

## An expression for the atomic fluorescence and thermal-emission intensity under conditions of near saturation and arbitrary self-absorption

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**Abstract**—An expression for the effect of self-absorption on the fluorescence and thermal emission intensities is derived by taking into account stimulated emission. A simple, idealized case is considered, consisting of a two level atomic system, in a flame, homogeneous with respect to temperature and composition, and uniformly illuminated by an external quasi-continuum radiation source.

### INTRODUCTION

THE EFFECT of self-absorption on the outgoing radiation intensity in a uniformly excited atomic vapor present in a flame of uniform temperature and composition, can be described in a most simple and elegant way by introducing the integral absorption,  $A_i$  (in  $s^{-1}$ ). This applies for both the thermal-emission intensity [1–5] and the fluorescence intensity of a resonance line [4]. The expression for  $A_i$ , which is the integral of the absorption factor over the whole line profile, reads according to Beer's law

$$A_i = \int_{\text{line}} [1 - \exp \{-k(\nu)l\}] d\nu \quad (1)$$

where  $k(\nu)$  (in  $\text{cm}^{-1}$ ) is the absorption coefficient at frequency  $\nu$  and  $l$  (in cm) is the flame thickness along the line of observation. In the usual expression for  $k(\nu)$ , the effect of stimulated emission is neglected, which seems justified for spectral lines in the u.v. visible regions, excited by conventional light sources or thermally-excited in analytical flames with temperatures,  $T_f$ , up to about 3000 K.

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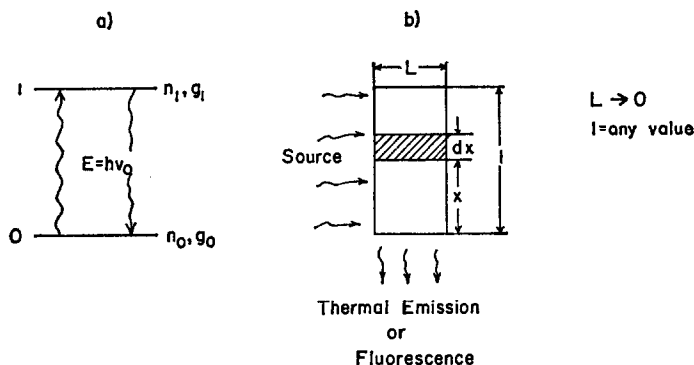


Fig. 1. Representation of Simple Two-Level Atomic System and Illumination Geometry. a. Energy Level Diagram b. Geometry of illumination and observation (diagrams apply to either emission or fluorescence processes).

The advent of intense (tunable) laser sources has made it possible to nearly saturate atom lines in the flame [6–9]. Under such conditions, (self-) absorption is accompanied by stimulated emission, which reduces the *net* absorption coefficient as measured, e.g., in a direction perpendicular to the laser beam. Stimulated emission induced by photons that are re-emitted as fluorescence in a direction perpendicular to the laser beam (see Fig. 1b) will thus partly offset the reduction of the fluorescence intensity due to self-absorption.

For a simple, idealized case, an expression will be derived for the effect of self-absorption on the fluorescence and thermal-emission intensities, while taking into account stimulated emission.

### Theory

A simple atomic system (see Fig. 1a) will be considered having only two energy levels (0 refers to the ground state), statistical weights  $g_0$  and  $g_1$ , and an energy separation  $E = h\nu_0$ , where  $\nu_0$  is the central frequency (in Hz) of the optical transition. In the case of fluorescence excitation by an external light source, the geometry of illumination and observation is as depicted in Fig. 1b. In order to avoid mathematical complications due to the gradual weakening of the primary light beam along its path through the flame or due to self-reversal of the fluorescence line [4, 10], it will be assumed that the whole flame section observed is uniformly illuminated. (This may be realized, for a given atom concentration, by keeping  $L$  sufficiently small and by choosing the width of the primary beam equal to  $l$ , which is itself not restricted; see Fig. 1b).

