

THE RELATIONSHIP BETWEEN THE FLUORESCENCE YIELD AND THE UNDERPOPULATION OF DOUBLET EXCITED STATES

H. P. HOOYMAYERS and P. L. LUNSE

Fysisch Laboratorium Rijksuniversiteit Utrecht, The Netherlands

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Abstract—The influence of radiative non-equilibrium on the occupation of excited metal states in flames can be investigated by measuring the deviation ΔT of line reversal (or excitation) temperature T_L from “true” (or translation) temperature T_f of the flame as a function of metal concentration. In this paper it is shown that, under certain conditions concerning the rates of the de-excitation processes, the measurements of ΔT for atoms with close lying upper levels (such as the alkali atoms) may be interpreted by assuming a single excitation level. In that case, the fluorescence yield Y_D , obtained when both lines are used in excitation and measured in fluorescence, occurs as a parameter in the expressions which describe the behavior of ΔT for low and high metal densities.

The theoretical relationships were checked by comparing the experimental values of Y_D and ΔT for the yellow sodium doublet in a typical hydrogen–oxygen–argon flame. Satisfactory agreement was found. In order to determine more reliably the low density asymptote of the excitation temperature, the variation of ΔT with atomic density was theoretically analysed to first order in the density.

Fluorescence yield factors were again measured for several alkali lines with an improved experimental set-up and agreed with our previous results,^(1,2,3) except for the sodium doublet. The effective cross sections (see Table 1) derived from these yield factors for the quenching of excited sodium ($3P_{1/2,3/2}$), potassium ($4P_{1/2,3/2}$) and rubidium ($5P_{-1/2,3/2}$) atoms by various flame molecules, are in satisfactory agreement with the results of Jenkins’ flame experiments.^(4,5)

INTRODUCTION

BECAUSE of the influence of radiative nonequilibrium on the occupation of the excited states in flames^(1,6,7) and shock heated gases,^(8,9) the line reversal temperature T_L will differ by an amount ΔT from the “true” flame temperature T_f . The latter temperature which is assumed to be constant throughout the colored central flame* can be obtained by extrapolating T_L to infinitely high concentrations. In our earlier paper,⁽⁶⁾ expressions have been derived for ΔT in the extreme cases of very low and very high metal densities, respectively. In these expressions the resonance fluorescence yield Y appears as a parameter. This yield factor is defined as the fractional probability that an excited atom loses its energy by radiation of a photon. From its value the quenching cross-sections of excited metal atoms by other atoms and molecules can be derived. The expressions given in the literature^(6–9) for the asymptotic behavior of ΔT are derived assuming a single excitation level and, in general, may not be applied to atoms with close lying upper levels, such as the alkali atoms.

* The colored central flame is supposed to be surrounded by a metal-free burning mantle flame in order to guarantee a uniform temperature in the central part of the flame. For brevity we will indicate in the following this central flame by “the flame”.

In the latter case one has to take into account the consequences of an inter-level transfer of excitation energy in addition to the quenching transition from each doublet level to the groundlevel. Altogether, there are nine different fluorescence experiments feasible for each doublet, corresponding to excitation by either one, or both, resonance lines combined with measurements of the fluorescence from either one or both levels. JENKINS⁽¹⁰⁾ has derived the relationship between the different Y values and the collision rates for the various quenching and mixing processes. Generally speaking, the temperature deviation ΔT for each doublet component can be expressed only as a complex combination of the various Y values. In this paper it will be shown, however, that under certain reasonable conditions concerning the relative rates of the de-excitation processes for the doublet states, the relations found for singlet excited levels are also valid for doublet levels, when measured together, if we replace Y by Y_D . Here Y_D is the yield factor when both resonance lines are used in excitation and measured in fluorescence. Under these conditions the experimental determination of Y_D enables us to predict the deviation of line reversal temperature from true flame temperature in the low density limit. This may be important, when dealing with low pressure flames⁽⁷⁾ or flames containing species with small quenching efficiency in major concentrations,^(1,4,5) such as inert gas atoms, water molecules and hydrogen molecules in collision with excited alkalis. In these cases large deviations of the occupation of the excited doublet states from Boltzmann equilibrium may be expected. Conversely, under the same conditions, Y_D can be found with satisfactory accuracy from the rise in the line reversal temperature (measured on one of the doublet lines) with increasing metal concentrations, provided that Y_D is not too small and that accurate line reversal measurements are possible. In this way one can obtain information about the collisional interaction of excited alkali atoms and various kinds of flame species from the low-density limit, ΔT_m , of ΔT .

For low metal concentrations the experimental error in the measurements of the line reversal temperature increases, so that the position of the low density asymptote and thus ΔT_m is rather uncertain. In order to determine ΔT_m more reliably it is necessary to analyse the deviations of the doublet state populations from the thermodynamic equilibrium populations. These deviations, in general, depend on the rates of all transitions, collisional and radiative, of the excitation levels involved. Solutions for the normalized population function (i.e. the population function as a fraction of the equilibrium population) can be obtained by numerical procedures as described by AVRETT and HUMMER⁽¹¹⁾ and others.⁽¹²⁾ These authors have given attention to the determination of the optical depth variation of the population function (source function) for the case of a plane-parallel homogeneous atmosphere containing two-level atoms, in order to get insight into the formation of spectral lines in stars. Recently FINN and JEFFRIES⁽¹³⁾ have outlined a numerical procedure for the solution of a coupled system of transfer equations in the case of a model three-level atoms, with two close lying upper levels, such as the alkalis. Their computer calculations have been performed for a semi-infinite atmosphere in the case of pure Doppler broadening of the doublet lines and for weak coupling between the thermal energy and the radiation field, i.e. for Y_D values, which are very close to unity ($(1 - Y_D) \approx 10^{-4}$). The results of these calculations show the influence of the coupling strength between both upper levels on the shape of the population functions. Under our flame conditions, however, the emission lines exhibit Voigt profiles with damping parameters of the order of unity, while a strong coupling exists between the thermal energy and the radiation field ($(1 - Y_D) \gtrsim 0.4$). This strong coupling enables us to derive approximate analytical expressions for the population functions in the low and high density case by

