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On the applicability of optical depth-atomic absorption relationship to measurements of alkali seeded combustion flames[1]

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Abstract

The applicability of the new depth-atomic absorption relationship to measurements of optical properties of an alkali metal in a non-uniform multi-component combustion flame was numerically studied. The relationship describes the equality between the ratio of the optical depths at far to near wing wavelengths and that of the atomic absorption coefficients at the respective wavelengths. An introduction of biases into theoretical wing intensities and the evaluation of the ratio of the atomic absorption coefficients with far wing temperatures are essential features in the formalism. It is shown that the relationship has sufficient sensitivities to the change of optical quantities to be measured under realistic flame pressures, temperatures and wing spectral levels when the two wavelengths are adequately separated.

Keywords: Spectroscopy; Flame; Alkali metal; Optical depth; AAC

1. Introduction

The knowledge of the flame temperature, the ground state atom density and the spectral properties of a specific radiating atom is of basic importance in combustion chemistry, radiation heat transfer and in the field of combustion plasma technology. The monochromatic emission absorption method developed by Strong and Bundy [1] has been widely used to measure flame temperature employing an isolated spectrum emitted from alkali atoms added to the flame as the emission source or the seed to enhance the flame's

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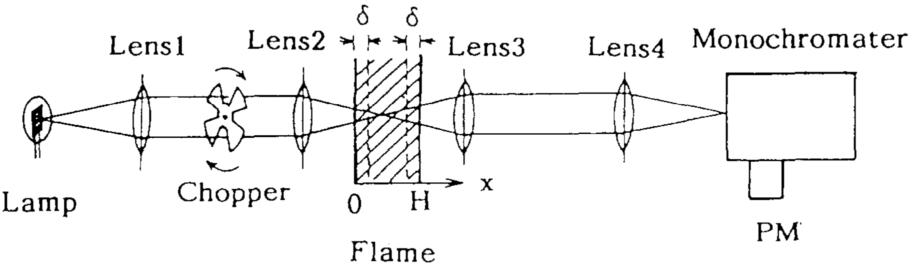

Fig. 1. A basic optical scheme of monochromatic emission-absorption measurement and the optical path coordinate.

electrical conductivity. In the optical scheme shown in Fig. 1, the flame temperature and the optical depth can be calculated by discriminatively measured monochromatic signals of each the lamp plus flame emission, flame emission only, and pre-flame lamp. Even when the flame temperature is non-uniform on the line of sight as in the case of channel flows with a hot core region bounded by cold boundary layers, it is known [2] that the temperature measured at an appropriately far wing wavelength is close to the hottest temperature in the core with definite errors of less than a few percent.

In principle, the ground state number density of the emitting species can be calculated by the optical depth per unit length divided by the atomic absorption coefficient (AAC). However, reliable measurement of the AAC requires correct identification of the collision dominated half width of the resonance line (Lorentz breadth), which further requires a correct optical cross section (OCS) of the emitting atom. The correct Lorentz breadth may be obtainable by taking the effect of flame constituents and the adequate modelling of the OCS dependence on the flame temperature. In the past, emission absorption density measurements of fossil fuel fired magnetohydrodynamic channel flows [3,4], constant OCS data of Hofmann and Kohn [5] or Hinnov and Kohn [6] obtained in a uniform acetylene–air flame based on Hinnov's intensity density method [7] have been employed. The contribution of flame constituents on the collision process has also been neglected. A part of the relatively large error of from several tens to a hundred percent may have resulted from the uncertainty in the OCS and the Lorentz breadth.

Recently, we have shown [8] in the two wavelength emission absorption method that the ratio of the far wing optical depth to the near wing counterpart was closely equal to the ratio of the AAC at the same wavelengths, provided that the latter ratio was evaluated by the temperature measured at the far wing wavelength. This depth–AAC relationship can be used to calculate the OCS and the Lorentz breadth with the measurements of two wing optical depths and the far wing temperature. However, the experimental applicability is crucially dependent on the sensitivity of the relationship to the variation of the quantity to be measured. This paper is devoted mainly to examine the appropriate range of the wavelength separation, the gas pressure, the temperature non-uniformity and the bias level. The use of biases has been proposed to describe actual wing spectra, which, as observed by Bauman [9], are higher than the theoretical values by an order of magnitude.

