

A theoretical study of coincidence laser spectroscopy (CLS) for the detection of ions in ICP-MS (ICP-MS-CLS).

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Electronic Supplementary Information

The second equation number (where one is given) in each bracket is that employed in the printed text.

Description of the programme “CO-IN” which models the CLS detector.

INPUT DATA

file INPUT containing following data:

- $\tau, \Delta\tau$
- $I, \sigma, \omega, A_{21}$
- $M, P_{bg}, I_{bg}, PART$

$\tau, \Delta\tau$ - estimated time of flight of an ion through the flow tube (τ), and detection volume ($\Delta\tau$) in seconds (s).

I – maximum laser intensity in (W/m^2), σ - cross section in (m^2), ω - angular frequency in (Hz), and A_{21} – transition probability in (s^{-1}).

M – ion mass in (amu), P_{bg} – photon background in (cps), ion flow rate in (cps), and $PART$ – fraction of total ions that are analyte ions in (%).

file DF.DAT containing the ion energy distribution function (EDF) as a set of discrete points

$E_1(eV)$	f_1
$E_2(eV)$	f_2
:	:
$E_N(eV)$	f_N

where $N < 102$. EDF is not be normalized because its normalization is performed later in the course of program operation.

SUBROUTINES

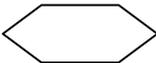
DISTRBTN: This subroutine converts the EDF to a discrete distribution in order to accelerate the whole algorithm. It means that the program works with a large, but finite number of energy values, usually 1024, which can be extended at 2048, 4096 or 8192. Besides, this subroutine provides works with an arbitrary EDF which is given in the file DF.DAT.

TIME0: This subroutine is used in several places in the program, whenever it is necessary to draw a time when some random process will occur (e.g appearance of a background photon in the photo detector, appearance of an ion in the detection volume, etc.). Each time, a new value is drawn in agreement with the known rate for this process.

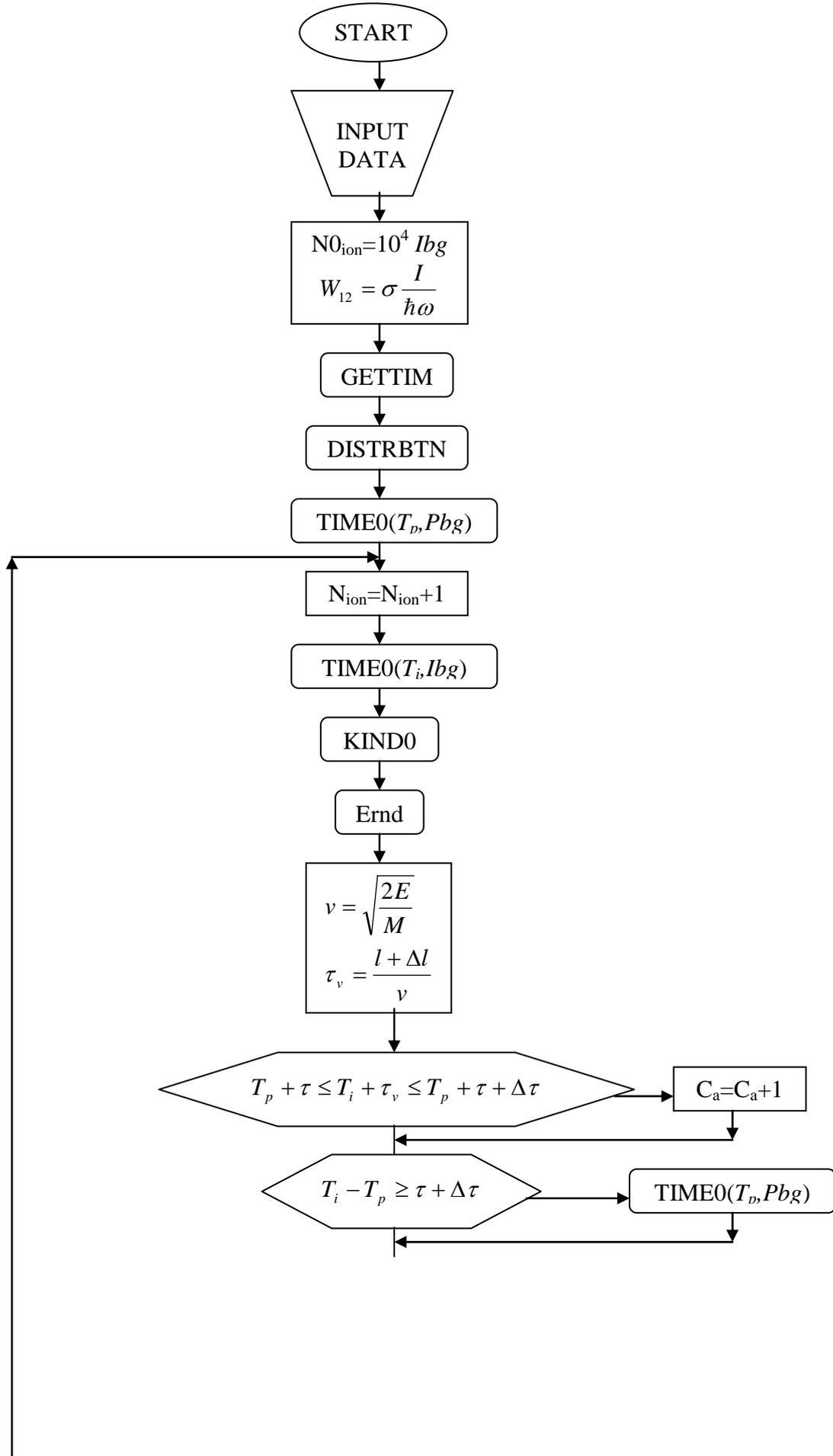
KIND0: This subroutine decides whether an ion is analyte or background ion, in agreement with the variable $PART$ which is given in file INPUT.