following an iteration procedure, because for small Y_D values the iteration procedure converges fast enough to make it useful. Making use of these approximate expressions, the asymptotic behavior of ΔT can be determined, which, in turn, makes a more reliable determination of ΔT_m possible.

RELATIONSHIP BETWEEN DOUBLET STATE POPULATIONS AND Y_D

The derivation of this relationship accounts for the influence of radiative nonequilibrium (which depends on Y_D and metal concentration) on the occupation of the alkali doublet levels. The deviations from equilibrium population (i.e. the population obeying Boltzmann's law at "true" flame temperature) depends on the spectral radiation density $\rho_\nu(\bar{r}, n_0)$ for each of the considered doublet lines as a function of frequency ν and groundstate atom concentration n_0 at any point \bar{r} of the colored flame part. This radiation density, in turn, is connected to the excited state population which again depends on spatial coordinates. In the calculation of the normalized population function $P(\bar{r}, n_0)$ we shall assume, that the translation temperature and the groundstate atom concentration is constant throughout the colored flame, and that at any point in the flame the population of the excited state is negligibly small relative to the groundstate population. The latter condition is easily fulfilled for optical alkali lines in flames and also permits us to neglect stimulated emission. In the steady state the total rate of de-excitation by radiation and collisions balances the total rate of excitation. We have, therefore, in the case of two non-overlapping doublet lines

$$\int_{\Delta\nu_2} \rho_\nu(\bar{r}, n_0)_2 (c/h\nu_0) k_2(\nu) d\nu + n_0 k_{02} + n_1 k_{12} = n_2 (A + k_{21} + k_{20}) \tag{1}$$

and

$$\int_{\Delta\nu_1} \rho_\nu(\bar{r}, n_0)_1 (c/h\nu_0) k_1(\nu) d\nu + n_0 k_{01} + n_2 k_{21} = n_1 (A + k_{12} + k_{10}) \tag{2}$$

where n_0 , n_1 and n_2 represent the values of metal atom concentrations in the groundstate (0) and the excited states (1) and (2), respectively. $k(\nu)$ and $\rho_\nu(\bar{r}, n_0)$ are the absorption coefficient and the spectral volume density of radiant energy at frequency ν for the two doublet lines. The integrations run the total widths $\Delta\nu_1$ and $\Delta\nu_2$ of $k_1(\nu)$ and $k_2(\nu)$, respectively. k_{ij} is the total collisional rate constant, defined as the number of collisions per atom per second leading to the transfer of atoms from the state (i) to the state (j). The A value is assumed to be the same for both doublet levels, incurring only an error of a few percent for rubidium and much less for the other alkalis. The values of k_{ij} are, in general, dependent on the energy distribution of the colliding species. Since, however, the metal-particles are present as a trace in the flame gases, it is not expected that any deviation of the population of the excited doublet states from Boltzmann equilibrium will upset the equilibrium distribution for the flame particles. Hence the values of k_{ij} will be the same as in complete thermodynamic equilibrium. In order to find the population of the doublet states we rewrite the equations (1) and (2), by applying detailed balancing in the case of complete equilibrium, as

$$\delta_2(\bar{r}, n_0) A (n_2)_e + (n_2)_e k_{20} + n_1 k_{12} = n_2 (A + k_{21} + k_{20}) \tag{3}$$

and

$$\delta_1(\bar{r}, n_0)A(n_1)_e + (n_1)_e k_{10} + n_2 k_{21} = n_1(A + k_{12} + k_{10}) \quad (4)$$

where $(n_i)_e$ is the equilibrium population of the doublet level (i) and

$$\delta_i(\bar{r}, n_0) \equiv \int_{\Delta\nu_i} \rho_\nu(\bar{r}, n_0)_i k_i(\nu) d\nu / \int_{\Delta\nu_i} \rho_{\nu_0}^b k_i(\nu) d\nu$$

with $\rho_{\nu_0}^b$ = spectral volume density of radiant energy of black-body at true flame temperature, at central line frequency ν_0 . Combining these equations and using $(n_1)_e k_{12} = (n_2)_e k_{21}$, we obtain for the normalized population function (fractional source function) of the upper doublet level

$$P_2(\bar{r}, n_0) \equiv \frac{n_2}{(n_2)_e} = \frac{k_{20} + A\delta_2(\bar{r}, n_0) + k_{21} \frac{k_{10} + A\delta_1(\bar{r}, n_0)}{A + k_{12} + k_{10}}}{A + k_{20} + \frac{k_{21}(A + k_{10})}{A + k_{12} + k_{10}}} \quad (5)$$

An analogous equation for the lower level follows directly from equation (5) by interchanging the subscripts 1 and 2. Then it appears, that the fractional underpopulation of both doublet levels, will not be the same.

