POWER BROADENING OF THE Na-D LINES IN A FLAME—II. THE FLUORESCENCE LINE WIDTH AS A FUNCTION OF THE SPECTRAL IRRADIANCE OF THE PULSED DYE LASER


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Abstract—Results are given of spectrally as well as temporally resolved measurements of Na-fluorescence in an H2-O2-Ar flame at 1 atm (T = 1760 K). The Na-atoms were excited with a spectrally broadband pulsed dye laser, tuned to resonance. The existence of radiation-power broadening of the Na-D lines, due to interaction of the Na-atoms with the intense (broadband) resonant laser field, has been established for the first time. Quantitative agreement is obtained between a simplified theory and experimental results if we account for the (measured) spatial inhomogeneity of the laser beam.

1. INTRODUCTION

During the last decade, dye lasers with high output power have become available, making it possible to study non-linear radiation processes in atomic fluorescence spectroscopy. The theory of one of these processes, i.e., broadening of spectral lines due to interaction of the atomic species with an intense broadband radiation field, has recently been studied by Nienhuis. Following Ya’Akobi, Alkemade, and Nienhuis, we shall refer to this type of line broadening as (radiation) power broadening. We use the term power broadening to distinguish this type of line broadening from saturation broadening. Saturation broadening is observed when a fluorescence-excitation profile is measured by scanning the wavelength of a narrow, strong (saturating) radiation beam over the absorption line profile. Power broadening is observed when the fluorescence of atoms excited by a broadband resonant laser beam with fixed central frequency is spectrally analyzed.

In this paper, we give a simplified theory of the power broadening, based on lifetime considerations of the atomic levels involved. This theory holds in the limit of a spectrally, temporally, and spatially uniform irradiation source. By using a (pulsed dye) laser with a pulse duration long compared to characteristic lifetimes of the atomic system and with a spectral width sufficiently large compared to the absorption line width, the first two conditions were fulfilled in good approximation.

The spatial inhomogeneity was accounted for by measuring the spatial profile of the laser irradiance (which varied during the laser pulse). By using the local value of the spectral irradiance in the theory of power broadening and integrating over space, we were able to compare the experiments with theoretical predictions. We give only a short description of the experimental set-up and measuring procedure; a more detailed description has been given in Part I and in Ref. 6.

The experimental results are reported and discussed, allowing for the time-dependence of the spectral as well as the spatial properties of the laser beam. Preliminary results of parts of these measurements have been presented in Ref. 7.

2. SIMPLIFIED THEORY

In order to derive theoretical expressions for the widths of Na-D lines as functions of the spectral volume density of the broadband resonant radiation beam, we use a three-level model for the Na-atom. Transitions from the Na-D levels to higher levels and the ionization continuum are neglected. We also assume that laser-enhanced chemical reactions of the Na-atoms with flame species do not influence the Na-line profile. Furthermore, we assume the spectrum of the irradiation source to be (quasi-) continuous with respect to the atomic
absorption line width, but small enough to excite only one of the Na-D lines. We denote the total transition rate constant from level \(i\) to level \(j\) by \(a_{ij}\), the ground level by index 1, and the laser-excited doublet component by index 3. The various transition rate constants \(a_{ij}\) are given by

\[ a_{13} = B_{13} \rho_r, \quad a_{31} = B_{31} + A_{31} + k_{31}, \quad a_{12} = 0 \] (i.e., we neglect excitation of the Na-D lines by thermal collisions), \(a_{21} = A_{21} + k_{21}, \quad a_{23} = k_{23}\), and \(a_{32} = k_{32}\). Here, \(B_{31}\) is the Einstein coefficient for stimulated emission (cm J\(^{-1}\) s\(^{-2}\)); \(B_{13}\) is the Einstein coefficient for absorption (cm J\(^{-1}\) s\(^{-2}\)); \(A_{31}\) and \(A_{21}\) are the Einstein coefficients for spontaneous emission (s\(^{-1}\)); \(k_{31}\) and \(k_{21}\) are the monomolecular quenching rate constants (s\(^{-1}\)); \(k_{32}\) and \(k_{23}\) are the monomolecular mixing rate constants (s\(^{-1}\)); \(\rho_r\) is the spectral volume density of the radiation field in the flame (J \(\cdot\) cm\(^{-3}\) Hz\(^{-1}\)) which is tuned to the 1-3 transition.

