Abstract: This report is the 14th in a series on Spectrochemical Methods of Analysis issued by IUPAC Commission V.4. Because of the complexity and the lack of uniformity of the present nomenclature (e.g. "2 step excited resonance fluorescence", "resonance enhanced multiphoton ionization", etc.) a new way is needed to describe these transitions. The aim of this document is therefore to present a new notation, the IUPAC Notation, to describe the various processes involved in atomic laser spectroscopy. Using a few assumptions as detailed below, this notation has the advantage of being simple and systematic. States and processes can be described in a general way irrespective of the type of laser spectrometry.

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1 INTRODUCTION

A series of documents dealing with nomenclature, symbols and units used in spectrochemical analysis have been issued by IUPAC.

Part I [Pure Appl. Chem., 30, 653-679 (1972)] is concerned mainly with general recommendations in the field of emission spectrochemical analysis.

Part III [Pure Appl. Chem. 45, 105-123 (1976)] deals extensively with the nomenclature of analytical flame (atomic emission and absorption) spectroscopy and associated procedures.

Part IV [Pure Appl. Chem. 52, 2541-2552 (1980)] concerns X-ray emission (and fluorescence) spectroscopy.

Part V [Pure Appl. Chem. 57, 1453-1490 (1985)] deals with the classification and description of radiation sources.


Part VII [Pure Appl. Chem. 60, 1449-1460 (1988)] is concerned with molecular absorption spectroscopy (UV/VIS).


Part X [Pure Appl. Chem. 60, 1461-1472 (1988)] deals with sample preparation for analytical atomic spectroscopy and other related techniques.


Part XII [Pure Appl. Chem. 64, 253-259, 1992] deals with terms related to electrothermal atomization.


This document, Part XIV, presents the IUPAC notation to describe the various processes involved in atomic laser spectroscopy. This notation has the advantage of being simple and systematic. States and processes can be described in a general way irrespective of the type of laser spectrometry.

2 BASIC CONCEPTS OF THE IUPAC NOTATION

The IUPAC notation describes any variety of laser-based atomic spectroscopy as a sequential series of processes which cause transitions between the states of an atom. The processes are symbolized by upper case letters (defined later) and modified by lower case subscripts which indicate the state transitions induced by the process, given in a series beginning with the initial state and ending in the final state. This system may be thought of as a means to describe with textual symbols the energy level diagrams often used for this purpose, where the states of an atom are symbolized by a stacked series of horizontal lines, and processes are shown as a variety of arrows connecting the states. As a general rule, it was felt useful to keep the symbols as few and simple as possible.

This notation is not intended to replace or enhance accepted atomic state and transition nomenclature. It is presented just as a simple system to describe spectrochemical processes.

The processes considered are those believed to be of analytical usefulness and already discussed in the literature. The names of these processes are given as an illustration of the notation and not as IUPAC nomenclature. Moreover, and more importantly, while the processes can be unambiguously characterized by the IUPAC Notation, the same cannot necessarily hold for the terms attributed to each process. In fact, in some cases (especially in the ionization processes) clarity and conciseness do not always coexist.

2.1 Assumptions

2.1.1 Monochromatic excitation

The excitation process is assumed to be monochromatic, i.e. the source emits only at the excitation transition(s) considered.

2.1.2 Homogeneous broadening

All atoms are assumed to participate in the absorption process considered, i.e. they contribute equally to the absorption at any frequency within the absorption profile.
2.2 Notation for the states

The following symbols will be used as subscripts in the Notation.

- \( g \) ground state
- \( a, b, c, d, \ldots \) excited states with energies \( a < b < c < d < \ldots \)
- \( v \) virtual state
- \( \Delta \) amount of detuning from resonant interaction
- \( \infty \) continuum of states
- \( i \) auto-ionizing level
- \( +, - \) ionized state, e.g. \( g^+, a^{2+} \)
- ( ) simultaneous processes

2.3 Processes

The following symbols will be used in the Notation:

- \( R \) radiatively induced transition
- \( F \) fluorescence
- \( C \) collisional excitation or collisional ionization (including specific ionization processes such as Penning ionization, associative ionization, energy-pooling collisions)
- \( M \) collisional intra-multiplet mixing
- \( Q \) quenching (collisional de-excitation)
- \( E \) ionization induced by an electric field
- \( S \) scattering
- ( ) simultaneous processes

