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Nomenclature, Symbols, Units, and their Usage in Spectrochemical Analysis - XIV

LASER-BASED ATOMIC SPECTROSCOPY: PROPOSAL FOR A NEW NOTATION

(IUPAC Recommendations 1996)

Prepared for publication by

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Nomenclature, Symbols, Units, And Their Usage In Spectrochemical Analysis - XIV. Laser-Based Atomic Spectroscopy: Proposal For A New Notation (IUPAC Recommendations 1996)

SYNOPSIS

This report is 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.

1 INTRODUCTION

A series of documents dealing with nomenclature, symbols and units used in spectrochemical analysis is 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 II [Pure Appl. Chem., 45, 99-103 (1976)] gives some basic rules on data interpretation.

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 VI [Pure Appl. Chem. 56, 231-345 (1984)] covers molecular luminescence spectroscopy.

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

Part VIII [Pure Appl. Chem. 63, 735-746 (1991)] deals with a new nomenclature system for X-ray spectroscopy.

Part IX [Pure Appl. Chem. 67, 1724-1744 (1995)] covers fundamental aspects of spectral dispersion and isolation of radiation.

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

Part XI [Pure Appl. Chem. 67, 1745-1760 (1995)] deals with the detection of radiation.

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

Part XIII [Pure Appl. Chem. 64, 261-264, 1992] deals with terms related to chemical vapour generation.

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 <u>not</u> as IUPAC nomenclature. Moreover, and more importantly, while the processes can be unambiguously characterised 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.

As a general rule, it was felt useful to keep the symbols as few and simple as possible.

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, ...:	excited states with energies $a < b < c < d < \ldots$
v:	virtual state
Δ:	amount of detuning from resonant interaction
∞:	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 hn_{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 n_{ga} and n_{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. As, in the context of this Notation, the question seems to be irrelevant, a "virtual" state has been retained because it is helpful in visualizing off-resonant processes. For example, R_{gva} 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.

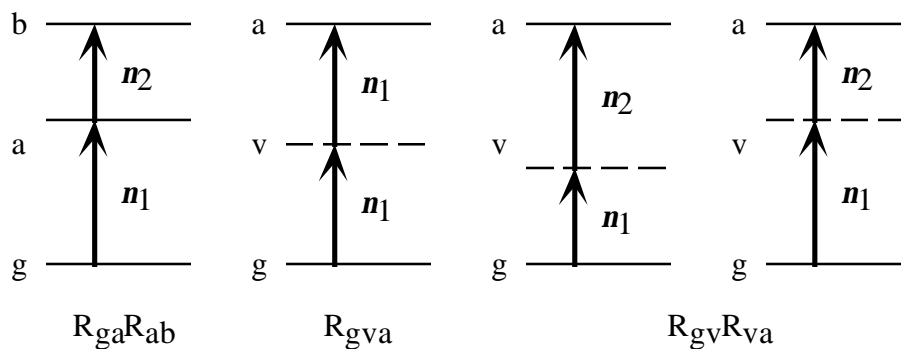The above described process are illustrated below in Fig. 1.

Fig.1 Radiative pumping processes

The two schemes for the process $R_{gv}R_{va}$ are intended to stress the fact that what matters in this instance is the condition $n_1 + n_2 = n_{ga}$, irrespective of whether n_1 is greater or less than n_2.

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 Δ, then the process can simply be written as $R_{g(a\pm\Delta)b}$. In other words, the letter v has been replace by $(a\pm\Delta)$.

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 $R_{g(a\pm\Delta)}R_{ab}$ 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.

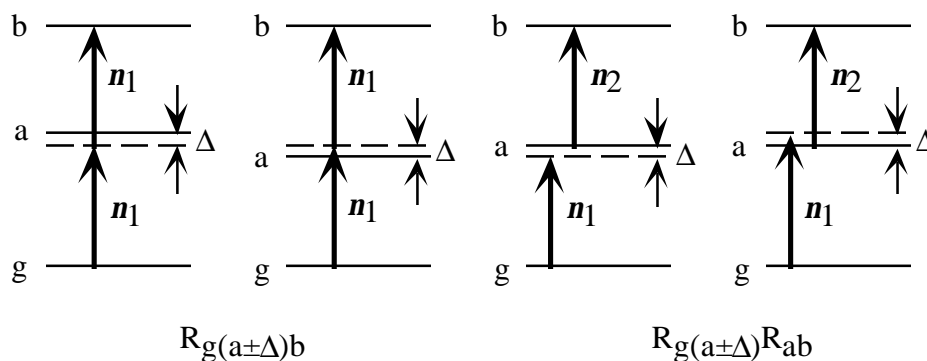$$R_{g(a\pm\Delta)b} \qquad\qquad R_{g(a\pm\Delta)}R_{ab}$$