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Furthermore, the simplification will be made that the flame is homogeneous as to temperature and composition, and that the atom concentration is uniform throughout the illuminated region in the flame. (The more general case of a non-uniform atom concentration will be dealt with separately in the Appendix.) The product of atom concentration and flame depth  $l$  is, however, not restricted, so that the extent of self-absorption of the outgoing fluorescence or thermal radiation may be arbitrarily high (assuming negligible radiation diffusion).

### General expression

Referring to Fig. 1b, the contribution of section  $dx$  to the spectral radiance,  $dB_\nu(\nu, x)$  (expressed in  $\text{erg s}^{-1} \text{cm}^{-2} \text{sr}^{-1} \text{Hz}^{-1}$ ) of the outgoing radiation at frequency  $\nu$  observed along the  $x$ -axis is given by

$$dB_\nu(\nu, x) = (A_{10}n_1h\nu/4\pi)S_\nu(\nu) \exp \left\{ \int_0^x -k^*(\nu) dx' \right\} dx \quad (2)$$

where  $n_1$  is the number density of excited atoms (in  $\text{cm}^{-3}$ ),  $A_{10}$  is the Einstein transition probability for spontaneous emission (in  $\text{s}^{-1}$ ),  $h$  is Planck's constant,  $S_\nu(\nu)$  is the normalized spectral distribution function (in  $\text{Hz}^{-1}$ ) of photons emitted by a downward transition  $1 \rightarrow 0$  ( $\int_{\text{line}} S_\nu(\nu) d\nu = 1$ ), and  $k^*(\nu)$  is the *net* absorption coefficient of the atomic vapor at vapor frequency  $\nu$ . The exponential factor in Equation (2) accounts for the attenuation of the atomic radiation generated at place  $x$ , due to the *net* effect of self-absorption and stimulated emission, when travelling over a path length  $x$ . From Einstein's radiation theory [11, 12],

$$k^*(\nu) = (B_{01}h\nu/c)S_\nu(\nu)\{n_0 - (g_0/g_1)n_1\}, \quad (3a)$$

or

$$k^*(\nu) = (B_{01}h\nu/c)S_\nu(\nu)n_0\{1 - (g_0/g_1)(n_1/n_0)\} \quad (3b)$$

where  $B_{01}$  is the Einstein coefficient for absorption (in  $\text{erg}^{-1} \text{cm}^3 \text{s}^{-1} \text{Hz}$ ), which equals the Einstein coefficient for stimulated emission,  $B_{10}$ , multiplied by  $(g_1/g_0)$ ,  $c$  is the velocity of light (in  $\text{cm s}^{-1}$ ), and  $n_0$  is the number density of ground-state atoms (in  $\text{cm}^{-3}$ ). In Equations (3), we have indirectly assumed that the normalized spectral distribution function of photons absorbed (from a hypothetical continuum radiation field), is the same as that for spontaneous emission,  $S_\nu(\nu)$ ; this assumption implies that coherence effects between absorbed and re-emitted photons are neglected which seems to be justified in flames at 1 atm pressure [13]. We have also neglected radiation diffusion effects in assuming that a photon re-absorbed at place  $x'$  ( $0 < x' < x$ ) on its way out, will have a negligible chance to leave the flame in the same direction after being re-emitted and re-absorbed in succession a number of times; this latter assumption seems to be justified if the efficiency of resonance fluorescence  $Y$ , is not too close to unity.

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With conventional external light sources and/or under usual flame conditions in atomic fluorescence and flame emission spectrometry, the second term between brackets { } in Equation (3b) is much less than unity. This is tantamount to assuming that stimulated emission is negligible in comparison with (real) absorption, and so to a good approximation

$$k^*(\nu) \approx k(\nu) \equiv (B_{01}h\nu/c)S_\nu(\nu)n_0. \quad (4)$$

Under (near-) saturation conditions, however, the (exact) equation for  $k^*(\nu)$  (Equations (3a, b) instead of Equation (4)) must be applied.