2.3.1 Radiative Pumping

The symbol \( R \) stands for radiatively induced transition, e.g. \( R_{ga} \) describes the transition in which an atom is changed from its ground state, \( g \), to an excited state, \( a \), by resonant absorption of a photon of energy \( h\nu_{ga} \). **Multiple excitation** is also described. This term refers to the possibility of reaching a given excited state by a series of sequential pumping processes which can take place with a single laser source or with multiple laser sources. Multiple excitation can be further qualified as a **multi-photon** and a **multi-step process**, depending on whether the intermediate level in the excitation process is a virtual or a real level. The terminology **multi-photon** is here preferred to **multi-step**, because the difference in the two processes can be clarified by the resonant or off-resonant character of the interaction. For example, \( R_{ga}R_{ab} \) means that atoms are transferred from the ground state, \( g \), to an excited state, \( b \), by resonant absorption of two photons of different frequencies \( \nu_{ga} \) and \( \nu_{ab} \), which is currently termed "resonant, two-photon excitation."

Although the very existence of a so-called "virtual" state might be questioned on purely theoretical grounds, it is common practice to refer to such states when describing multi-photon processes. In the context of this Notation a "virtual" state has been retained because it is helpful in visualizing off-resonant processes. For example, \( R_{gv}R_{va} \) means that atoms are transferred from the ground state, \( g \), to an excited state, \( a \), by an absorption process proceeding through an intermediate virtual state, \( v \), and involving two identical photons of the same frequency. This process is currently termed "off-resonant, two-photon excitation." Only one laser is needed. Contrary to the resonant case above, here the name off-resonant, single frequency, two-photon excitation is appropriate. Indeed, atoms can also be transferred from the ground state, \( g \), to an excited state, \( a \), by an absorption process proceeding through an intermediate virtual state, \( v \), and involving two photons of different frequencies. In this instance, this process would be denoted as \( R_{gv}R_{va} \) and termed "off-resonant, two frequency, two-photon excitation." Two lasers are needed.

The above described process are illustrated below in Fig. 1.
2.3.2 Near-resonant excitation

In the off-resonant process described under section 2.3.1 as \( R_{gva} \), the possible existence of a real level in the vicinity of the virtual state, \( v \), was not taken into account. However, from excitation studies with a single laser source, it is well known that, when the laser excitation frequency comes close to resonance with a real state, a sharp increase in the two-photon excitation probability occurs. To distinguish this process from that already described, the term "near-resonant, single frequency, two-photon excitation" is currently used. If the detuning between the virtual state reached by the laser and the real state is indicated by \( \Delta \), then the process can simply be written as \( R_{g(a+\Delta)b} \). In other words, the letter \( v \) has been replaced by \( (a+\Delta) \).

Moreover, when the atoms are present in a collision-dominated environment such as atmospheric pressure atomizers (e.g., flames, furnaces, plasmas), it is well known that, if the atoms excited by the laser near to resonance collide with other atoms (molecules), the scattered light has a component at the resonant frequency (known as fluorescence). This process is known as collisional redistribution of radiation. Atoms transferred by collisions into the real state can then absorb another photon of a different frequency and be further excited. Such a mechanism would then be denoted as \( R_{g(a+\Delta)b} \) and is termed "near-resonant, two-frequency, two-photon excitation." For the sake of simplicity, the "near resonant" level is indicated with dashed lines (as if it were a virtual level), although, in this particular case, one should speak of resonant dipole absorption in the quasi-molecule (collision complex). The above described processes are exemplified below in Fig. 2.

2.3.3 Radiationless depopulation of excited states

The following symbols are used to describe these processes:

- **C**: collisional excitation or collisional ionization (including specific ionization processes such as Penning ionization, associative ionization, energy-pooling collisions, etc.)
- **M**: collisional intra-multiplet mixing
- **Q**: collisional de-excitation
- **E**: ionization induced by an electrical field (the symbol \( W \) could be used in those cases where ionization is accomplished with a microwave field)

Some additional explanations for the symbols seem to be necessary here. \( C \) refers to (endoergic) collisional transfer of atoms to states higher in energy than the radiatively excited level, and which occurs

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1Note: The similarity of the notation \( R_{gab} \) (involving a real intermediate level \( a \)) with \( R_{gva} \) (involving one virtual level) should not be taken as an indication that the two processes are also conceptually similar. In fact, except for the fact that two lasers tuned at two different frequencies are involved, \( R_{gva} \) is conceptually similar to \( R_{gva} \). In this last case, as only one laser is involved but a two-photon event occurs, one could also replace the notation \( R_{gva} \) with \( R_{g2a} \).