Fig. 2. Examples of near-resonant excitation

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 therefore, only after radiative excitation (e.g. C_{ab}). 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_{ba}). Both C and Q define transitions between states belonging to a different spectroscopic term [e.g. Na $(3^2P_{3/2} - 3^2S_{1/2})$]. When a collision induces a transition between different components of the same multiplet [e.g. Na $(3^2P_{3/2} - 3^2P_{1/2})$], the symbol M (mixing collisions) is used.

2.3.4 Radiative de-excitation by spontaneous emission

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. $R_{ga}F_{ag}$, where ga is the reverse of ag.

Non resonance fluorescence is divided into direct line fluorescence, represented by e.g. $R_{gb}F_{ba}$ where there is only one common level, b, and stepwise fluorescence, denoted by e.g. $R_{gb}Q_{ba}F_{ag}$, $R_{gb}M_{ba}F_{ag}$, or $R_{ga}C_{ab}F_{bg}$.

2.3.5 Radiative de-excitation by Rayleigh or Raman scattering

The symbol S is used to denote scattering transition. 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 $d > 1$, scattering is due to particulates. Elastic scattering has both Mie scattering and Rayleigh scattering components.

– For $d < 1$, 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:

1.) $R_{ga}F_{ag}$ 2.) $R_{ab}F_{ba}$ 3.) $R_{ga}R_{ab}F_{ba}$ 4.) $R_{ab}R_{bc}F_{cb}$ 5.) $R_{g(a\pm\Delta)}F_{ag}$

6.) $R_{g(a-\Delta)}R_{ab}F_{ba}$ 7.) $R_{a(b-\Delta)}R_{bc}F_{cb}$ 8.) $R_{ga}C_{ab}R_{bc}F_{cb}$ 9.) $R_{gb}Q_{ba}R_{ac}F_{ca}$
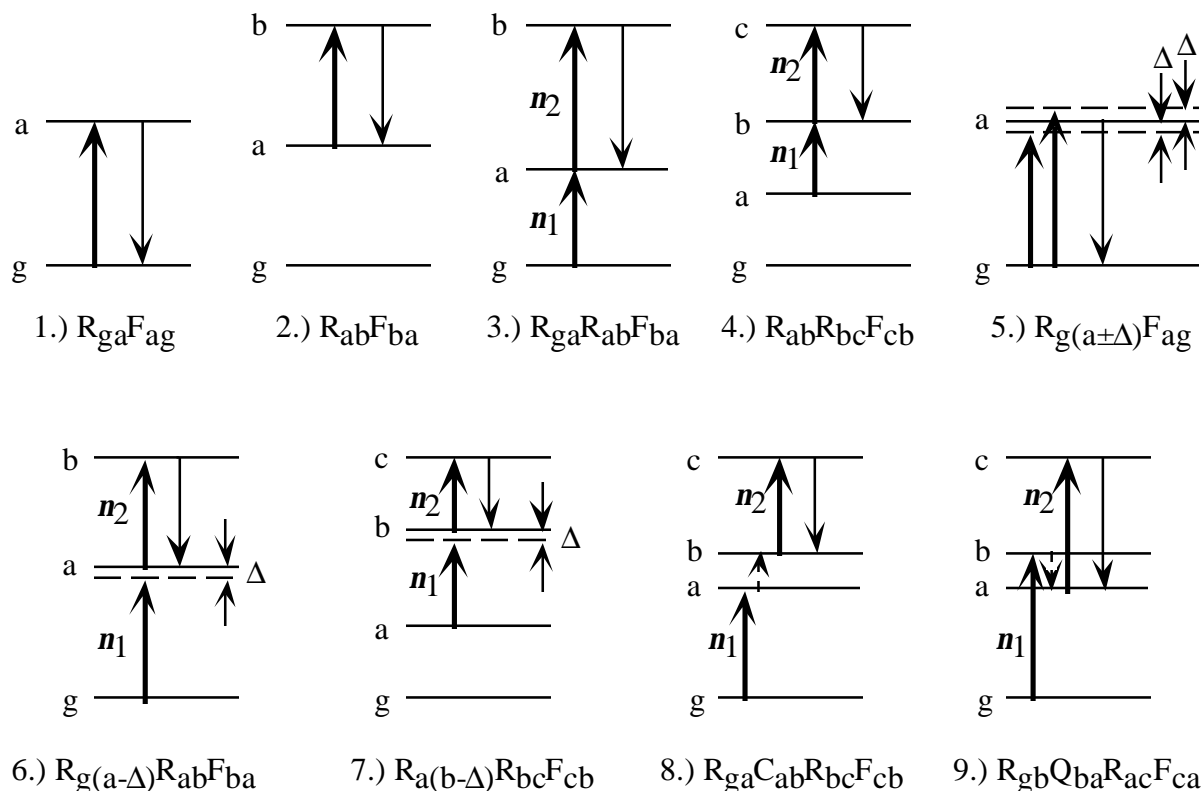
Fig. 3. Examples of resonance fluorescence processes