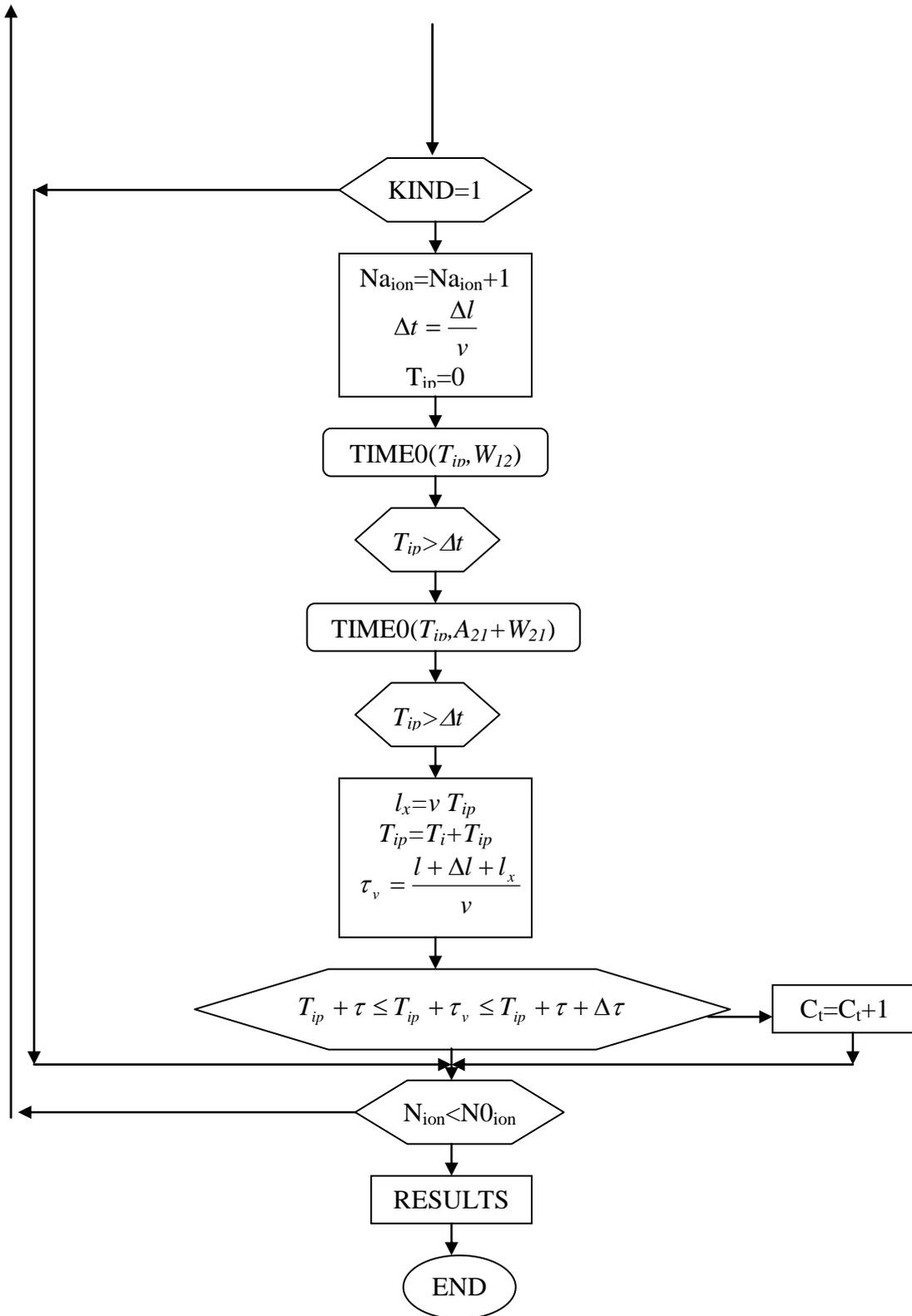
Ernd: The main task of this subroutine is establishing a correspondence between random numbers with uniform distribution, and energy values with a given EDF.