Using the relation \(B_{13} = (g_3/g_1)B_{31}\), where \(g_1\) and \(g_3\) are the corresponding statistical weights, we find the following expressions for the inverse mean lifetime of levels 1, 2 and 3, respectively:

\[ \tau_3^{-1} = A_{31} + k_{31} + B_{31} \rho_r, \] (1)
\[ \tau_2^{-1} = A_{21} + k_{21} + k_{23}, \] (2)
\[ \tau_1^{-1} = (g_3/g_1)B_{31} \rho_r. \] (3)

From these equations, we calculate the contribution of inelastic collisions and radiative transitions to the Lorentz part of the spectral width (full-width-at-half-maximum, FWHM) of the Na-D lines to be

\[ \Delta \nu_{31} = \frac{1}{2\pi} \left[ (1 + g_3/g_1)B_{31} \rho_r + A_{31} + k_{31} + k_{32} \right] \] (4)

for transition from the laser-excited level and

\[ \Delta \nu_{21} = \frac{1}{2\pi} \left[ (g_3/g_1)B_{31} \rho_r + A_{21} + k_{21} + k_{23} \right] \] (5)

for the other one. Elastic collisions also contribute to the Lorentz part of the line profile and the total Lorentz width (FWHM) is given by

\[ \Delta \nu_{L,i} = \Delta \nu_{it} + \Delta \nu_{C,i}, \] (6)

where \(i = 2\) or \(3\) and \(\Delta \nu_{C,i}\) is the contribution from the elastic collisions.

The total line profile is obtained by the convolution of the Lorentz profile with a Doppler profile which has a width (FWHM) given by

\[ \Delta \nu_D = (2\nu_0/c)(2RT\ln 2/M)^{1/2}, \] (7)

where \(\nu_0\) is the central frequency of the spectral line, \(c = \) the speed of light in vacuo, \(R = \) the gas constant, \(T = \) the absolute temperature and \(M = \) the molar mass. For the Na-D lines, we find a Doppler width of 3.19 \pm 0.04 GHz (36.9 \pm 0.4 mÅ), at \(T = 1760 \pm 50\ K\).

In good approximation (better than 1.2\%\), the line width of the convoluted profile (Voigt profile) is given by

\[ \Delta \nu_{V,i} = \frac{1}{2}(\Delta \nu_{L,i} + \sqrt{\frac{1}{4}(\Delta \nu_{L,i})^2 + (\Delta \nu_D)^2}). \] (8)

Finally, the Voigt profile must be convoluted with two delta functions (1772 MHz or 20.55 mÅ apart and 10:11 with intensity ratio 5:3) to allow for the hyperfine structure of the ground level; only splitting of the ground level produces noticeable broadening in our flame.

Neglecting the energy difference between the two doublet levels, which is small compared to \(kT\), we can write \(k_{32}/k_{12} = g_3/g_2\). We simplify Eqs. (4) and (5) by substituting this expression and
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making the approximations \( A_{31} = A_{21} = A, \ k_{31} = k_{21} = k \), while writing \( B_{31} = B \):

\[
\Delta \nu_{31} = \frac{1}{2\pi} [(1 + g_3/g_1)B\rho_\nu + A + k + k_{32}],
\]

\[
\Delta \nu_{21} = \frac{1}{2\pi} [(g_3/g_1)B\rho_\nu + A + k + (g_3/g_2)k_{32}],
\]