The usual names used for the processes in Fig. 3 are: 1.) Resonant[1] 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.[2]

3.2 Non-resonance fluorescence

The illustrative examples of non-resonance fluorescence are given in Fig. 4:

$$1.) R_{gb}F_{ba} \quad 2.) R_{ab}F_{bg} \quad 3.) R_{ga}R_{ac}F_{cb} \quad 4.) R_{gvb}F_{ba} \quad 5.) R_{gv}R_{vb}F_{ba}$$

$$6.) R_{gb}R_{bc}F_{ca} \quad 7.) R_{gb}Q_{ba}F_{ag} \quad 8.) R_{ga}C_{ab}F_{bg} \quad \begin{array}{c}9.) \\ R_{ga}C_{ab}R_{bc}F_{ca}\end{array} \quad \begin{array}{c}10.) \\ R_{gb}Q_{ba}R_{ac}F_{cb}\end{array}$$
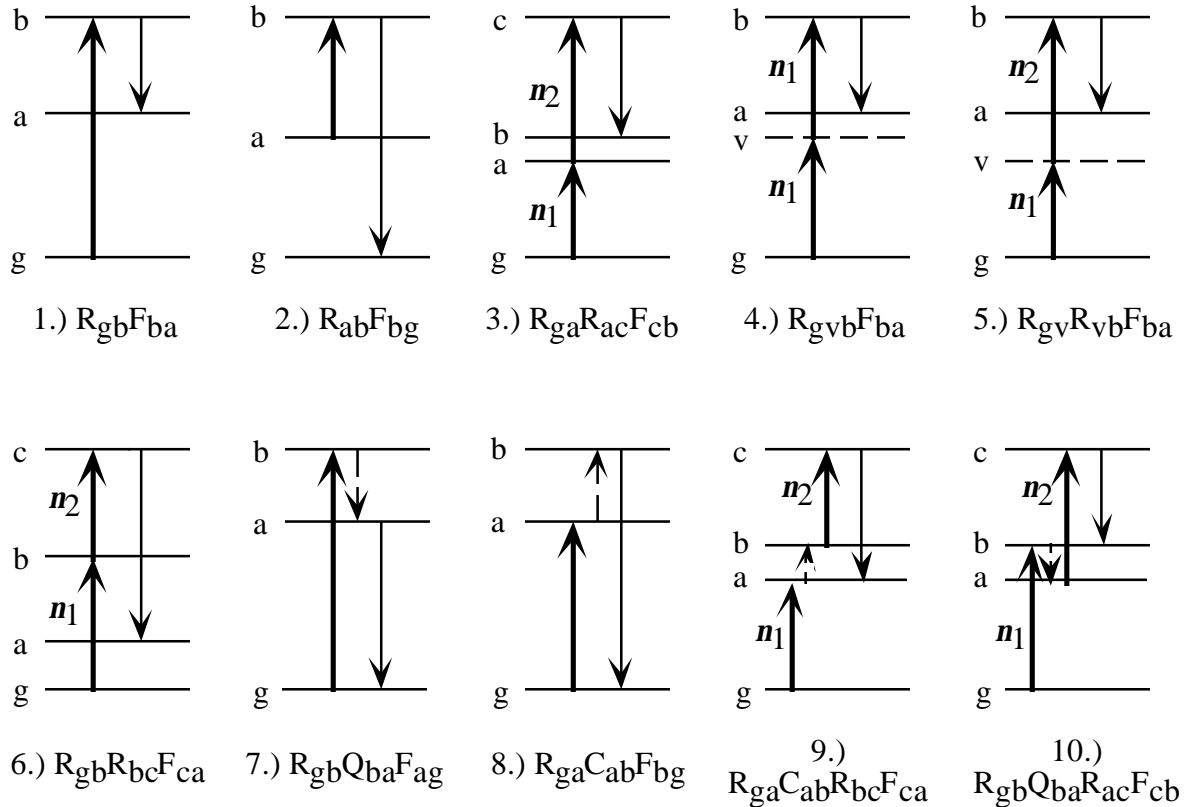
Fig. 4. Examples of non-resonance fluorescence processes