From the general assumptions made, it can be concluded that  $n_0$ ,  $n_1$ ,  $S_\nu(\nu)$  and thus  $k^*(\nu)$  [see Equations (3a, b)] are independent of position,  $x$ . Therefore from Equations (2),  $dB_\nu(\nu, x)$  is given by

$$dB_\nu(\nu, x) = (A_{10}n_1h\nu/4\pi)S_\nu(\nu) \exp \{-k^*(\nu)x\} dx. \quad (5)$$

Integration of the latter equation over  $x$  then yields for the spectral radiance  $B_\nu(\nu)$  of the outgoing radiation at frequency  $\nu$

$$B_\nu(\nu) = (A_{10}n_1h\nu/4\pi)S_\nu(\nu) [1 - \exp \{-k^*(\nu)l\}]/k^*(\nu) \quad (6)$$

Substituting the expression for  $k^*(\nu)$  given by Equation (3a) in the denominator of the right-hand side of Equation (6), gives

$$B_\nu(\nu) = \left(\frac{c}{4\pi}\right) \left(\frac{A_{10}}{B_{01}}\right) \left(\frac{n_1}{n_0 - (g_0/g_1)n_1}\right) [1 - \exp \{-k^*(\nu)l\}]. \quad (7)$$

Making use of the general relationship between  $A_{10}$  and  $B_{01}$  [11, 12] and substituting into Equation (7) gives

$$B_\nu(\nu) = \left(\frac{2h\nu_0^3}{c^2}\right) \left(\frac{n_1(g_0/g_1)}{n_0 - (g_0/g_1)n_1}\right) [1 - \exp \{-k^*(\nu)l\}] \quad (8)$$

The radiance,  $B$ , (in  $\text{erg s}^{-1} \text{cm}^{-2} \text{sr}^{-1}$ ) of the whole atom line is obtained by integrating Equation (8) over frequency and so

$$B = \int_{\text{line}} B_\nu(\nu) d\nu = \left(\frac{2h\nu_0^3}{c^2}\right) \left(\frac{n_1(g_0/g_1)}{n_0 - (g_0/g_1)n_1}\right) A_i^*, \quad (9)$$

where the *net* integral absorption  $A_i^*$  is defined by

$$A_i^* \equiv \int_{\text{line}} [1 - \exp \{k^*(\nu)l\}] d\nu \quad (10)$$

Equations (9) and (10) describe the influence of self-absorption on the radiance of the outgoing radiation, *while taking the contribution of stimulated emission exactly into account*. These equations replace the previously derived expression for the self-absorption of fluorescence radiation. This previous expression is again found from Equations (9) and (10) by neglecting the term  $(g_0/g_1)n_1$  with respect to  $n_0$  in Equation (9) as well as in the expression for  $k^*(\nu)$  given by Equation (3a).

### Case of fluorescence

When the atomic vapor is uniformly illuminated by a quasi continuum source with spectral irradiance  $E_{\nu_0}$  (in  $\text{erg s}^{-1} \text{cm}^{-2} \text{Hz}^{-1}$ ) at  $\nu \approx \nu_0$  and with a spectral

bandwidth much larger than the atomic line-width, then [8]

$$\frac{n_1(g_0/g_1)}{n_0 - (g_0/g_1)n_1} = \frac{1}{2} \left( \frac{E_{\nu_0}}{E_{\nu_0}^s} \right) \quad (11)$$

if thermal excitation is neglected;  $E_{\nu_0}^s$  is the "saturation parameter" (expressed as spectral irradiance) defined [8] by

$$B_{\nu_0}^s \equiv 4\pi h\nu_0^3/c^2 Y \quad (12)$$

where  $Y$  = quantum efficiency of fluorescence. Substitution of Equations (11) and (12) in Equation (9) yields

$$B = (Y/4\pi)E_{\nu_0}A_i^* \quad (13)$$

The factor  $A_i^*$  is, in general, dependent on  $E_{\nu_0}$  too, as  $A_i^*$  contains  $k^*(\nu)$  which again depends on the degree of saturation through the factor  $\{n_0 - (g_0/g_1)n_1\}$  occurring in Equation (3a). The latter factor is found from Equation (11) to be given by

$$n_0 - (g_0/g_1)n_1 = n_i / \{1 + \frac{1}{2}(E_{\nu_0}/E_{\nu_0}^s)(g_1 + g_0)/g_0\} \quad (14)$$

where  $n_i (\equiv n_1 + n_0)$  is the total number density of atoms.