The flame is a kerosene oxygen combustion gas in chemical equilibrium seeded with 48% KOH aq. by 1 wt.% of potassium. An example of the calculated mole fractions of

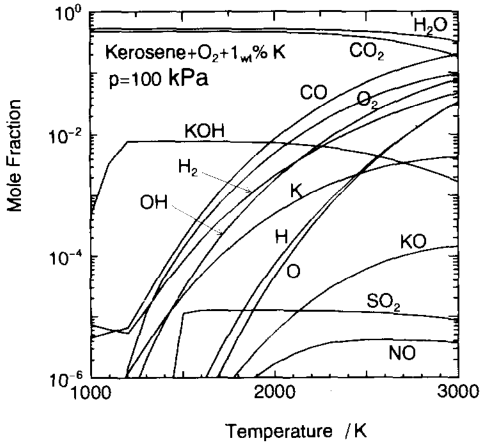

Fig. 2. Major chemical constituents of kerosene-oxygen combustion flame with 1 wt.% potassium under atmospheric pressure and an O_2 equivalence ratio of 1.0.

the major constituents is given in Fig. 2. In the following calculations, we considered 27 neutral species in thermodynamic equilibrium. It is assumed that the flame has non-uniform temperature distribution on the optical path with boundary layers of the 1/7th temperature profile and a constant temperature core layer (see Fig. 1).

2. Emission absorption theory and the depth-AAC relationship

The optical depth $\tau(\lambda)$ at the wavelength λ is defined as the integration of the absorption coefficient $\kappa(\lambda,x) = N(x)\kappa(\lambda,x)$ along the optical path x:

$$\tau(\lambda) \equiv \int_0^H k(\lambda, x)\,\mathrm{d}x = \int_0^H N(x)\kappa(\lambda, x)\,\mathrm{d}x \tag{1}$$

where $\kappa(\lambda,x)$ and $N(x)$ are the AAC and the potassium number density, respectively. The AAC $\kappa(\lambda,x)$ is a function of x due to temperature non-uniformity. For potassium D-lines the total absorption coefficient may be the sum of each contribution from the resonance line λ_1 (766.5 nm) and λ_2 (769.9 nm). Introducing a constant bias κ_n per emitting atom, the AAC is given by

$$\kappa(\lambda, x) = \sum_{i=1}^{2} G_i P_i + \kappa_n \tag{2}$$

Here, $G_i \equiv \lambda_i^2 \cdot (g_h / g_l) \cdot A_{hl} / 8\pi$,, g_h and g_l are the statistical weight of the excited and ground levels, and A_{hl} is Einstein's coefficient of spontaneous emission. According to Radzig and Smirnov [10], $G_1 = 1.87 \times 10^{-5}$ m^2 s^{-1} and $G_2 = 0.92 \times 10^{-5}$ m^2 s^{-1}. The probability function P_i is generally given by the following Voigt function [11]:

$$P_i^V 2\frac{\sqrt{\ln 2/\pi}}{\Delta\nu_{Di}}\frac{a_i}{\pi}\int_{-\infty}^{\infty}\frac{\exp(-y^2)}{a_i^2+(\omega_i-y)^2}\mathrm{d}y \tag{3}$$

For wing spectra, Eq. (3) can be simplified by the approximation $\omega_i >> y$ to result in the following Lorentz function:

$$P_i^L = \frac{2}{\pi}\frac{\Delta\nu_p}{\Delta\nu_p^2+4(\nu-\nu_i)^2} \tag{4}$$

Here, $a_i \equiv \Delta\nu_{Di}\sqrt{(\ln 2)}/\Delta\nu_p$, $\Delta\nu_{Di} = \sqrt{(8\pi RT\ln 2)}/\lambda_i$ is the Doppler breadth, $\Delta\nu_p$ is the Lorentz breadth, R is the potassium gas constant, T is the temperature $\omega_i = (\nu - \nu_i)\sqrt{(\ln 2)}/\Delta\nu_{Di}$, $\nu_i = c/\lambda_i$ is the frequency of the ith resonance center, $\nu = c/\lambda$, and c is the speed of light. The Lorentz breadth $\Delta\nu_p$ is defined by

$$\Delta\nu_p = \sum_{s\neq K} N_s\langle\nu_{sK}\rangle Q_{sK} \tag{5}$$

where N_s is the number density of neutral species except potassium, and $\langle\nu_{sK}\rangle = \sqrt{(8k_BT/\pi m_{sK})}$ is the relative speed, where k_B and $m_{sK} = m_s m_K/(m_s + m_K)$ are the Boltzmann constant and the reduced mass, respectively.