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therefore, only after radiative excitation (e.g., C<sub>ab</sub>). Although, in a general sense, these processes might also include quenching collisions, the symbol Q is used here in the restricted meaning of exoergic collisional (quenching) transfer of atoms to state lower in energy than the radiatively-excited state (e.g., Q<sub>ba</sub>). Both C and Q define transitions between states belonging to a different spectroscopic term [e.g., Na (3<sup>2</sup>P<sub>3/2</sub> - 3<sup>2</sup>S<sub>1/2</sub>)]. When a collision induces a transition between different components of the same multiplet [e.g., Na (3<sup>2</sup>P<sub>3/2</sub> - 3<sup>2</sup>P<sub>1/2</sub>)], the symbol M (mixing collisions) is used.

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\[ R_{g(a \pm \Delta)b} \]
\[ R_{g(a \pm \Delta)R_{ab}} \]

Fig. 2. Examples of near-resonant excitation

2.3.4 Radiative de-excitation by spontaneous emission

Despite the fact that stimulated emission from the laser excited level can occur and can indeed be used in many (mainly molecular) experiments, it is omitted here. Only spontaneous radiative de-excitation processes are therefore considered. The symbol F represents fluorescence and other spontaneous emission transitions. The processes will be written in a sequential way as illustrated with the following examples:

- Resonance fluorescence is represented by e.g. R<sub>gaFag</sub>, where ga is the reverse of ag.
- Non resonance fluorescence is divided into direct-line fluorescence, represented by e.g. R<sub>gbFba</sub> where there is only one common level, b, and stepwise fluorescence, denoted by e.g. R<sub>gbQbaFag</sub>, R<sub>gbMbaFag</sub>, or R<sub>gaCabFbg</sub>.

2.3.5 Radiative de-excitation by Rayleigh or Raman scattering

The symbol S is used to denote scattering transitions. It is used in this Notation to emphasize the fundamentally different character of these radiative scattering processes from the fluorescence processes. As resonance fluorescence is often considered to be a special case of scattering, the following distinctions are suggested:

- Scattering is a single act. Absorption and re-emission of light occur almost at the same time (delay measured in fs). A redirection of the light quanta is observed.
- Fluorescence is a double act. Absorption is followed by re-emission after a delay.

Classification of the various cases of scattering is made in this Notation according to the diameter, \( d \), of the particle involved.

- For \( d > \lambda \), scattering is due to particulates. Elastic scattering has both Mie scattering and Rayleigh scattering components.
- For \( d < \lambda \), scattering is mostly due to interactions with atoms or molecules. Elastic scattering corresponds to Rayleigh scattering and inelastic scattering to Raman scattering.

3 EXAMPLES OF USE

To illustrate the use of this IUPAC Notation, examples pertinent to both fluorescence and ionization methods will be used. For each process, we give the proposed Notation and the currently used term. In some instances, some more qualifying attributes can be added to these terms, e.g. Stokes and anti-Stokes, excited state, thermally assisted, etc. Note that in describing a process as "anti-Stokes" when more
excitation transitions are involved, the fluorescence frequency is compared with the excitation frequency of the last exciting photon. The possible processes shown are not intended to be exhaustive, only illustrative.

3.1 Resonance fluorescence

The illustrative examples of resonance fluorescence are given in Fig. 3:

3.2 Non-resonance fluorescence

The usual names used for the processes in Fig. 3 are: 1.) Resonant$^2$ fluorescence; 2.) Excited-state resonant fluorescence; 3.) Resonant, two-photon fluorescence; 4.) Excited-state resonant two-photon fluorescence; 5.) Near-resonant fluorescence (Stokes and anti-Stokes); 6.) Near-resonant, two-photon fluorescence; 7.) Excited-state, near-resonant, two-photon fluorescence; 8.) and 9.) Resonant, disconnected, two-photon fluorescence.$^3$

3.3 Other fluorescence processes

$^2$Note: The words "resonance" and "resonant" are used interchangeably in the literature.