CONDITIONS



Flow diagram of Coincidence Simulation code





Calculation of the Hyperfine Splitting

The splittings may be calculated from a knowledge of the I, J, and F quantum numbers and the hyperfine splitting constants, thus

$$\Delta E = \frac{1}{2} A [F(F+1) - J(J+1) - I(I+1)], \quad \vec{F} = \vec{J} + \vec{I}. \quad (1; 3)$$

$$A = a_0 \frac{S(S+1) + s(s+1) - S_1(S_1+1)}{2S(S+1)} \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{for s-state}), \quad (2)$$

$$A = a_1 \left[2 - g - \sigma \frac{6\Xi(2-g) - 2(g-1)L(L+1)}{(2L-1)(2L+3)} \right] \quad (\text{for p-state}), \quad (3)$$

where

$$\Xi = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \quad (4)$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{Lande factor}) \quad (5)$$

$$\sigma = \sqrt{\frac{1}{S(L+1)(2S+1)}}. \quad (6)$$

Factor $a_{(l=0,1)}$ is given by Fermi-Segre formula:

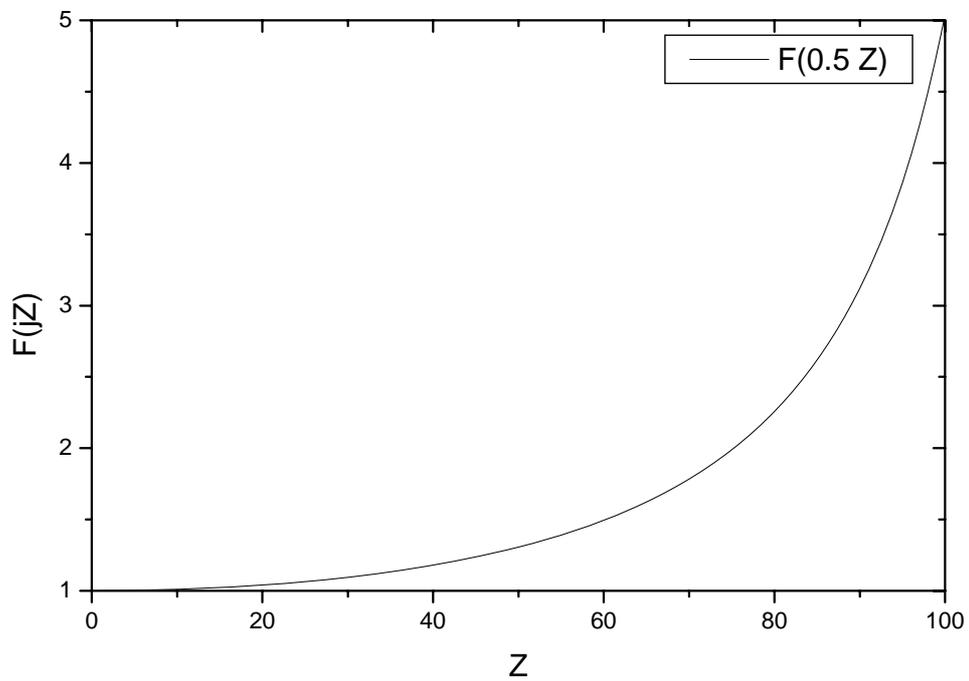
$$a_l = \frac{\alpha^2 g_l Z_a^2 Z}{n_*^3 (l + \frac{1}{2})(j+1)} \left(\frac{m}{m_p} \right) (1 - \delta) F(j, Z) Ry \quad (7)$$

where $F(j,Z)$ (see plot below) and δ are relativistic corrections:

$$F(jZ) = \frac{2j(j+1)(2j+1)}{\gamma(4\gamma^2-1)}, \quad \gamma = \sqrt{\kappa^2 - \alpha^2 Z^2}, \quad \kappa = |j + \frac{1}{2}| \quad (8)$$