In many past emission absorption studies on the potassium seeded combustion plasmas, a constant optical cross section Q_{sK} has been assumed, i.e. $Q_{sK} = 6.0 \times 10^{-19}$ m^2 for λ_1 or $Q_{sK} = 5.77 \times 10^{-19}$ m^2 for λ_2 [5]. Also, the effect of each component on the Lorentz breadth has been neglected. However, as mentioned above, the OCS of potassium may be different in each flame with different temperature and collision partners. Therefore, according to Margnau and Watson [12], we assume here the temperature dependence of the OCS as $Q_{sK} = C\langle\nu_{sK}\rangle^{-2/5}$, where C is a constant of the order of 10^{-37} m^6 s^{-1}, that relates to Van der Waals' force and the model of the interaction potential. However, no rigorous expression of C has yet been given for alkali metals in combustion gases. Neglecting the difference in Q_{sK} for λ_1 and λ_2, we can write Eq. (5) as

$$\Delta\nu_p = \alpha pT^{-0.7}\sum_{s\neq K} X_s\left(\frac{1}{M_s}+\frac{1}{M_K}\right)^{0.3} \tag{6}$$

Here, the new constant coefficient is defined as $\alpha \equiv C(8R_0/\pi)^{0.3}/k_B$, R_0 is the universal gas constant, p is the pressure, M_s and M_K are the molecular weight of s and K, respectively. X_s is the mole fraction of s, which is calculated by the equilibrium combustion analysis as function of the temperature and pressure. The flame temperature can be evaluated by the following formula [13]:

$$T_m(\lambda) = T_L\left(1-\frac{\lambda k_B T_L}{hc}\ln\left(\frac{K_1\phi_g(\lambda)}{\phi_g(\lambda)+\phi_L(\lambda)-\phi_{g+L}(\lambda)}\right)\right)^{-1} \tag{7}$$

where the suffix m stands for the measured value, h is Planck's constant, K_1 is the transmissivity of the incident system (lenses 1 and 2 in Fig. 1) and T_L is the brightness temperature of the lamp filament. $\phi_L(\lambda)$ is the lamp light intensity defined under the condition of no absorption (no potassium). The intensities $\phi_{g+L}(\lambda)$ and $\phi_g(\lambda)$ are the emissions with and without the incidence of the lamp light, respectively. Assuming no optical loss in the detection system after lens 3, $\phi_{g+L}(\lambda)$ and $\phi_g(\lambda)$ are given approximately by the solution of the one-dimensional radiation transfer equation [2] as follows:

$$\phi_g(\lambda) = \exp(-\tau(\lambda))\int_0^H (k(\lambda,x)B(\lambda,x)\exp(\int_0^x k(\lambda,x')\,dx'))\,dx \tag{8}$$

$$\phi_{g+L}(\lambda) = \phi_L(\lambda)\exp(-\tau(\lambda)) + \phi_g(\lambda) \tag{9}$$

where $B(\lambda,x)$ is Planck's blackbody function, which is given under Wien's approximation $hc/k_B T\lambda >> 1$ as

$$B(\lambda,x) = \frac{2hc}{\lambda^3}\exp\left(-\frac{hc}{\lambda k_B T(x)}\right) \tag{10}$$

The lamp emission is given by $\phi_L(\lambda) = B(\lambda,T_L)$. The experimental formula of the optical depth $\tau(\lambda)$ can be obtained from Eq. (9) as

$$\tau(\lambda) = \ln\left(\frac{\phi_L(\lambda)}{\phi_{g+L}(\lambda) - \phi_g(\lambda)}\right) \tag{11}$$

The temperature given by Eq. (7) is derived from the ratio $B(\lambda,T_m)/B(\lambda,T_L)$ by assuming constant properties at T_m in Eq. (8). For wavelengths outside the center region, typically at optical depths of less than unity, T_m and absorption coefficients evaluated with T_m well describe the values corresponding to the core region [2]. Therefore, if the coefficient α, namely the Lorentz breadth is known, the core potassium density can be approximately evaluated by

$$N_m(\lambda) = \frac{\tau(\lambda)}{H\kappa(\lambda,\alpha,T_m(\lambda))} \tag{12}$$

where the absorption coefficient per atom is defined by Eq. (2). In cases where an exact AAC is known, the error in $N_m(\lambda)$ relative to the core value is about 10% at wing wavelengths, where $\tau(\lambda) \leq 1.0$.

A method so far known to determine the Lorentz breadth is the intensity density method developed by Hinnov [7], which, unfortunately, cannot be applied to nonuniform gases and fixed potassium density.