In the derivation of equation (5) it is implicitly assumed that the radiation field in the flame caused by any external light source may be neglected relative to the radiation field produced by the flame itself. Even for low metal densities, where the terms containing δ_1 and δ_2 are negligibly small, the general expressions for P_1 and P_2 are related in a rather complex way to the fluorescence yield factors obtained when one of the resonance lines is used for excitation and either one or both are measured in fluorescence. P_1 and P_2 are, in general, not uniquely related to the fluorescence yields obtained from excitation of both doublet levels together, because these yield factors depend on the profiles of the exciting spectral lines⁽¹⁰⁾ which under the above assumption is certainly not the case for the population functions. We shall now consider equation (5) under some less general, but still realistic assumptions concerning the relative rates of the de-excitation processes.

CASE OF EQUAL QUENCHING CROSS SECTIONS FOR THE DOUBLET COMPONENTS

When the quenching cross sections for both doublet levels are the same for all quenching species in the flame, equation (5) changes into

$$P_2(\bar{r}, n_0) = \frac{k}{A+k} + \frac{A}{A+k} \left(\frac{\delta_2 + \delta_1 k_{21}/(k_{12} + k + A)}{1 + k_{21}/(k_{12} + k + A)} \right) \quad (6)$$

where $k_{10} = k_{20} \equiv k$.

Under this condition Y_D is given by the same expression as for a single line

$$Y_D = \frac{A}{A+k} \quad (7)$$

So we can rewrite equation (6) as

$$P_2(\bar{r}, n_0) = 1 - Y_D + Y_D \frac{\delta_2 + \delta_1 k_{21}/(k_{12} + k + A)}{1 + k_{21}/(k_{12} + k + A)} \quad (8)$$

$P_1(\bar{r}, n_0)$ simply follows from this equation by interchanging the subscripts (1) and (2). From equation (8) it is seen that in the low density limit (that is for vanishing δ -values) $P_1 = P_2$ is constant and equal to $1 - Y_D$. For high metal densities δ_1 will approach δ_2 at any place in the flame, because ρ_1 as well as ρ_2 approach $\rho_{v_0}^b$ at line frequency. As a consequence the expressions for P_1 and P_2 both reduce to the "single excitation level" expression

$$P(\bar{r}, n_0) = 1 - Y_D + \delta Y_D \quad (9)$$

where $\delta = \delta_1 \approx \delta_2$.

From the computer calculations performed by FINN *et al.*⁽¹³⁾ it follows, that for equal quenching rates, P_1 and P_2 differ by at most 6 per cent from the "single excitation level" expression for all optical depths in a semi infinite atmosphere. Strictly speaking, this result only holds for a weak coupling of the thermal and radiation field in the case of pure Doppler broadening of the spectral lines. But it may be expected that the deviations of P_1 and P_2 from the "single excitation level" expression in flames are smaller rather than larger, because for small Y_D values the underpopulation of the excited states is less pronounced.

So we can conclude that for equal quenching cross sections, a doublet may be treated as a singlet, at least in the extreme cases mentioned. This means that for high metal densities $P(\bar{r})$ will decrease monotonously for both doublet lines from unity at the flame center to $\sqrt{(1 - Y_D)}$ at the very flame border, independently of line shape.⁽¹⁴⁾

For intermediate concentrations, however, P_1 and P_2 differ from each other and depend on the k -values for mixing and quenching and the spectral radiation densities of the individual doublet lines.

CASE OF STRONG COLLISIONAL MIXING OF DOUBLET STATES

When the probability of de-excitation of excited alkali atoms by photon emission and quenching to the ground state is small relative to the probability for the interlevel energy transfer of the doublet states, we have

$$k_{12}, k_{21} \gg k_{10}, k_{20} \quad \text{and} \quad A. \quad (10)$$

Accounting for this inequality, equation (5) reduces to

$$P_2(\bar{r}, n_0) = \frac{k_{20} + k_{10}k_{21}/k_{12} + A\{\delta_2(\bar{r}, n_0) + \delta_1(\bar{r}, n_0)k_{21}/k_{12}\}}{A + k_{20} + (A + k_{10})k_{21}/k_{12}}. \quad (11)$$

From interchanging the subscripts (1) and (2) it follows that $P_2 = P_1 \equiv P$ in the entire range of concentration values (see also Ref. 13). Furthermore, under the above conditions Y_D is given by

$$Y_D = \frac{A(1 + k_{21}/k_{12})}{A + k_{20} + (A + k_{10})k_{21}/k_{12}} \quad (12)$$

so that combination of equations (11) and (12) leads to

$$P(\bar{r}, n_0) = 1 - Y_D + Y_D \frac{\delta_2 + \delta_1 k_{21}/k_{12}}{1 + k_{21}/k_{12}}. \quad (13)$$

By the principle of detailed balancing, k_{21} and k_{12} are related to each other by the expression

$$k_{21}/k_{12} = (g_1/g_2)e^{-\Delta E/kT_i} \quad (14)$$

where $g_{1,2}$ are the statistical weights of the two excited states, and $\Delta E = (E_1 - E_2)$ is the energy difference between the lower (1) and upper (2) doublet state. Comparison of equation (8) and equation (13) shows that the considerations concerning the asymptotic behavior of $P(\bar{r}, n_0)$ for low and high metal densities in the case of equal quenching cross sections also hold for strong doublet mixing. However, the parameter Y_D is given in this case by equation (12) instead of equation (7).