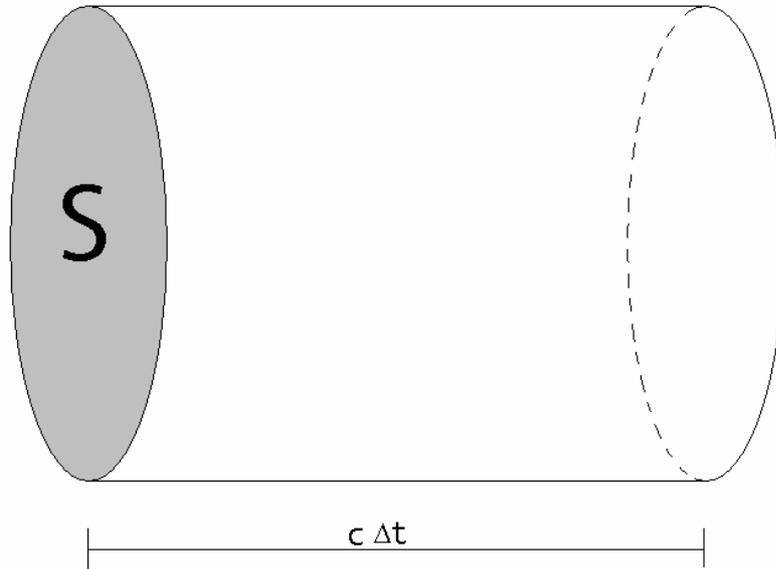
and

$$\delta = \frac{2\gamma(\kappa - \gamma)(2\gamma + 1)}{[\Gamma(2\gamma + 1)]^2 (2\kappa - 1)} \left(\frac{2Zr_0}{a_0} \right)^{2\gamma-1} \quad (9)$$



Plot of Relativistic Correction $F(j,Z)$ versus Atomic Number

Modelling the Laser Beam and Line Shape



Schematic of the beam

Consider a spatially homogenous laser beam implying that the radiation intensity I (W/m^2) satisfies the criteria

$$I = \begin{cases} I(r) = \text{const} & r \leq R \\ I(r) = 0 & r > R \end{cases} \quad (1)$$

Let E (Joules) be the energy passing through the area S (m^2) in a time Δt (s):

$$E = IS\Delta t \equiv \frac{I}{\underbrace{c}_{\substack{\text{energy} \\ \text{density}}}} \underbrace{Sc\Delta t}_{\text{volume}}. \quad (2)$$

$\rho(Jm^{-3}) = \frac{I}{c}$ is the spatial energy density and is related to the spectral energy density, $\tilde{\rho}(\omega)$ by the relationship

$$\rho = \int_0^{\infty} \tilde{\rho}(\omega) d\omega. \quad (3)$$

Taking into account these definitions, $\tilde{\rho}(\omega)(Jm^{-3}Hz^{-1})$ can be expressed in terms of the laser line shape function $f(\omega - \omega_l)$ as $\tilde{\rho}(\omega) = \frac{I}{c} f(\omega - \omega_l)$ which satisfies the relation

$$\int_0^{\infty} f(\omega - \omega_l) d\omega = 1 \quad (4; 19)$$

Examples:

- 1) The laser approximates a monochromatic source with circular frequency ω_l in which case

$$f(\omega - \omega_l) = \delta(\omega - \omega_l) \quad (5, 20)$$

2) Another possible laser shape function is an inverse Voigt profile (see Schematic)

$$f(\omega - \omega_l) = A \left[P\left(\frac{4}{5}, \frac{\omega - \omega_l}{\Delta\omega_l}\right) f_G(\omega - \omega_l) + Q\left(\frac{4}{5}, \frac{\omega - \omega_l}{\Delta\omega_l}\right) f_L(\omega - \omega_l) \right] \quad (6; 21)$$

with

$$f_G(\omega - \omega_l) \propto \exp\left(-2 \frac{(\omega - \omega_l)^2}{\Delta\omega_l^2}\right) \quad (7)$$

