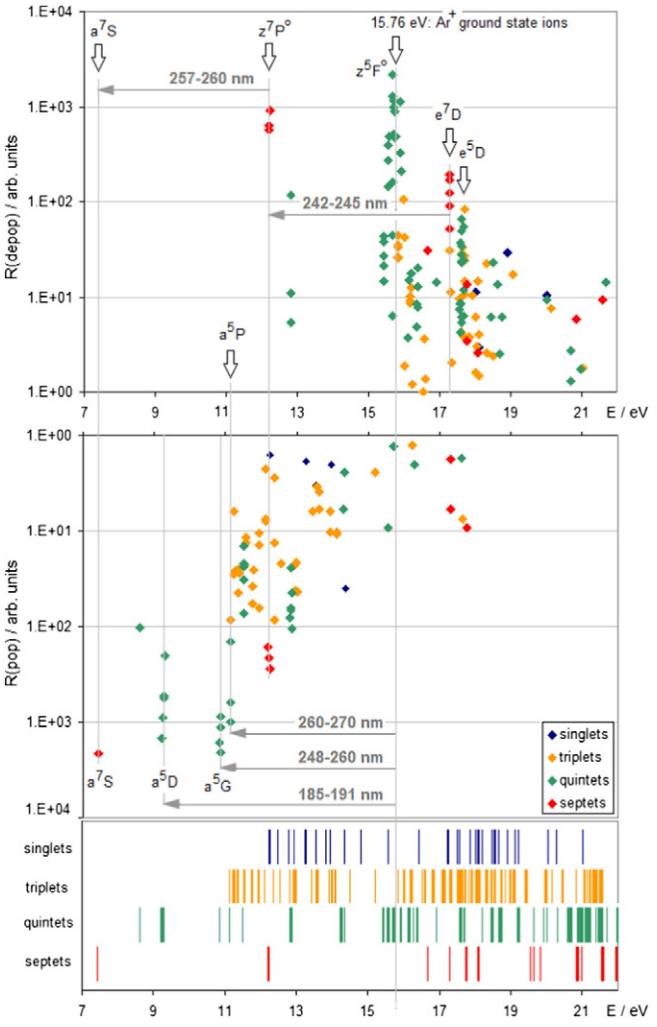

Fig. 1. Transition rate diagram of Mn II in a Grimm-type glow discharge in argon (700 V, 20 mA, a 4 mm-diameter anode).

the corresponding transitions. Also wavelength intervals of those multiplets are indicated. An example of a cascade process in the Mn II spectrum is the sequence

$$3d^5\,(^6S)4d\ e^7D\ (\sim 17.30\ eV) \rightarrow 3d^5\,(^6S)4p\ z^7P^\circ\ (12.19-12.24\ eV) \rightarrow 3d^5\,(^6S)4s\ a^7S\ (7.43\ eV), \quad (4)$$

ending in the Mn II ground state, $3d^5(^6S)4s\ a^7S$, at 7.43 eV (see Fig. 1, top). It makes sense to distinguish individual levels in a TR diagram by their spin multiplicities, $2S + 1$, where S is the spin angular momentum. Spin multiplicity is preserved in electric dipole transitions, hence, most spectral lines are associated with transitions between levels with the same multiplicity.[b] It is then easier to track major cascade de-excitation paths in the TR diagram, considering separately the points (levels) with a given multiplicity. A TR diagram inherently reflects the electronic structure of the atom or ion investigated. Some collisional processes responsible for excitation are selective [4], i.e., occur at certain energies only and/or can excite only states with certain multiplicity. Therefore, it helps to show the TR diagram together with a plot depicting energies of all existing levels, sorted according to their

[a] Radiative power of that line, emitted by the plasma and collected by the spectrometer. The fraction collected of the total power emitted is given by the optical setup and is the same for all lines in the spectrum at any plasma conditions. Hence, the signal produced by the spectrometer is a good measure of the total power radiated by that line. The word '*true*' means that the intensity, as defined above, is corrected for the instrument sensitivity function (sensitivity as function of the wavelength).

[b] For transition group elements, there are transitions from higher lying levels not preserving multiplicity, because of level mixing. If LS coupling is violated, terms may contain admixtures of different L's and S's. Then, if terms are designated by their dominant LS components, the $\Delta S = 0$ selection rule may appear to break down because of transitions occurring through non-dominant components[16].