Again it follows from Ref. (13) that under the conditions already mentioned P differs by at most 1 per cent from the singlet level expression for all optical depth in a semi infinite atmosphere if the mixing rates exceed the quenching rates (and A) by a factor 10.

APPROXIMATE SOLUTION OF POPULATION FUNCTION

For the case of relatively strong doublet mixing, where equation (13) applies, we shall derive an approximate expression for the population function, which holds in first order of metal concentration. At sufficiently low concentrations we have

$$\frac{\delta_2(n_0, \bar{r})}{\delta_1(n_0, \bar{r})} = \frac{f_2}{f_1} \quad (15)$$

where $f_{1,2}$ are the f -values for absorption of the separate doublet lines. As a consequence equation (13) reduces to the form

$$P(\bar{r}, n_0) = 1 - Y_D + Y_D \delta_2 \gamma. \quad (16)$$

Using the detailed balancing relation (14) we find for γ the expression

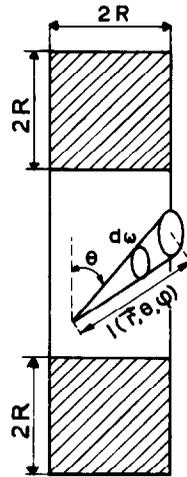
$$\gamma = \frac{1 + (f_1/f_2)(g_1/g_2) \exp[-\Delta E/kT_i]}{1 + (g_1/g_2) \exp[-\Delta E/kT_i]}. \quad (17)$$

The spectral radiation density for the strongest of the doublet lines $\rho_v(\bar{r}, n_0)_2$ is found by integrating the spectral radiance $(B_v)_2$ at the place \bar{r} over all solid angles according to

$$\rho_v(\bar{r}, n_0)_2 = \frac{1}{c} \int_{4\pi} (B_v)_2 d\omega. \quad (18)$$

Here c is light velocity. For a given place and direction, $(B_v)_2$, in turn, depends on the normalized population function P which varies with spatial coordinates. In the low density case we find $\rho_v(\bar{r}, n_0)_2$ in first order approximation with respect to n_0 by assuming in the calculation of B_v the population to equal its zeroth order value $1 - Y_D$. Applying Kirchoff's law, this yields for a cylindrical flame with radius R (see Fig. 1)

$$\rho_v(\bar{r}, n_0)_2 = (1 - Y_D) B_{v_0}^b \frac{1}{c} \int_{4\pi} (1 - \exp[-k_2(v)l(\bar{r}, \theta, \varphi)]) d\omega \quad (19)$$



COLORED INNER FLAME

FIG. 1. Cross-section through cylindrical flame with radius R . $l(\bar{r}, \theta, \varphi)$ is the distance of considered point at place \bar{r} to the flame surface, measured along the direction (θ, φ) . Equation (21) (see text) holds at any place \bar{r} in the colored flame part, except for the areas shaded in the figure.

where $B_{\nu_0}^b = \frac{c}{4\pi} \rho_{\nu_0}^b$ is the black body spectral radiance at the central frequency ν_0 of the spectral line at true flame temperature. $l(\bar{r}, \theta, \varphi)$ is the distance of the place \bar{r} to the flame border, measured along the direction (θ, φ) , where φ is the azimuthal angle and θ is the angle between l and the direction of the flame axis. The integrand represents the absorption factor at frequency ν of a column of flame gases with length l . In order to find an approximate solution for $\rho_{\nu}(\bar{r}, n_0)$ we shall restrict ourselves to such low concentrations, that $2Rk(\nu_0) \lesssim 0.2$, where $k(\nu_0)$ is the peak absorption coefficient. Doing this, we can sandwich the integral in equation (19) for any concentration within the considered concentration, between two limits, which can be computed rather easily. The upper limit is obtained by replacing the absorption factor by the leading term of its series expansion and is given by $k_2(\nu)l(\bar{r})$ where $l(\bar{r}) \equiv \frac{1}{4\pi} \int_{4\pi} l(\bar{r}, \theta, \varphi) d\omega$ is the average distance of the place r to the flame surface, weighted by a solid angle factor. This limit holds in the entire range of concentration values. The lower limit, which holds only for concentrations within the restricted concentration range is given by $\overline{l_{2R}(\bar{r})}k_2(\nu)$. Here $\overline{l_{2R}(\bar{r})}$ is a similar integral as $l(\bar{r})$, however, with the difference, that the contribution of the points lying beyond the distance $2R$ from \bar{r} is disregarded. Numerical calculations of \overline{l} and $\overline{l_{2R}}$ for a cylindrical flame with a height large compared to its radius R , show, that the sandwiched integral deviates from the value $1.5R k_2(\nu)$ by less than 20 per cent for any point in the flame, if we exclude points that lie within a distance of $2R$ from the top or the bottom of the flame (see shaded areas in Fig. 1). The quantity $1.5R$ represents a sort of weighted average of l , that holds for all considered points. Accordingly $\rho_{\nu}(\bar{r}, n_0)_2$ can be approximated in first order of $k_2(\nu)$ and thus of n_0 by

$$\rho_{\nu}(\bar{r}, n_0) = (1 - Y_D)\rho_{\nu_0}^b k_2(\nu) 1.5R. \tag{20}$$

Substituting this relation into equation (16), we obtain an expression for the population function which is uniform throughout the considered flame part and may be written as

$$P(n_0) = (1 - Y_D)(1 + Y_D 1.5R \overline{k_2(v)\gamma}) \quad (21)$$

where

$$\overline{k_2(v)} \equiv \frac{\int_0^{\infty} k_2(v)^2 dv}{\int_0^{\infty} k_2(v) dv}$$

is the weighted average of $k_2(v)$. For $n_0 = 0$, this leads immediately to the trivial result $P(0) = 1 - Y_D$. The quantity $k(v)$ is proportional to the groundstate concentration n_0 and can be expressed theoretically in the parameters of the atomic doublet line considered.