and

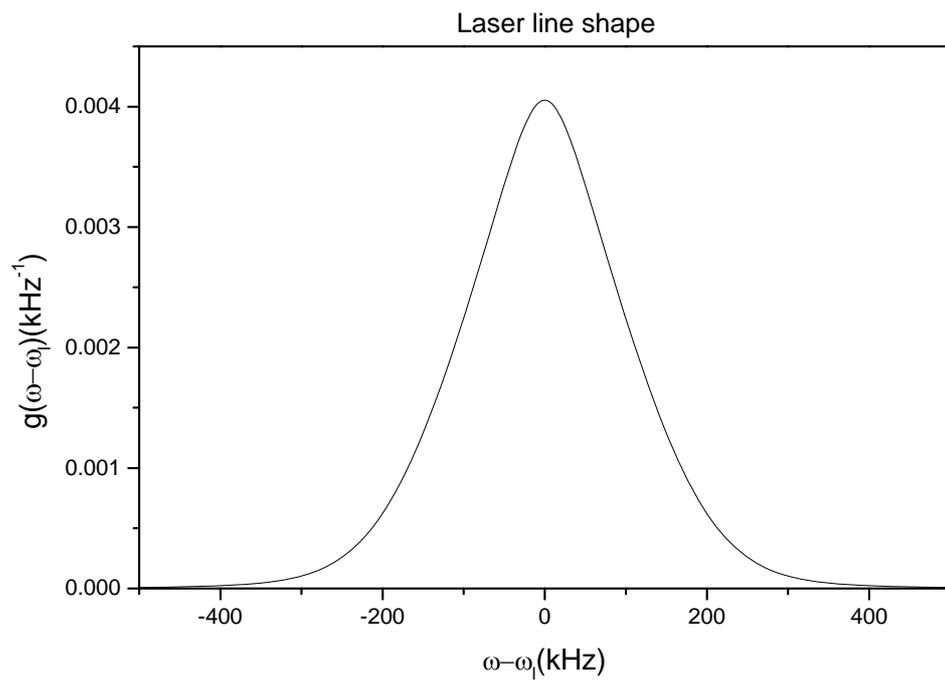
$$f_L(\omega - \omega_l) \propto \frac{1}{1 + 4 \frac{(\omega - \omega_l)^2}{\Delta\omega_l^2}} \quad (8)$$

where $P(a, x)$ and $Q(a, x)$ are incomplete gamma functions defined as:

$$P(a, x) = \frac{1}{\Gamma(a)} \int_0^x e^{-t} t^{a-1} dt, \quad Q(a, x) = 1 - P(a, x). \quad (9)$$

A is the normalisation constant given by:

$$A = \left\{ \int_0^\infty \left[P\left(\frac{4}{5}, \frac{\omega - \omega_l}{\Delta\omega_l}\right) f_G(\omega - \omega_l) + Q\left(\frac{4}{5}, \frac{\omega - \omega_l}{\Delta\omega_l}\right) f_L(\omega - \omega_l) \right] d\omega \right\}^{-1}$$

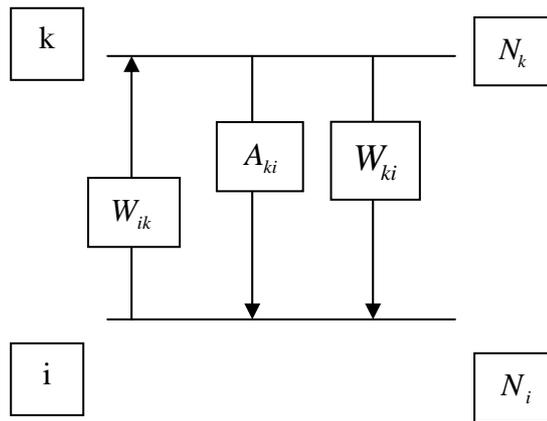


Schematic of the laser line shape

Calculation of Saturation Power and Fluorescence Yield

1 Pumping Parameters

A system comprising only two spectroscopic states, the ground state and one excited state, without hyperfine splitting (applicable only to isotopes with even Z) is the simplest model for the proposed detection scheme, viz:



Schematic - A Model Two Level System.