$^3$Note: By analogy, processes 3.3.) and 3.4.) can be qualified as "connected," i.e. process 3.3.) can be called "Resonant, connected, two-photon fluorescence."
It is also possible to observe two fluorescence transitions at the same time, especially in the case of collisional intra-multiplet mixing, as in Fig. 5:

![Diagram showing fluorescence transitions]

1. $R_{gb}F_{ba}$
2. $R_{ab}F_{bg}$
3. $R_{ga}R_{ac}F_{cb}$
4. $R_{gv}F_{ba}$
5. $R_{gv}R_{vb}F_{ba}$
6. $R_{gb}R_{bc}F_{ca}$
7. $R_{gb}Q_{ba}F_{ag}$
8. $R_{ga}C_{ab}F_{bg}$
9. $R_{ga}C_{ab}R_{bc}F_{ca}$
10. $R_{gb}Q_{ba}R_{ac}F_{cb}$

Fig. 4. Examples of non-resonance fluorescence processes

![Diagram showing non-resonance fluorescence processes]

Fig. 5. Simultaneous observation of two fluorescence transitions
1. $R_{ga}M_{ab}(F_{ag}+F_{bg})$
2. $R_{gb}M_{ba}(F_{bg}+F_{ag})$

3.4 Rayleigh and Raman scattering

Only a few examples of these processes are given in Fig. 6:

![Diagram showing Rayleigh and Raman scattering]

1. $R_{gv}S_{vg}$
2. $R_{gv}S_{va}$
3. $R_{av}S_{vg}$
4. $R_{gv}vS_{va}$

Fig. 6. Examples of Rayleigh and Raman scattering
The usual names for these processes are: 1.) Rayleigh scattering; 2.) Spontaneous Raman scattering; 3.) Spontaneous anti-Stokes Raman scattering; and 4.) Hyper-Raman scattering.

3.5 Laser enhanced ionization

As indicated previously, C is used here for collisional ionization proceeding from the single state reached in the excitation process and the continuum of states above the ionization potential of the atom. However, a summation, ∑, of states is involved in the ionization process which cannot, therefore, be referred to one particular state. As this is not easy to denote in a Notation system, it has to be understood that C is in fact ∑C, the summation being extended to several levels whose collisional ionization rate is enhanced by the laser excitation process considered. By way of example, the processes illustrated in Fig. 7 are given:

Fig. 7. Examples of laser enhanced ionization processes

The usual names for these processes are: 1.) Resonant excitation, collisional ionization; 2.) Excited-state resonant excitation, collisional ionization; 3.) Resonant, connected, two-photon excitation, collisional ionization; 4.) Off-resonant, single-frequency, two-photon excitation, collisional ionization; 5.) Resonant, disconnected, two-photon excitation, collisional ionization; and 7.) Off-resonant, single-frequency, three-photon excitation, collisional ionization.

3.6 Photo-ionization

Contrary to the collisional ionization processes, photo-ionization processes can be resonant when an auto-ionizing state is reached. Some of these processes are illustrated in Fig. 8:

The usual names for these processes are: 1.) Single-frequency, resonant excitation, photo-ionization; 2.) Single-frequency, off-resonant, two-photon excitation, photo-ionization; 3.) Two-frequency, resonant excitation, photo-ionization; 4.) and 5.) Disconnected, two-frequency, resonant excitation, photo-ionization; 6.) Two-frequency, off-resonant, two-photon excitation, photo-ionization; 7.) Two-frequency,

4Note: Collisional ionization is intended to be, by definition, non-resonant.
resonant excitation, resonant ionization; 8.) Three-frequency, resonant, two-photon excitation, photo-ionization; and 9.) Two-frequency, off-resonant, three-photon excitation, resonant ionization.

Fig. 8. Examples of photo-ionization processes

3.7 Other ionization processes

An example of other ionization processes is given in Fig. 9:

Fig. 9. Field ionization as an example of other ionization processes

This process is usually named resonant, two-photon excitation, field ionization.

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