Its value can also be obtained from curve-of-growth calculations.⁽¹⁵⁾ This holds because at sufficiently low concentrations the fraction of radiation that is lost by self absorption is then proportional to $\overline{k_2(v)}$ and thus to n_0 . Results of computer calculations of equivalent widths have been tabulated by JANSSON *et al.*⁽¹⁵⁾ for several values of the wellknown damping parameter a , and can be used in the computation of $\overline{k_2(v)}$.

For the strongest of the two yellow sodium lines ($\lambda_0 = 5.9 \cdot 10^{-5}$ cm, $f = \frac{2}{3}$) and in a typical hydrogen-oxygen-argon flame with $a = 1$, $Y_D = 0.6$ and $R = 0.9$ cm, $\overline{k_2(v)}$ was calculated to equal 0.1 cm^{-1} for an optical thickness $k_2(v_0)2R = 0.2$. Substituting the values for $\overline{k_2(v)}$, Y_D and R into equation (21) shows, that $P(n_0) = 1.07(1 - Y_D)$. In other words, the population function exceeds its zero concentration value $(1 - Y_D)$ with 7 per cent for the considered optical thickness. Moreover, it appears that a 20 per cent error in the adopted average value $1.5R$ causes a variation in the population function of only 2 per cent. This implies that for a *homogeneous* cylindrical flame $P(n_0)$ is constant within few per cents throughout the considered flame part, at least for values of the optical thickness up to 0.2 at center frequency ν_0 . Instead of expressing $\overline{k_2(v)}$ theoretically in the parameters of the atomic line, its value can also be found from self-absorption measurements for this doublet line.

For strong mixing, for instance: $\overline{k_2(v)}$ can be obtained for an arbitrary but sufficiently low concentration n_0 , by measuring the loss $\Delta Y_D(n_0)$ in fluorescence yield, due to self absorption (Fig. 2), when both doublet lines are used in excitation and measured in fluorescence. In that case, we have, namely (see Appendix)

$$\overline{k_2(v)} = \frac{\Delta Y_D(n_0)}{Y_D} \frac{4}{\pi R \gamma} \quad (22)$$

where γ is defined by equation (17). Substitution of equation (22) into equation (21) finally gives

$$P(n_0) = (1 - Y_D) \left(1 + \frac{6}{\pi} \Delta Y_D(n_0) \right). \quad (23)$$

RELATIONSHIP BETWEEN ΔT AND Y_D

In our earlier paper⁽⁶⁾ expressions have been derived for the fractional shortage $\alpha(n_0)$ in the "total line intensity" (i.e. the line intensity integrated over its frequency band-width) when compared to the Boltzmann equilibrium intensity. This was done for both the low and high-density case for atoms with a single excitation level. The deviation ΔT of line-reversal temperature T_L from true flame temperature T_f follows from $\alpha(n_0)$ through Boltzmann's law

$$\Delta T = \frac{(kT_f^2/h\nu_0) \ln[1 - \alpha(n_0)]^{-1}}{1 + (kT_f/h\nu_0) \ln[1 - \alpha(n_0)]^{-1}} \quad (24)$$

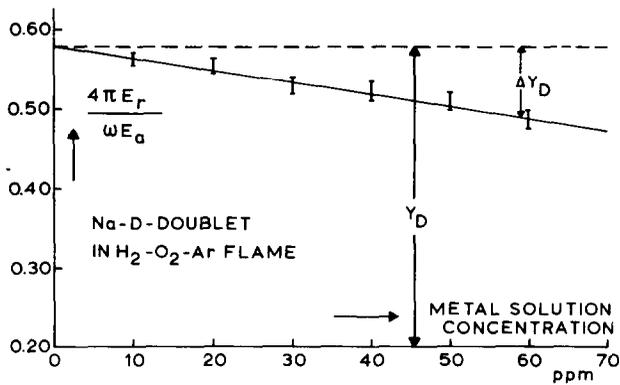


FIG. 2. Ratio of fluorescence intensity $(4\pi/\omega)E_f$ and absorbed primary radiation E_a as a function of metal solution concentration for the sodium D-doublet in a shielded stoichiometric hydrogen-oxygen-argon flame. The intersection of the experimental line with the ordinate-axis yields the Y_D value free from self absorption. ΔY_D is the loss in fluorescence yield, due to self absorption, when both lines are used in excitation and measured in fluorescence.

where ν_0 is the central frequency of the spectral line and h and k are Planck's and Boltzmann's constant, respectively. In the high-density case and for a Lorentz profile of the emitted spectral line, we have found,⁽⁶⁾ that equation (24) can be approximated by the asymptotic relation

$$\Delta T = \text{const } n_0^{-\frac{1}{2}} \quad (25)$$

For very low metal densities $\alpha(n_0)$ approaches its asymptotic value $\alpha(0) = Y$, where Y is the fluorescence yield factor of the considered spectral line. As a consequence the maximum temperature deviation ΔT_m , that is the difference between T_f and the asymptotic value of T_L for vanishing metal concentration, can be obtained by inserting $\alpha = Y$ into equation (24). In order to state as to how far these "singlet level" expressions apply for doublets we shall again distinguish the cases of strong mixing and of equal quenching cross-sections for the doublet states, respectively.