With \( A = 6.2 \times 10^7 \text{ s}^{-1} \) (see Ref. 12), \( B = (c^3/8\pi\hbar \nu_0^3)A \) (\( \hbar = \text{Planck's constant} \)) and using the values \( k = 3.7 \times 10^7 \text{ s}^{-1} \) (see Ref. 13) and \( k_{32} = 3 \times 10^8 \text{ s}^{-1} \) (see Ref. 8) as measured for a similar flame, we calculate (with \( \rho_\nu \) expressed in \( \text{J cm}^{-3} \text{ Hz}^{-1} \)) for the width \( \Delta \nu \) (expressed in Hz) of the Lorentz part of the line profiles the following values:

\[
\Delta \nu_{31} = 3.64 \times 10^{26} \rho_\nu + 0.6 \times 10^8, \tag{11}
\]

for the \( D_2 \)-line, if the \( D_2 \)-line is excited;

\[
\Delta \nu_{21} = 2.42 \times 10^{26} \rho_\nu + 1.0 \times 10^8, \tag{12}
\]

for the \( D_1 \)-line, if the \( D_2 \)-line is excited;

\[
\Delta \nu_{31} = 2.42 \times 10^{26} \rho_\nu + 1.0 \times 10^8, \tag{13}
\]

for the \( D_1 \)-line, if the \( D_1 \)-line is excited;

\[
\Delta \nu_{21} = 1.21 \times 10^{26} \rho_\nu + 0.6 \times 10^8 \tag{14}
\]

for the \( D_2 \)-line, if the \( D_1 \)-line is excited.

Figure 1 shows a plot of the total line width (FWHM) of the Na-D lines as a function of the spectral volume density of the laser, including contributions of elastic collisions, the Doppler width and the hyperfine structure. For \( \Delta \nu_{\nu,0} \) in the absence of an intense laser field, we use the experimental values of 8.0 GHz (93 mÅ) for the \( D_2 \)-line and 8.5 GHz (98 mÅ) for the \( D_1 \)-line (see Section 6).

![Fig. 1. The calculated spectral width (FWHM) (including contributions due to Doppler-effect, elastic collisions and hyperfine structure) of the Na-D lines as a function of the spectral volume density of a broadband uniform laser beam. (a) The width of the \( D_2 \)-line when the \( D_2 \)-line is excited. (b) The width of the \( D_1 \)-line when the \( D_2 \)-line or the \( D_2 \)-line is excited. (c) The width of the \( D_1 \)-line when the \( D_1 \)-line is excited.](image-url)
We conclude that power broadening of the D₂-line does not depend on which of the two lines is excited by the laser irradiation. On the other hand, the broadening of the D₂-line is much larger when the D₂-line is excited than when the D₁-line is excited.

3. EXPERIMENTAL SET-UP

A general lay-out of the experimental arrangement (see also part 1 and Ref. 6) is shown in Fig. 2. The measurements were carried out in a premixed, laminar, shielded H₂-O₂-Ar flame at 1 atm (T = 1760 K), burning on a Mékèr burner and into which a NaCl-solution was nebulized. This type of flame has been described by Lijnse. 14

We used a flashlamp-pumped pulsed dye laser as excitation source with Rh-6G in methanol dye solution. An interference filter and a Fabry-Pérot etalon were mounted in the laser cavity as bandwidth-restricting elements. Measurements on the time-dependent spectra of the dye laser revealed a spectral width of about 360 mÅ (FWHM) and a shift of the central wavelength over about 80 mÅ during the laser pulse. 3 The (instantaneous) spectral width of the laser beam was compared with the (instantaneous) power-broadened spectral width of the fluorescence line. We discarded all measurements for which the laser bandwidth was smaller than the actual spectral width of the fluorescence line. For these measurements, the assumption of (quasi-)continuous irradiation is certainly invalid and our simplified theory is inapplicable.