With conventional light sources,  $E_{\nu_0} \ll E_{\nu_0}^s$ , so that  $k^*(\nu)$  and thus  $A_i^*$  can be approximated by  $k(\nu)$  and  $A_i$ , respectively, which are independent of  $E_{\nu_0}$ . Therefore, according to Equation (13), the fluorescence intensity is simply proportional to the source intensity. The dependence of fluorescence intensity on  $(n_0 l)$  is then described by the usual curve-of-growth theory through the factor  $A_i$ .

With very high intensity sources,  $E_{\nu_0}/E_{\nu_0}^s \rightarrow \infty$ , it can be seen from Equation (3a) and (14) that, for a given  $n_i$ ,  $k^*(\nu) \rightarrow 0$ . But  $k^*(\nu) \rightarrow 0$  implies that self-absorption is removed, that is,  $A_i^*$  becomes simply proportional to  $n_i$  [which is found from the usual series expansion [3, 10] of the exponential term in Equation (10)]. This was to be expected; under saturation conditions, the atomic vapor becomes transparent to the resonance line radiation which has great analytical value [10].

### Case of thermal emission radiation

Equation (9) for the outgoing radiation intensity is valid irrespective of the particular process(es) by which the atoms are actually excited. It can thus also be applied in order to derive an *exact* expression for the thermal emission radiation intensity (i.e., without external light source); in which case, the effects of self-absorption as well as stimulated emission are taken into account. For this case, it is only necessary to replace the ratio  $n_1/n_0$  in Equation (9) by the thermal equilibrium ratio as given by Boltzmann's law\*

$$\frac{n_1^{\text{th}}}{n_0^{\text{th}}} = \frac{g_1}{g_0} \exp \{-E/kT\} \quad (15)$$

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\* This law is obeyed exactly only if the flame were placed inside a cavity at the same temperature. In practical flames, it is obeyed in reasonable approximation at any atom concentration, if the fluorescence efficiency is not higher than, say 10% [3, 13].

From Equations (9) and (15) and substituting  $E = h\nu_0$ , the thermal radiance is given by

$$\begin{aligned} B^{\text{th}} &= (2h\nu_0^3/c^2) \left( \frac{\exp \{-h\nu_0/kT_f\}}{1 - \exp \{-h\nu_0/kT_f\}} \right) A_i^* \\ &= (2h\nu_0^3/c^2) [\exp \{h\nu_0/kT_f\} - 1]^{-1} A_i^*. \end{aligned} \quad (16)$$

According to Planck's law, the spectral radiance of a blackbody at temperature  $T_f$  and frequency  $\nu_0$  is given by

$$B_{\nu_0}^{Pl}(T_f) = (2h\nu_0^3/c^2) [\exp \{h\nu_0/kT_f\} - 1]^{-1} \quad (17)$$