CASE OF EQUAL QUENCHING CROSS SECTIONS

As we showed above for this case, the asymptotic behavior of the population function for low and high metal densities is described for both doublet components by the same "singlet level" expression, with the difference, that Y_D instead of Y appears as a parameter. The value of Y_D is given here by equation (7). This implies that the asymptotic expressions for ΔT (i.e. equation (24) with $\alpha = Y_D$ and equation (25)) may be applied safely for both doublet lines. However, for intermediate concentrations the ΔT values are different for the individual doublet components and cannot be calculated from the "singlet level" expressions.

CASE OF STRONG COLLISIONAL MIXING OF THE DOUBLET STATES

From our above considerations concerning the population function it appeared that for strong mixing ΔT is the same for the two doublet components in the entire range of concentration values. The asymptotic expressions for ΔT are again given by the "singlet level" expressions with Y_D instead of Y , where Y_D is presented by equation (12). For intermediate concentration values, ΔT is determined by the spectral radiation densities of both doublet components.

The expression for $P(n_0)$ given in equation (23) enables us to calculate ΔT as function of n_0 for concentrations where equation (23) applies, i.e. where $k_2(v_0)2R \lesssim 0.2$.

Because $P(n_0)$ holds uniformly at any place inside the considered flame part, we have

$$\alpha(n_0) = 1 - P(n_0). \quad (26)$$

Combining equations (23), (24) and (26) we find

$$\Delta T = \frac{(kT_i^2/hv_0) \ln[(1 - Y_D)(1 + (6/\pi)\Delta Y_D(n_0))]^{-1}}{1 + (kT_i/hv_0) \ln[(1 - Y_D)(1 + (6/\pi)\Delta Y_D(n_0))]^{-1}}. \quad (27)$$

Since the factor $kT_i^2/hv_0 \ln(1 - Y_D)^{-1}$ occurring in this equation is equal to $\Delta T_m(1 - \Delta T_m/T_i)^{-1}$, which follows from the expression for ΔT_m , we can rewrite equation (27) into the form

$$\Delta T_m \left(\frac{T_i - \Delta T}{T_i - \Delta T_m} \right) = \Delta T + \left(1 - \frac{\Delta T}{T_i} \right) \frac{kT_i^2}{hv_0} \ln \left[1 + \frac{6}{\pi} \Delta Y_D(n_0) \right]. \quad (28)$$

If $\Delta T_m \lesssim 200$ K, which holds in most practical cases when dealing with atmospheric flames, we have $(T_i - \Delta T)/(T_i - \Delta T_m) \approx 1$ with an error less than 3 per cent, so that equation (28) finally can be written as

$$\Delta T_m - \Delta T = \left(1 - \frac{\Delta T}{T_i} \right) \frac{kT_i^2}{hv_0} \ln \left[1 + \frac{6}{\pi} \Delta Y_D(n_0) \right]. \quad (29)$$

Here ΔT depends on the concentration through ΔY_D (see Figs. 2 and 3).

Recapitulating we can say, that equation (29) may be expected to hold true for strong mixing of the doublet states and within the concentration range where $k_2(v_0)2R \lesssim 0.2$ with an error less than 5 per cent. From our fluorescence and absorption measurements it appeared, that this concentration range is equal to roughly half the concentration range where ΔY_D is proportional to n_0 (see Fig. 2).

EXPERIMENTAL

Determination of Y_D

The apparatus used in the experimental determination of Y_D has been described in Ref. 1. The values of the yield factor Y_D for the first resonance doublet of Na and Rb and for the first and second resonance doublet of K were obtained by measuring the ratio of the fluorescence power E_r of both doublet lines together emerging from the flame through a solid angle ω , to the absorbed primary radiation power E_a as a function of alkali concentration. Considerable effort was made to check carefully the solid angle factor of the detector and the optical alignment. In Fig. 2, $(4\pi/\omega)E_r/E_a$ for the yellow sodium doublet is plotted versus metal concentration in a H_2-O_2-Ar flame. The linear dependence of $(4\pi/\omega)E_r/E_a$ on alkali concentration found in the low concentration range can be explained by the effect of self-absorption. In these measurements the major source of error stems from the fluctuations of the thermal emission of the colored flame. It should be noted that the Y_D -values found for the sodium D-doublet in our present experiments exceed our earlier values⁽¹⁾ by a factor 1.85.*