The probability per unit time, W_{ki} , that a photon of energy $\hbar\omega$ will be absorbed, in the most general case is given by expression:

$$W_{ki} = \int_0^{\infty} B_{ki} \tilde{\rho}(\omega) g(\omega - \omega_0) d\omega \quad (1)$$

where $B_{ki} (J^{-1} m^3 Hz s^{-1})$ is the Einstein coefficient for absorption, and $g(\omega - \omega_0)$ - the atomic spectral line shape function (Lorentzian), which satisfies relation:

$$\int_0^{\infty} g(\omega - \omega_0) d\omega = 1. \quad (2; 19)$$

Further discussions are limited to the case where $f(\omega) = \delta(\omega - \omega_l)$, thus:

$$W_{ik} = B_{ik} \tilde{\rho}(\omega_l) \equiv B_{ik} \frac{I}{c} g(\omega_l - \omega_0) \quad (3)$$

where ω_l is the frequency of monochromatic laser.

The rate at which excited states are created through the absorption of photons is therefore given by:

$$\text{Upward rate} = N_i \tilde{\rho}(\omega_l) B_{ik} \quad (4)$$

where N_i is the number density of lower state atom/ions (m^{-3}) and

$$N_i + N_k = N_o \quad (5)$$

N_o is the total atomic/ionic density (m^{-3}).

When considering one ion/atom N_i is defined as the fractional population of the ground state at any instant.

The population generated by thermal processes (radiational and collisional) can be ignored for transitions in the visible and UV parts of the spectrum..

The de-population of the excited state occurs through spontaneous emission (the signal to be measured) and stimulated emission (potentially a much larger signal than spontaneous emission, but indistinguishable from the source laser photons). The probability per unit time for the decay of an excited state is given by:

$$W_{ki} = A_{ki} + \tilde{\rho}(\omega_l)B_{ki} \quad (6)$$

Thus the downward rate becomes:

$$\text{Downward rate} = N_k (A_{ki} + \tilde{\rho}(\omega_l)B_{ki}) \quad (7)$$

1.1 Rate equation for a two-level system in the presence of a laser beam

These equations can be simplified by expressing the radiation-induced probabilities as:

$$W_{ik} = B_{ik} \tilde{\rho}(\omega_l) \quad (8)$$

$$W_{ki} = B_{ki} \tilde{\rho}(\omega_l) \quad (9)$$

with

$$g_i B_{ik} = g_k B_{ki} \quad (10)$$

and also recognising that

$$\tau = \frac{1}{A_{ki}} \quad (11)$$

Then the rate at which the upper state is populated is given by:

$$\frac{dN_k}{dt} = -W_{ki}N_k + W_{ik}N_i - \frac{N_k}{\tau} \quad (12)$$

and similarly the rate at which the lower state is de-populated is given by:

$$\frac{dN_i}{dt} = -W_{ik}N_i + W_{ki}N_k + \frac{N_k}{\tau} \quad (13)$$

In steady-state condition, $\frac{dN_k}{dt} = \frac{dN_i}{dt} = 0$, then we have

$$\frac{N_k}{N_i} = \frac{W_{ik}\tau}{(1 + W_{ki}\tau)} \quad (14)$$

Taking into account $W_{ki} = B_{ki} \frac{I}{c} g(\omega)$, and applying equations (8 - 11), and (13), equation (14) becomes:

$$\frac{N_k}{N_i} = \frac{B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)} \quad (15)$$

2 Definition of Saturation Intensity I_s

Saturation intensity is defined in terms of the laser gain coefficient $\gamma(\omega)$ (equivalent to negative value absorption coefficient), Assuming $\gamma_0(\omega)$ is the small signal ($I = 0$) gain/absorption coefficient, generally we have, for a two-level atomic system:

$$\gamma(\omega) = \frac{\gamma_0(\omega)}{1 + \frac{I}{I_s(\omega)}} \quad (16; 22)$$

When $\frac{\gamma(\omega)}{\gamma_0(\omega)} = \frac{1}{2}$, the intensity $I(\omega) = I_s(\omega)$ is called the saturation intensity, which is

$$\frac{1}{I_s(\omega_l)} = \left(1 + \frac{g_k}{g_i} \right) \tau \frac{1}{c} g(\omega_l - \omega_0) B_{ki} \quad (17; 23)$$

Two different expressions have been derived subject to different laser conditions, i.e. small laser intensity and the large laser intensity.

2.1 Small Laser Intensity Case ($N_k \approx 0$)

When a laser beam with a photon flux F goes through a medium with length dz and cross-section S having two arbitrary energy levels, in the steady-state case, the decrease in the number of photons must be equal to the difference between the absorption and the stimulated emission, thus:

$$SdF = -(W_{ki}N_k - W_{ik}N_i)Sdz \quad (18)$$

Additionally, it can be stated that:

$$\begin{aligned} W_{ik} &= \sigma_{ik}F, \\ W_{ki} &= \sigma_{ki}F. \end{aligned} \quad (19)$$

and

$$g_i\sigma_{ik} = g_k\sigma_{ki} \quad (20)$$

where σ_{ik} and σ_{ki} are stimulated absorption and emission cross-sections, respectively (see Appendix 1 for further details).