Combining Equations (16) and (17),  $B^{\text{th}}$  is given by

$$B^{\text{th}} = A_i^* B_{\nu_0}^{Pl}(T_f) \quad (18a)$$

Thus, in the thermal case, the effect of stimulated emission is *exactly* taken into account, if Equations (3b) and (15) are used in the calculation of  $k^*(\nu)$ , and Equation (10) is used in the calculation of  $A_i^*$ , while using Planck's law [Equation (17)] for the blackbody spectral radiance. The criterion for the applicability of the approximate Wien's law, instead of Planck's law, results when  $\exp \{h\nu_0/kT_f\} \gg 1$ , and holds generally in analytical flame emission spectroscopy. But the same criterion also holds for the replacement of  $k^*(\nu)$  by  $k(\nu)$ , while neglecting in Equation (3b) the term  $(g_0/g_1)(I_1^{\text{th}}/n_0^{\text{th}}) = \exp \{-h\nu_0/kT_f\}$  with respect to unity. The presence of the  $(-1)$  term in the denominator of the right-hand side of Equation (17) is intrinsically related to the occurrence of stimulated emission transitions. If  $\exp \{h\nu_0/kT_f\} \gg 1$ , then the  $(-1)$  term as well as stimulated emission can be neglected, and instead of Equation (18a) the more common approximative expression for  $B^{\text{th}}$  is obtained

$$B^{\text{th}} \approx A_i B_{\nu_0}^W(T_f) \quad (18b)$$

where the superscript index  $W$  refers to Wiens's law.

By series expansion of  $A_i^*$  and  $A_i$  to first order of  $(n_0 l)$  (i.e., for  $n_0 l \rightarrow 0$ ), Equations (18a) and (18b) become, in fact identical. This does not hold, however, to higher orders of approximation. Therefore, it is suggested that whenever we use the term  $A_i$  instead of the exact term  $A_i^*$ , we should consistently replace Planck's law by Wien's law, too.

## APPENDIX

### *Derivation of Equation (7) for non-uniform atom distribution*

When  $n_0$  and  $n_1$  are assumed to be arbitrary functions of the position coordinate,  $x$ , then also the net absorption coefficient  $k^*(\nu)$  will vary with  $x$  [compare Equation (3b)]. If, however, the other initial assumptions are retained (uniform illumination, flame temperature and composition),  $S_\nu(\nu)$  as well as the ratio  $n_1(x)/n_0(x)$  are independent of place and the same as before.

Instead of Equations (5) and (6), the appropriate expressions for  $dB_\nu(\nu, x)$  and  $B_\nu(\nu)$  are now

$$dB_\nu(\nu, x) = (A_{10}h\nu/4\pi)S_\nu(\nu)n_1(x) \exp \left\{ -\int_0^x k^*(\nu, x') dx' \right\} dx \quad (\text{A-1})$$

and

$$B_\nu(\nu) = (A_{10}h\nu/4\pi)S_\nu(\nu) \int_0^l n_1(x) \exp \left\{ -\int_0^x k^*(\nu, x') dx' \right\} dx \quad (\text{A-2})$$

respectively. The latter equation can be solved by putting:  $y(x) \equiv \int_0^x k^*(\nu, x') dx'$ , so that  $y'(\equiv dy/dx) = k^*(\nu, x)$ . Equation (A-2) then becomes

$$B_\nu(\nu) = (A_{10}h\nu/4\pi)S_\nu(\nu) \{n_1(x)/k^*(\nu, x)\} \int_0^l \exp \{-y\} y' dx \quad (\text{A-3})$$

where according to Equation (3b)

$$n_1(x)/k^*(\nu, x) = \frac{c\{n_1(x)/n_0(x)\}}{B_{01}h\nu S_\nu(\nu)[1 - (g_0/g_1)\{n_1(x)/n_0(x)\}]} \quad (\text{A-4})$$

which is independent of  $x$ , (because  $n_1(x)/n_0(x)$  is independent of  $x$  see above). The integral:

$$\int_0^l \exp \{-y\} y' dx$$

can be solved by choosing  $y$  as a new integration variable with  $y' dx = dy$ . The integral then becomes

$$\int_0^{y(l)} \exp \{-y\} dy = 1 - \exp \{-y(l)\} = 1 \exp \left\{ -\int_0^l k^*(\nu, x') dx' \right\} \quad (\text{A-5})$$

Substituting Equations (A-4) and (A-5), into Equation (A-3), Equation (7) and all equations after Equation (7) result again except that  $\exp \{-k^*(\nu)l\}$  is now replaced everywhere by:  $\exp \{-\int_0^l k^*(\nu, x') dx'\}$ .