On the other hand, we have shown numerically that there exists the following approximate equality in two wavelength emission absorption spectroscopy [8]:

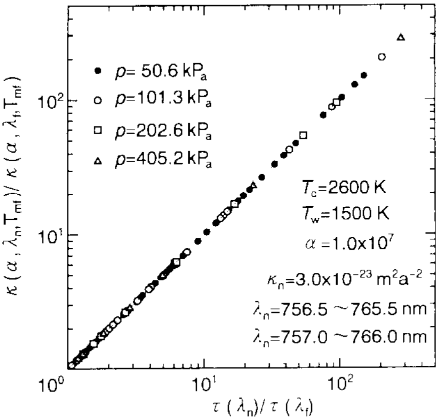

Fig. 3. Relationship between the ratio of optical depths $T(\lambda_n)/T(\lambda_f)$ and the ratio of atomic absorption coefficients $\kappa(\lambda_n,\alpha_a,T_m(\lambda_f))/\kappa(\lambda_f,\alpha_a,T_m(\lambda_f))$ for various wavelength separations $\lambda_n - \lambda_f$ and pressures.

$$\frac{\tau(\lambda_n)}{\tau(\lambda_f)} \cong \frac{\kappa(\lambda_n, \alpha, T_m(\lambda_f))}{\kappa(\lambda_f, \alpha, T_m(\lambda_f))} \tag{13}$$

where λ_n and λ_f are the near and far wing wavelengths, respectively. It is to be noted that the temperature dependence of the AAC at λ_n is described by $T_m(\lambda_f)$. Together with an appropriate modelling of the temperature dependence of the Lorentz breadth as in Eq. (6), the accuracy of Eq. (13) is assured by the use of $T_m(\lambda_f)$ in $\kappa(\lambda,\alpha,T)$ at λ_n. Assuming the non-uniform temperatures in boundary layers as $T_g(x) = T_w + (T_c - T_w)(x/\delta)^{1/7}$, we can calculate emission absorption spectra from Eqs. (8) and (9), the optical depth from Eq. (11) and the AAC from Eq. (2). The coefficient α, the bias κ_n, the pressure p, the boundary and core temperatures T_w and T_c are considered as given parameters with fixed δ and H in the following calculation. The ratios $\tau(\lambda_n)/T(\lambda_f)$ and $\kappa(\lambda_n,\alpha,T_m(\lambda_f))/\kappa(\lambda_f,\alpha,T_m(\lambda_f))$ thus calculated for $\delta = 0.02$ m and $H = 0.1$ m are plotted in Fig. 3 under various wavelength separation $\Delta\lambda = \lambda_n - \lambda_f$ and pressures. This result clearly demonstrates the equality (13). The equality has been confirmed also for a wide range of temperatures $T_w = 900$–2000 K, $T_c = 2000$–3000 K and biases $\kappa_n = 1.0 \times 10^{-25}$–$1.56 \times 10^{-21}$ m^2 atom^{-1}.

3. Sensitivity of the depth–AAC relationship

The depth–AAC relationship (Eq. 13) can be regarded as an algebraic equation with respect to the coefficient α. However, experimental determination of α with measured optical depths and temperatures requires a high sensitivity of the relationship to the variation of α. We define the sensitivity S as

$$S(\alpha) \equiv \frac{\tau(\lambda_n)}{\tau(\lambda_f)} - \frac{\kappa(\lambda_n, \alpha, T_m(\lambda_f))}{\kappa(\lambda_f, \alpha, T_m(\lambda_f))} \tag{14}$$

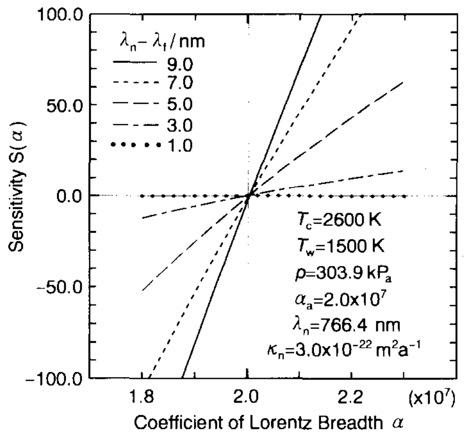

Fig. 4. Sensitivity of the depth–AAC relationship to α at different separations of far and near wavelengths.

Fig. 4 shows the sensitivity to the coefficient α under various wavelength separations, Here, α_a is the prescribed "true" coefficient and the horizontal axis are arbitrarily assumed values. The ratio $\tau(\lambda_n)/\tau/(\lambda_f)$ and $T_m(\lambda_f)$ are calculated with α_a. The point where the curve intersects the line $S(\alpha) = 0$ gives experimental values of α. We see that the sensitivity decreases when λ_n and λ_f are close to each other. However, it is sufficiently high when $\lambda_n - \lambda_f \geq 5.0$ nm with λ_n fixed at 766.4 nm in the present case. That the α value of the intersection is close to the prescribed value irrespective of $\Delta\lambda$ may indicate that quite accurate measurements of the Lorentz breadth can be expected by this formalism.