Equation (18) may be rewritten as

$$\frac{dF}{F} = -\sigma_{ik} \left[N_k - \frac{g_k}{g_i} N_i \right] dz \quad (21)$$

For small laser intensity, equation (21) may be simplified by assuming that, $N_k = 0$ and $n = N_i S dz$ where n is the number of the ions in the interaction region. Allowing the additional simplification that $g_i = g_k$ yields:

$$\frac{dF}{F} = \frac{\sigma_{ik} N_i S dz}{S} = \frac{n \sigma_{ik}}{S} \quad (22)$$

Thus dF represents the loss of flux from the beam passing through an assembly of absorbers and is therefore numerically equal to the fluorescence flux in photons $s^{-1}cm^{-2}$. This formula is in complete agreement with equation (1) given by Eastham *et al.*¹ Note dF is expressed in terms of the laser beam geometry and therefore the geometry of the system has to be considered when calculating the detectable number of photons.

2.2 *Large Laser Intensity Case ($N_k \neq 0$)*

The treatment that follows can be applied to individual ions, which can, for optical purposes be regarded as a point source.

In this case, the resonance fluorescence rate R is defined as:

$$R = \frac{N_k}{N_o} A_{ki} \quad (23)$$

Or:

$$R = \frac{N_k}{N_i + N_k} A_{ki} = \frac{\frac{N_k}{N_i}}{1 + \frac{N_k}{N_i}} A_{ki} \quad (24; 24)$$

Then substitute equation (5) and (15) into (24),

$$R = \frac{B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0) / [1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)]}{1 + B_{ik} \tau \left(\frac{I}{c} \right) / [1 + B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)]}$$

$$\begin{aligned}
& \frac{B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)} \\
= & \frac{\frac{B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}}{1 + B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0) + B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)} A_{ki} \\
& \frac{1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)} \\
= & \frac{B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + \left(1 + \frac{g_k}{g_i} \right) B_{ki} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)} A_{ki} \tag{25}
\end{aligned}$$

Introducing equation (16), equation (25) is written in terms of the saturation power as:

$$\begin{aligned}
R = \frac{\frac{g_k}{g_i} B_{ik} \tau \left(\frac{I}{c} \right) g(\omega_l - \omega_0)}{1 + \frac{I}{I_s(\omega_l)}} A_{ki} &= \frac{\frac{g_k}{g_i} \frac{g_i}{(g_i + g_k)} \frac{I}{I_s(\omega_l)}}{1 + \frac{I}{I_s(\omega_l)}} A_{ki} \\
& \tag{26}
\end{aligned}$$

At saturation, $\frac{I}{I_s(\omega)} \gg 1$, equation (26) becomes:

$$R = R_s = \frac{g_k A_{ki}}{g_i + g_k} \quad (27; 25)$$

R_s is called the saturation fluorescence rate. In terms of equation (27), equation (6) may be rewritten as

$$R = R_s \left(\frac{I}{I_s(\omega_l)} \right) \frac{1}{1 + \left(\frac{I}{I_s(\omega_l)} \right)} \quad (28; 26)$$

This result is in complete agreement with equations (1), (2) given by She *et al.*²

With the relationship between Einstein Coefficients $\frac{A_{ki}}{B_{ki}} = \frac{\hbar\omega^3}{\pi^2 c^3}$, and noticing that $\tau = \frac{1}{A_{ki}}$, equation (16) may be re-written as:

$$I_s(\omega) = \frac{c}{\left(1 + \frac{g_k}{g_i}\right) \frac{B_{ki}}{A_{ki}} g(\omega_l - \omega_0)} = \frac{c}{\left(1 + \frac{g_k}{g_i}\right) \frac{\pi^2 c^3}{\hbar\omega^3} g(\omega_l - \omega_0)}$$

(29)

Replacing the general shape function $g(\omega_1 - \omega_0)$ by the natural line shape which as described above is relevant to conditions in the beam, yields the desired expression:

$$I_s(\omega) = \frac{c}{\left(1 + \frac{g_k}{g_i}\right) \frac{\pi^2 c^3}{\hbar \omega_0^3} g_N(\omega - \omega_0)}$$