The duration of the pulse was about 500 ns (FWHM). Since the actual lifetimes of the excited states are smaller than 10 ns, a quasi-stationary state may be anticipated. Due to the pulsed character of the dye laser, the fluorescence had to be resolved spectrally as well as temporally. Time resolution was achieved by using a fast photomultiplier tube and detection circuit. Using an impedance transformer and a load resistance of 1000Ω, the rise time of the detection system was found to be less than 10 ns.

Spectral resolution was achieved by using a Fabry-Pérot interferometer that was controlled by a stabilization system in order to maintain a finesse of 50 for many days. In this way, the contribution of the instrumental profile to the measured fluorescence profiles was only 20 mÅ (1.8 GHz). All experimental results were corrected by deconvolution for this instrumental broadening.

4. SPATIAL CORRECTION

The theoretical curves shown in Fig. 1 are only valid in the case of uniform (in space, time and frequency) irradiation of the fluorescence volume that is detected by the photomultiplier tube. In practice, as far as spatial homogeneity is concerned, this condition will not be fulfilled because the laser irradiance is not uniform across the laser beam. The fluorescence detected is thus composed of contributions from volume elements within the observation region showing different power broadening. The intensities of the volume elements are equal because of the high degree of saturation and the uniform atomic density in the observation region. Moreover, the spatial profile of the laser beam turned out to vary during the laser pulse.

In order to account for this spatial inhomogeneity, we measured the spatial profiles of the laser beam as a function of time. Using these profiles, we calculated theoretically the intensity and spectral width of the fluorescence line emitted by each volume element in the observation region as a function of time. We chose each volume element to be so small that the laser beam irradiation was virtually uniform within it. Finally, we computed the appropriate integrals over space within the known boundaries of the observation volume.

In order to reduce the effects of spatial inhomogeneity of the laser beam, we used a beam expander with a linear expansion factor of about two. Greater expansion would cause too much loss of spectral volume density and consequently of power broadening effect. The time-dependent spatial properties of the laser beam were determined by moving a pinhole across the beam at the location of the flame and measuring the transmitted light with a fast photodiode. The results are shown in Fig. 3.

The normalized cross sectional spatial profiles of the expanded beam were well described by Gaussian distributions along two perpendicular axes with different, time-dependent widths (FWHM). The centers of these distributions, which determined the position of the beam axis, turned out to vary with time during the laser pulse (see Fig. 3). The corresponding maximum spectral volume density will be referred to as the axial spectral volume density. Knowing this
Fig. 2. Schematic diagram of the experimental arrangement. 1, light source; 2, detection system; 3, data storage; 4, stabilization system.
Fig. 3. The spatial width (FWHM) and centre position of the laser beam as a function of time. (a) The width in the direction in which the fluorescence was detected. (b) The relative position of the beam centre in the same direction. (c) The width in the direction perpendicular to the previous one and the beam axis. (d) The relative position of the centre of the beam in the same direction as under (c). The time domain in which the width is rather constant is indicated by stable region. Inclusion of the open circles in the calculations would introduce errors as in general they do not reproduce very well.
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value and the normalized spatial distribution at each moment, we calculated the line profile in each volume element using the theory for the homogeneous case. By integrating these profiles over all volume elements, we calculated the width of the composite fluorescence signal at each moment. Each profile was multiplied by a weight factor determined only by the geometry of the detection channel. In principle, the spectral profile of the composite fluorescence cannot be described by the convolution of single Lorentz and Doppler profiles.

In our experiments, one of the integration boundaries for the composite fluorescence was determined by the pinhole behind the Fabry–Pérot interferometer (see Figs. 2 and 4). This pinhole was imaged in the flame with a magnification factor of one, as indicated in Fig. 2. The diameter of the pinhole was 0.50 mm and the diameter of the laser beam was about 3.5 mm. Hence, any inaccuracy in the measured spatial distribution along the y-axis (see Fig. 4), which is perpendicular to the propagation of the beam and to the direction of detection, had no effect on the calculation of the composite fluorescence, as far as the integration boundaries were concerned. This inaccuracy, however, did affect the absolute calibration (see Section 5) of the axial spectral volume density.