The usual names used for these processes are: 1.) Resonant, Stokes, direct-line fluorescence; 2.) Resonant, anti-Stokes, direct-line fluorescence; 3.) Resonant, two-photon, Stokes, direct-line fluorescence; 4.) Off-resonant, single-frequency, two-photon, Stokes, direct-line fluorescence; 5.) Off-resonant, two-frequency, two-photon, Stokes, direct-line fluorescence; 6.) Resonant, two-photon, anti-Stokes, direct-line fluorescence; 7.) Resonant stepwise fluorescence; 8.) Resonant, thermally-assisted, stepwise fluorescence; 9.) Resonant, disconnected, two-photon, Stokes, direct-line fluorescence; and 10.) Resonant, disconnected, two-photon, anti-Stokes, direct-line fluorescence.

3.3 Other fluorescence processes

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:

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[1]Note: The words "resonance" and "resonant" are used interchangeably in the literature.
[2]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.

Fig. 5. Simultaneous observation of
two fluorescence transitions

1.) $R_{ga}M_{ab}(F_{ag}+F_{bg})$ 2.) $R_{gb}M_{ba}(F_{bg}+F_{ag})$
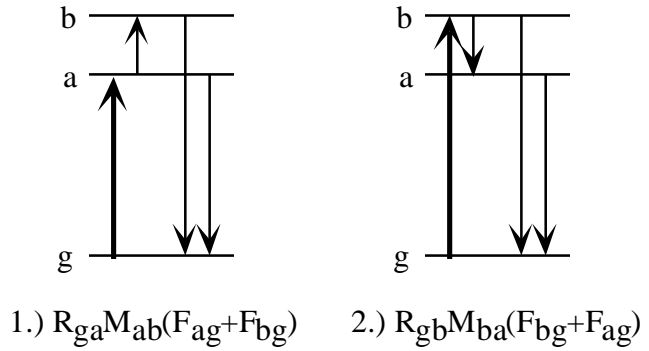
3.4 Rayleigh and Raman scattering

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

1.) $R_{gv}S_{vg}$ 2.) $R_{gv}S_{va}$ 3.) $R_{av}S_{vg}$ 4.) $R_{gvv}S_{va}$
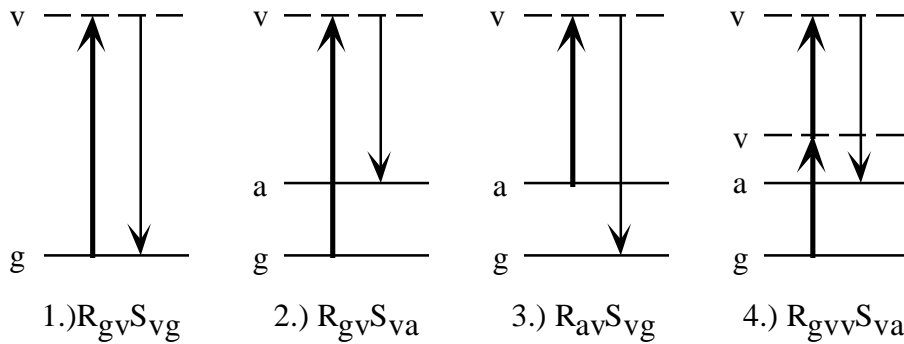
Fig. 6. Examples of Rayleigh and Raman scattering