(30)

For a narrow laser line such as that given by the Ti:Sapphire laser, I_s at the centre of the absorption profile becomes:

$$I_s(\omega_0) = \frac{c}{\left(1 + \frac{g_k}{g_i}\right) \frac{\pi^2 c^3}{\hbar \omega_0^3} g_N(0)}$$

(31)

where $g_N(0)$ is given by equation 13 in the printed document

Using $\hbar = \frac{h}{2\pi}$, $g(\omega) = (2\pi)^{-1} g(\nu)$, and $\lambda = \frac{c}{\nu}$, here ν is the laser frequency and λ is the laser wavelength. Equation (30) can also be expressed as:

$$I_s(\nu_l) = \frac{8\pi h c}{\left(1 + \frac{g_k}{g_i}\right) \lambda^3 g_N (\nu - \nu_l)} \quad (32)$$

This equation is in agreement with the equation (3) given by She *et al*². Taking into account real laser spectral shape, the last formula can be rewritten in the form

$$I_s(\nu_l) = \frac{8\pi h c}{\int_0^{\infty} \left(1 + \frac{g_k}{g_i}\right) \lambda^3 g_N (\nu - \nu_0) f(\nu - \nu_l) d\nu} \quad (33)$$

The cross sectional area of the laser beam S is given simply by:

$$S = 10^{-6} \frac{\pi d^2}{4} \quad (34)$$

The maximum laser intensity is:

$$I^{\max} = \frac{2P}{S} \quad (35)$$

and therefore:

$$P_s = \frac{I_s \cdot S}{2} \quad (36)$$

Defining the ratio between the beam intensity and the saturation intensity as:

$$r = \frac{I^{\max}}{I_s} \quad (37)$$

The actual fluorescence rate for the laser intensity I^{\max} is given by:

$$F_r = R_s \frac{r}{1+r} \quad (38)$$

compared with the saturated fluorescence given by equation (27).

Calculation of Detection Limits

The procedure for calculating detection limits was as follows:

Use equation 29 in the printed manuscript to establish the signal count N_S required to give a signal-to-noise ratio of 3 for a given background count of N_B . This was accomplished using the Solver function in Excel (Microsoft Office 2003).

The value of N_B for a 10 minute count period was determined according to the origin of the background:

- (i) For isobaric ions the background was set at 10^6 cps for non-CLS detection, but attenuated by the factor $4 \cdot 10^{-4}$ for CLS detection.
- (ii) For ions at ± 1 amu of any element the background was set at 10^{10} cps attenuated by the mass spectrometric abundance sensitivity of 10^{-5} for non-CLS detection.

- (iii) CLS discriminates between ions of other elements and ions of the same element because the latter can potentially be pumped and trigger the CLS channel. Thus for CLS detection of ions at ± 1 amu, only ions of the same element are considered in Table 7 as these represent a worse case scenario. The effective background is calculated by the product of the ± 1 amu count rate, the mass spectrometric abundance sensitivity and the element specific optical abundance sensitivity for CLS detection (hence element specific N_S values in the Table 7).
- (iv) The case of ions at ± 1 amu for different elements with CLS detection has not been specifically dealt with in the table because the calculation is the same as for isobaric ions of a different element. The number of background ions increases by the background count at ± 1 amu attenuated by about 4×10^{-9} , this being the product of the mass spectrometric abundance sensitivity and the CLS attenuation factor, which yields only a small increase in background in most circumstances.

Having obtained N_S the actual number of ions necessary to achieve N_S counts was calculated taking into account:

- (i) Photon burst capability: optical detector becomes 100% efficient, no radiation trapping and no hyperfine components are present so that the detectable ion flux represents only the mass spectrometric ion transport efficiency (beaker to detector) modified by the degree of ionisation.
- (ii) Optical trapping occurs: as for (i) above but now including the effect of the optical detection efficiency.
- (iii) Odd numbered ions with hyperfine structure: as for (ii) above but modifying the detection efficiency by a factor equal to one half the number of hyperfine components.

Branching was not factored in to the equation because it was demonstrated that in nearly all cases it would still yield at least one detectable photon.

References

1. D.A. Eastham, P.M. Walker, J.R.H. Smith, J.A.R. Griffith, D.E. Evans, S.A. Wells, M.J. Fawcett and I.S. Grant, *Optics Comm.*, 1986, **60**, 293.
2. C.Y. She and J.R. Yu, *Appl. Optics*, 1995, **34**, 1063.