In the direction of beam propagation (the z-axis in Fig. 4), the spectral volume density of the beam was almost constant because the (saturated) absorption in the optically thin Na-vapour was negligible and the beam cross section was constant within the observation region. In the direction of the detection channel (the x-axis in Fig. 4), the boundaries of the observation volume were determined by the diaphragm in the laser beam just in front of the flame. This diaphragm had a diameter of 6 mm and could not be made much smaller because of the resultant loss of signal. Hence in this direction, accurate knowledge of the beam radius was important.

In the experiments, the position of the laser beam axis was not exactly coincident with the image of the pinhole in the flame. The deviation was measured and accounted for in the calculations. Figure 5 shows the calculated deviation, due to spatial inhomogeneity of the laser beam, from the ideal theoretical curve as depicted in Fig. 1 and reproduced in Fig. 5(a). Even for the expanded beam used in our experiments, the influence of inhomogeneity was strong (curve b). For an unexpanded laser beam (curve c), power-broadening is hardly observable, even when there is a considerable power broadening on the beam axis.
5. EXPERIMENTAL PROCEDURE

At a large number of mirror positions (within one free spectral range) of the interferometer, each corresponding to a different wavelength, fluorescence intensities were measured as a function of time. The measurements were then digitized and stored with the aid of a transient digitizer and a mini-computer system. In each pulse registration, the instantaneous fluorescence intensity was averaged over every consecutive 50 ns interval and all registrations were combined to form a set of spectra, each labelled by a time (see Fig. 6).

The width (FWHM) of the composite fluorescence profiles was determined by fitting a Lorentz curve to the experimental points. Although these profiles were not strictly Lorentzian, the errors in the widths (corrected for the Doppler-contribution according to Eq. 8) obtained by this procedure appeared to be less than 5%. Figure 7 shows an example of such fits for a power-broadened and an unperturbed line profile, respectively. The wavelength scale was calibrated by measuring the free-spectral-range of the interferometer. 6

Absolute spectral intensity calibrations of the laser beam at each moment were obtained by measuring the total energy of a laser pulse, together with the (time-dependent) spectral width and (time-dependent) spatial distribution of the laser beam. The error in the calibration of the axial spectral volume density was estimated to be 10%.

6. EXPERIMENTAL RESULTS

In order to avoid possible self-absorption effects, 15 we first measured the unperturbed line width of the Na–D lines in fluorescence at weak irradiation for a number of Na-concentrations. In these measurements, we used a low-pressure Na-vapour discharge lamp. The observed part of the flame was uniformly illuminated by the lamp.

Figure 8 shows the apparent line width (FWHM) as a function of the Na-concentration in the nebulized solution. At a concentration of 20 ppm, the width of the D2-line in fluorescence was $93 \pm 2 \text{ mÅ (8.0 \pm 0.2 GHz)}$. According to measurements of Jongerius et al. 16 the ratio of the unperturbed widths of the Na-D lines in our flame was 1.06. We therefore expect a width of $98 \pm 2 \text{ mÅ (8.5 \pm 0.2 GHz)}$ for the unperturbed D1-line. Measurements of the width of the
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thermal emission lines at large Na-concentrations (> 200 ppm) agreed within the experimental error of 10% with the corresponding fluorescence measurements. At lower concentrations, the thermal emission was too weak to be spectrally analyzed. All line-width measurements with the pulsed dye laser were performed at a concentration of 20 ppm.

Figure 9 shows the instantaneous spectral width of the Na–D2 line as a function of the corresponding axial spectral volume density in the stable region (see Fig. 3), when the D2 and

Fig. 6. A 3-dimensional plot of the intensity of the D2-line in fluorescence measured as a function of time and wavelength on an arbitrary time scale. Spectra are constructed by making cross sections at various times during the pulse after averaging over consecutive 50 ns intervals. The appearance of a peak in the time behaviour of the fluorescence is caused by depletion of excited Na-atoms due to enhanced collisional ionization rate. This depletion plays no role in the derivation of the spectral line width as a function of time and thus as a function of spectral laser density.