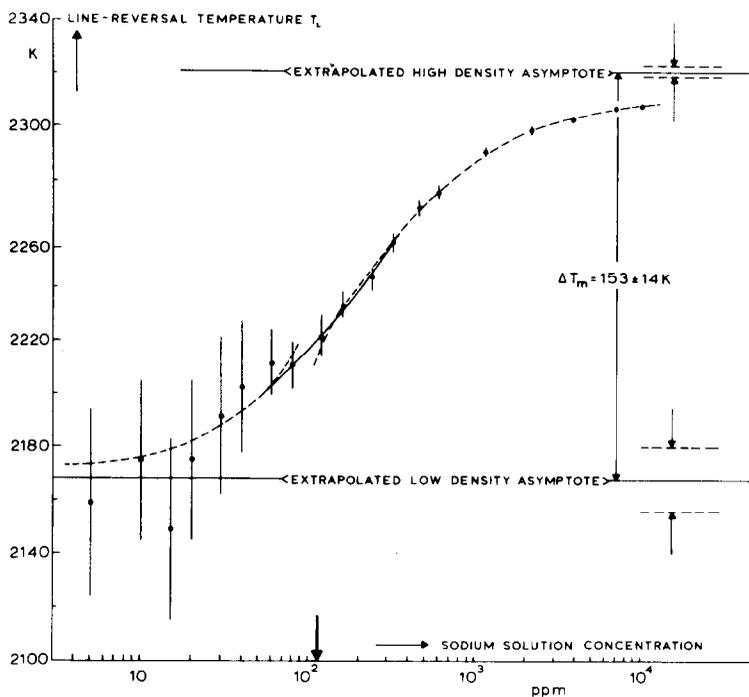


FIG. 3. Line reversal temperature T_L , measured on the sodium D_2 -line ($\lambda = 5690 \text{ \AA}$) is plotted as a function of the sodium solution concentration for a shielded stoichiometric hydrogen-oxygen-argon flame. The symbol ΔT_m represents the maximum deviation of T_L from the true (translation) temperature T_i in the limiting case of low metal concentrations. Using equations (29) and (25), the low and high density asymptotes were found by extrapolation from the low and high density values of T_L . The sodium concentration indicated with an arrow corresponds with the intersection point of the initial and final asymptote of the emission curve-of-growth.

* The yield values for the sodium D-doublet given previously were affected by systematic errors in the solid angle factor and higher impurities in the quenching gases than were thought possible.

Calculation of effective quenching cross sections

From the Y_D -values measured in a set of flames of different composition and temperature (1800–2100 K), we calculated the effective specific quenching cross-sections σ_{qu} for each of the major flame species by solving a set of equations of the form $Y_D = A/(A + k_{ij})$ (see equation (7)), where k_{ij} is the collisional rate constant summed over all types of quenching species present in the flame. Only when the quenching cross sections are the same for both doublet levels, the values deduced from these equations refer to specific processes. In the other cases these values are more or less complex averages of the actual cross-sections for quenching and mixing of the two states. From measurements^(16–21) in vapor bulbs at a temperature of about 300 K, the condition of equal quenching cross sections seems to be fulfilled in good approximation for the quenching of the first resonance doublets of Cs, Rb and K by N_2 . At present, however, there are insufficient data available to decide as to how far this condition is valid for the other alkalis and other quenching species. But for Na with relatively small doublet separation this assumption is expected to be reasonable. In the derivation of σ_{qu} -values it was assumed that the quenching effect of argon atoms could be neglected compared with that of the other predominant flame molecules H_2O , O_2 and H_2 in the argon cooled flames (for flame characteristics, see Ref. 1).

Moreover, we should make allowance for the unknown temperature dependence of each σ_{qu} separately. This problem was solved by an iteration procedure.⁽¹⁾ The cross sections derived are listed in Table 1. The values for H_2O apply to a temperature of about 2000 K, while the values for the other molecules are believed to be valid at about 1900 K. The error limits given in Table 1 include the uncertainty in the dependence of σ_{qu} on temperature, provided that this dependence is not much stronger than $\sigma_{qu} \sim T^{-1}$ as was found in our previous experiments⁽¹⁾ for N_2 and CO_2 . For comparison, also the σ values for excited ($4P_{1/2,3/2}$, $5P_{1/2,3/2}$) potassium and excited ($5P_{1/2,3/2}$) rubidium atoms are presented in Table 1.

These values were found to coincide with our earlier values within the error limits. Comparing our specific quenching cross-sections with the results obtained by Jenkins in flames of about 1600 K, it appears that there is a satisfactory mutual agreement (in most cases within 10 per cent). On the other hand, the cross sections for quenching of Na, K, Rb by N_2 and H_2 found by KRAUSE *et al.*,^(20,21) HULPKE *et al.*,⁽²²⁾ DEMTRÖDER⁽²³⁾ and

TABLE 1. SPECIFIC QUENCHING CROSS SECTION σ_{qu}

Quenching species	$\sigma_{qu} \times 10^{16}(\text{cm}^2)$ for			
	Na($3P_{1/2, 3/2}$)	K($4P_{1/2, 3/2}$)	K($5P_{1/2, 3/2}$)	Rb($5P_{1/2, 3/2}$)
H_2	8 ± 1 (9)	3.4 ± 0.3 (3.3)	60 ± 10	3.6 ± 0.4 (1.9)
O_2	34 ± 2 (38)	49 ± 3 (49)		83 ± 5 (79)
N_2	21 ± 1 (22)	19 ± 1 (17.5)	48 ± 10	25 ± 2 (19)
CO	41 ± 2 (37.5)	44 ± 3 (39)		
CO_2	50 ± 2 (53)	66 ± 2 (67)		
H_2O	2.2 ± 0.3 (1.6)	2.6 ± 0.3 (2.8)	10 ± 4	4.0 ± 0.8 (4.0)

The σ_{qu} values for water molecules may be considered as valid for a temperature of about 2100 K, while σ_{qu} is valid for about 1900 K for the other molecules. The error limits given allow also for the uncertainty in the dependence of σ_{qu} on temperature. Cross sections values in brackets refer to Refs. 4 and 5.