In Figs. 5–7 the sensitivity is calculated with varying the pressure, the boundary temperature and the bias level, respectively, under fixed λ_n and λ_f. Figs. 5 and 6 indicate that the sensitivity is high enough, and it is insensitive to the gas pressure and especially to

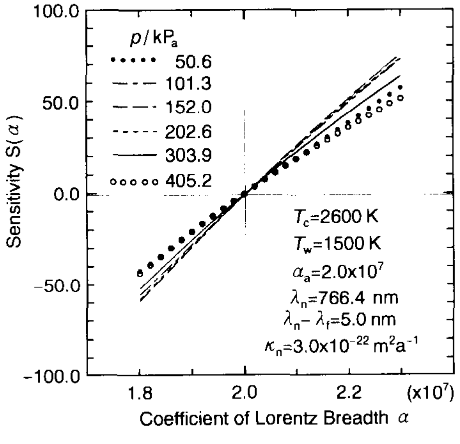

Fig. 5. Sensitivity of the depth–AAC relationship to α at different gas pressures.

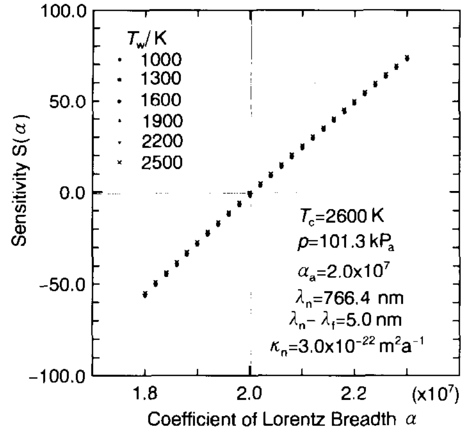

Fig. 6. Sensitivity of the depth–AAC relationship to α at different boundary edge temperatures.

the temperature non-uniformity. However, it is sensitive to the bias. Fig. 7 shows that in cases of extremely low or extremely high bias levels the applicability of the depths–AAC relationship becomes doubtful. The highest sensitivity can be expected for the bias of order 10^{-23}–10^{-22} m^2 atom^{-1}. Referring to Ref. [4], this order of κ_n well describes the wing intensity of the potassium seeded coal combustion plasmas.

The sensitivity has a common tendency to increase with the increase in the wave length difference. However, it is also affected by λ_n as well as λ_f itself. If λ_n is set extremely close to the center, the separation of the flame emission from the flame plus lamp emission becomes difficult due to self-absorption effects [2]. Also, when λ_f is extremely far away from the center a large error may be introduced due to low signal to noise ratio

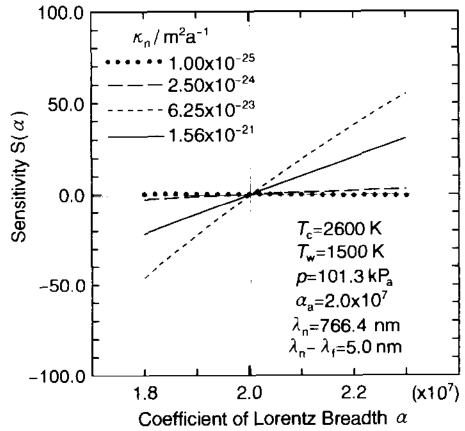

Fig. 7. Sensitivity of the depth–AAC relationship to α at different wing bias levels.

in the flame emission. The determination of optimum sets of λ_n and λ_f is an important subject of further experimental work.

4. Concluding remarks

The depth–atomic absorption relationship, the equality of the ratio of the near wing to the far wing optical depths to the ratio of the respective atomic absorption coefficients, has been outlined. It is emphasized that the formalism is based on the appropriate modelling of both the Lorentz breadth and the optical cross section.

The evaluation both of the atomic absorption coefficient with the far wing temperature and the wing spectra with the bias are essential in the proposed measurement scheme. The appropriate bias can be calculated by comparing the measured spectra with the theoretical values.

Numerical studies on the applicability of the new formula to the measurement of the Lorentz breadth and the optical cross section of alkali atoms in a non-uniform combustion flame have shown that, when the separation of two wing wavelengths is adequate, the relationship has sufficient sensitivity against the coefficient of the Lorentz breadth which is to be determined experimentally under realistic pressures, the temperature non-uniformities and the level of wing spectral intensities.

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