Fig. 7. An example of the fit of a Lorentz curve to the experimental points of a power-broadened composite fluorescence profile and an unperturbed profile, respectively.
the $D_1$ lines were excited. For a given value of the axial spectral volume density, various theoretical widths may be obtained for different spatial profiles of the laser beam. Since these profiles differ only slightly in the stable region (see Fig. 3), the corresponding theoretical curves also differ slightly. They all lie within the shaded area shown in Fig. 9.

In a similar way, Fig. 10 represents the spectral width of the Na–$D_1$ line as a function of the axial spectral volume density of the laser beam in the stable region for the same two cases of laser excitation.

Fig. 8. The spectral width (FWHM) of the $D_2$-line in fluorescence as a function of the Na-concentration in the nebulized solution. The slope of the curve at high concentrations tends to $\arctan(1/2)$, as predicted in Ref. 15.

Fig. 9. The spectral width of the $D_2$-line as a function of the axial spectral volume density in the stable region of the laser pulse with $D_2$-line and $D_1$-line excitation, respectively. The theoretically calculated (and for spatial inhomogeneities corrected) values of the line width are all within the shaded area of the figure. The indicated error is typical for high irradiances.
7. DISCUSSION

Our spectrally resolved measurements clearly demonstrate the occurrence of radiation-power broadening of the Na-D lines when either doublet component is excited by an intense, broadband laser beam. Although the scatter of the individual experiments was rather large, the general trend of the experimental line width as a function of spectral density was quantitatively in reasonable agreement with the simplified theory (see Figs. 9 and 10). Strictly speaking, this theory holds only for the limiting case of an infinitely large laser bandwidth. Quantitative agreement with the theory was still found, however, when the power-broadened atomic line width approximated the laser bandwidth (360 mÅ) within a factor of two. This outcome is not incompatible with preliminary computer calculations based on the exact theory.\(^\text{17}\) Experiments in an Na-vapour cell are under way now to check this general theory with variable laser bandwidth and detuning.

Upon closer inspection of Figs. 9 and 10, it seems that, in the range of low spectral densities, the experimental points tend to lie systematically above the theoretical curves. At medium and high spectral densities, the experimental values for the D₂-line with excitation at the D₁-line seem to be somewhat smaller than the theoretical values. Since these deviations are of the order of the experimental scatter and since the calculated values depend critically on the assumed spatial inhomogeneity of the laser beam, no definite conclusions can be drawn. This critical dependence on spatial inhomogeneity explains why we found no power broadening at all when the laser beam was focused in the flame. The application of a beam expander was essential for observing this broadening effect in our flame.

The scatter in the (individual) experimental points in Figs. 9 and 10 was mainly due to fluctuations of the spatial and spectral properties of the laser beam. No systematic differences were found between the positions of the experimental points that were obtained early and late, respectively, within the stable region (see Fig. 3).

In the H₂-O₂-Ar-flame at 1 atm pressure, power-broadening sets in at a spectral volume density of the order of \(10^{-17} \text{ J cm}^{-3} \text{ Hz}^{-1}\). This value is about 3 orders of magnitude larger than the saturation parameter for the Na-doublet in the same flame.\(^\text{8}\) It may be recalled that, in power-broadening experiments, the broadening caused by the (increased) induced emission and absorption rates must compete with adiabatic as well as with nonadiabatic collision broadening.
The natural line width is negligible in our flame. In saturation experiments, the induced emission rate has to compete only with the rate for nonadiabatic (or quenching) collisions and the spontaneous emission rate. Since the efficiency of fluorescence is rather close to unity in our Ar-diluted flame, the quenching rate is small compared to the rate of adiabatic collisions.

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