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, Σ, of states is involved in the ionization process which cannot, therefore, be referred to one particular state. Because this is not easy to denote in a Notation system, it has to be understood that C is in fact ΣC, 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:
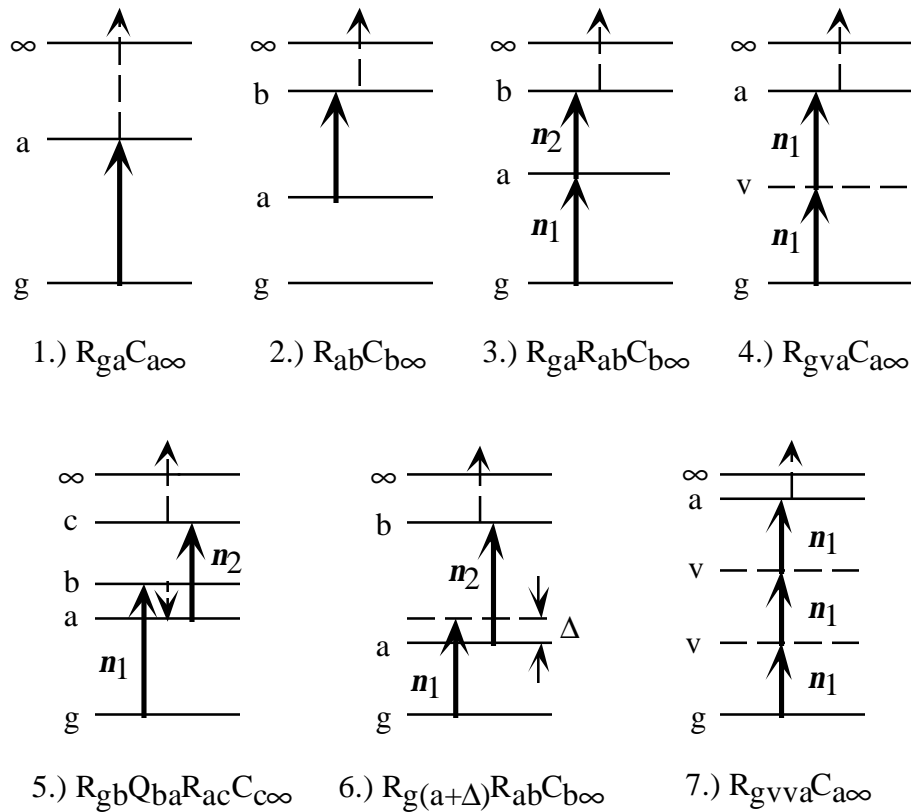
1.) $R_{ga}C_{a\infty}$ 2.) $R_{ab}C_{b\infty}$ 3.) $R_{ga}R_{ab}C_{b\infty}$ 4.) $R_{gva}C_{a\infty}$

5.) $R_{gb}Q_{ba}R_{ac}C_{c\infty}$ 6.) $R_{g(a+\Delta)}R_{ab}C_{b\infty}$ 7.) $R_{gvva}C_{a\infty}$

Fig. 7. Examples of laser enhanced ionization processes

The usual names for these processes are: 1.) Resonant excitation, collisional ionization; [3] 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; 6.) Near-resonant, 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:

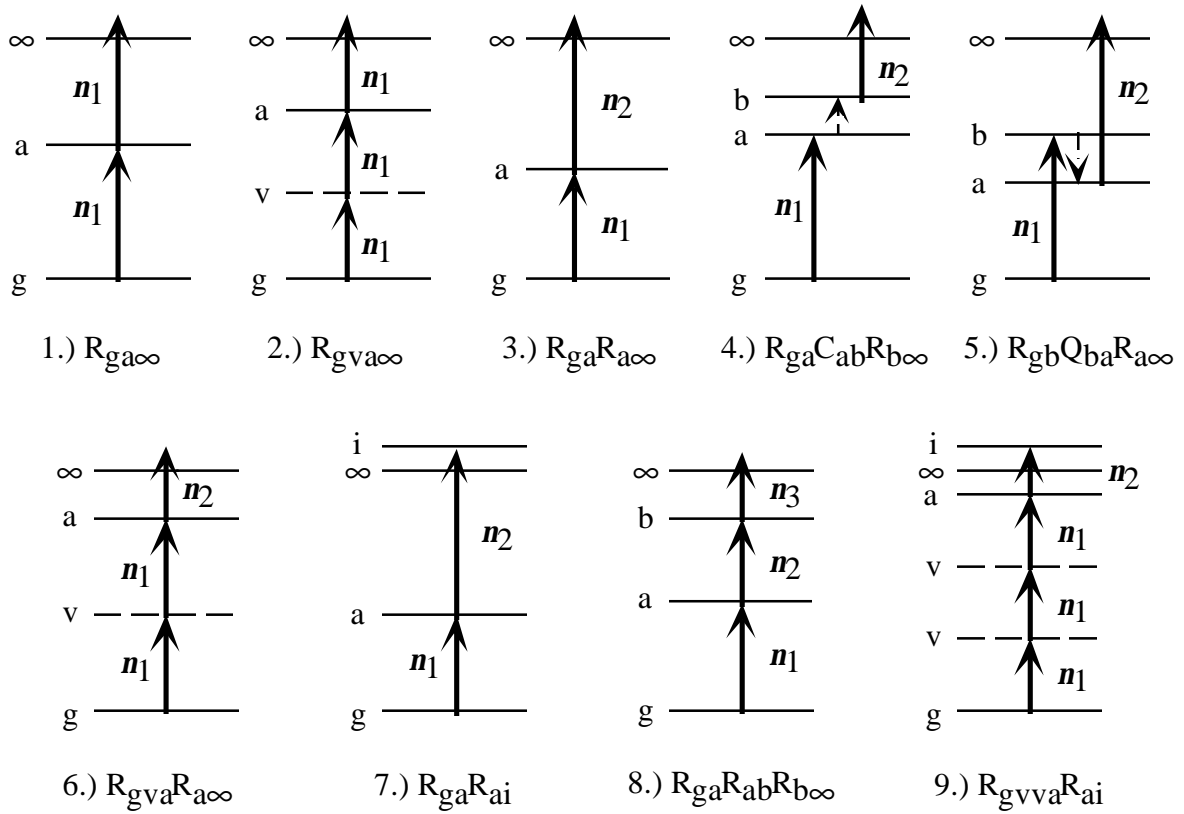[3]Note: Collisional ionization is intended to be, by definition, non-resonant.

Fig. 8. Examples of photo-ionization processes

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, resonant excitation, resonant ionization; 8.) Three-frequency, resonant, two-photon excitation, photo-ionization; and 9.) Two-frequency, off-resonant, three-photon excitation, resonant ionization.

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

$R_{ga}R_{ab}E_{b\infty}$
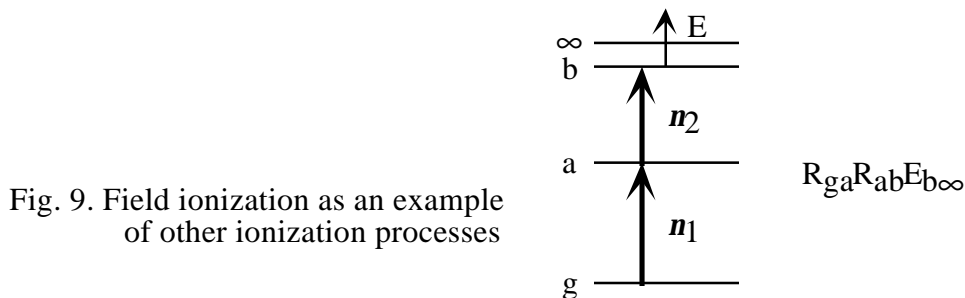
This process is usually named resonant, two-photon excitation, field ionization.

4. INDEX OF TERMS