BELLISIO *et al.* ⁽²⁴⁾ in vapor bulbs at about 350 K are all larger than our values by about a factor 2. This systematic difference might reveal a possible temperature dependence of the σ -values. In order to corroborate this conclusion, it is necessary to measure the cross sections in a larger range of temperatures. For this reason, fluorescence experiments with the sodium D-doublet have been started in hydrogen–oxygen–nitrogen flames covering a temperature range of about 1000 K.

Experimental check of the relations between ΔT and Y_D

In order to check the validity of the derived expressions for ΔT we compared the theoretical results with actual line-reversal temperature measurements as a function of sodium concentration in a stoichiometric hydrogen–oxygen–argon flame. The temperature measurements were performed on the strongest of the two doublet lines with the use of the accurate photo-electric device developed by SNELLMAN.^(25,26) A H_2 – O_2 –Ar flame, exhibiting a large Y_D value (Fig. 2), was chosen because the deviation of T_L is expected to be pronounced here.

To decide if the limiting condition⁽¹⁰⁾ concerning the relative magnitude of the de-excitation processes applies, we can use the values for mixing cross-sections, obtained by KRAUSE and coworkers.^(16,21,27) It appears from experiments on sodium and potassium that the quenching cross sections for these alkalis in collision with inert species are over an order of magnitude smaller than the corresponding mixing cross-sections. The latter cross-sections are also much larger than the cross-sections for the quenching of these alkalis by water molecules. As a consequence the collisional rates in stoichiometric H_2 – O_2 –Ar flames at atmospheric pressure will satisfy condition (10), so that the asymptotic behavior of ΔT is given by equation (24) (with $\alpha = Y_D$) and equation (25), while for concentrations with $k_2(v_0)2R \lesssim 0.2$, equation (29) is valid. Although equation (25) has been derived, strictly speaking, (see Ref. 1) for a pure Lorentz line profile, we may use this equation for a Voigt profile of the emitted spectral line as well. Earlier, it has been shown⁽¹⁾ namely, experimentally, that this asymptotic expression also holds for mixed Lorentz and Doppler broadening of the strongest sodium doublet line, at least if the damping parameter $a \gtrsim 1$.

Making use of equation (25), the true flame temperature can be obtained by extrapolation of the measured line-reversal temperature to infinitely high concentrations with an accuracy of two degrees. The dashed curve in the high density range of Fig. 3 shows as to how far the experimental temperature curve follows the $\sqrt{n_0}$ relationship as predicted by this equation. The factor of proportionality is obtained from the experimental points at high metal densities.

For low concentrations (that is small optical thickness) the experimental error in the measurements of the line reversal temperature increases, to such extent that the position of low intensity asymptote of T_L and thus ΔT_m is uncertain by about 35 K. However using equation (29) we can find ΔT_m with satisfactory accuracy from ΔT and ΔY_D measurements at such low concentrations that $k(v_0)2R \lesssim 0.2$. Direct absorption measurements in our H_2 – O_2 –Ar flame, showed that the latter condition is fulfilled for sodium concentration up to about 50 ppm. Moreover, our experiments pointed out that ΔY_D is proportional to metal density in a concentration range up to about 80 ppm. Because of this proportionality, ΔY_D can be evaluated from Fig. 2 with a statistical error being less than 10 per cent. Once

ΔY_D is determined, $(\Delta T_m - \Delta T)$ can be calculated from equation (29) for any concentration within the restricted concentration range.

The position of the low density asymptote of T_L can be found by shifting the theoretical $(\Delta T_m - \Delta T)$ vs. n_0 curve (dashed curve in low density range of Fig. 3) so as to fit best with the experimental points. As a result we obtained for ΔT_m the value $153(\pm 15)$ K (Fig. 3). On the other hand, calculating ΔT_m from equation (24) with $\alpha = Y_D = 0.58$ (Fig. 2) leads to the value $\Delta T_m = 170(\pm 6)$ K.

So we may conclude that there is a reasonable agreement (within experimental error) between the values of ΔT_m measured by line reversal and calculated from Y_D .

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APPENDIX

Theoretical relationship between $\overline{k_2(\nu)}$ and ΔY_D

In the derivation of equation (23) we start from the evident relation

$$\Delta Y_D = \Delta Y_1 + \Delta Y_2. \quad (30)$$

Here $\Delta Y_{1,2}$ is the loss in fluorescence yield, due to self absorption that would occur, if both resonance lines are used in excitation, while fluorescence is measured for each line,

separately. The subscripts (1) and (2) correspond to the lower and upper level, respectively. From the appendix of our earlier paper,⁽¹⁾ it follows for a cylindrical flame within the concentration range where the ΔY values are proportional to n_0 , that

$$\Delta Y_1 + \Delta Y_2 = \frac{\pi R}{4} (Y_1 \overline{k_1(v)} + Y_2 \overline{k_2(v)}). \quad (31)$$

Here Y_1 and Y_2 are the fluorescence yield factors if both lines are excited by the primary light source, while their fluorescence is measured for each line, separately. Equation (31) holds independently of the shape of the exciting doublet lines. For strong mixing we have (see Ref. 10)

$$Y_1 = (k_{21}/k_{12})Y_2 \quad (32)$$

combining equations (30), (31), (32), and using the evident relations $Y_1 + Y_2 = Y_D$, and $\overline{k_2(v)}/\overline{k_1(v)} = f_2/f_1$, we finally arrive at equation (22),

$$\overline{k_2(v)} = \frac{\Delta Y_D}{Y_D} \frac{4}{\pi R \gamma}.$$