J. Phys. B: At. Mol. Opt. Phys. 26 (1993) 3679–3692. Printed in the UK

# The non-Lorentzian wings of alkali resonance lines: the determination of the atom number density in pure and mixed alkali vapours

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Received 19 April 1993, in final form 2 July 1993

**Abstract.** The improved method for the determination of the atom number densities in pure and mixed alkali vapours has been proposed. It has been shown that in order to obtain the correct results one has to go beyond the simple Lorentzian shape of the quasistatic absorption profile. The method has been tested by the white-light absorption measurements in the pure K, Rb and Cs vapours. The statistical accuracy of the obtained data for the atom number density is found to be ±3%. The method has been applied for determining the atom number densities in the vapour over the Rb–Cs mixture. The obtained values have been used in the evaluation of the effective $C_6$ constants for Rb*–Cs interaction: $C_6^{\mathrm{eff}} = (4.9 \pm 0.3) \times 10^{-30}\ \mathrm{cm^6\,s^{-1}}$ for the Rb D1 line and $C_6^{\mathrm{eff}} = (2.4 \pm 0.3) \times 10^{-30}\ \mathrm{cm^6\,s^{-1}}$ for the D2 line. The theory predicts $C_6^{\mathrm{eff}} = 4.95 \times 10^{-30}\ \mathrm{cm^6\,s^{-1}}$ for the D1 line and $C_6^{\mathrm{eff}} = 2.37 \times 10^{-30}\ \mathrm{cm^6\,s^{-1}}$ for the D2 line.

## 1. Introduction

An accurate knowledge of the atom number density is frequently needed in the investigations of various physical processes in alkali vapours. At the same time, the uncertainty in the determination of the atom number density usually introduces the major error in the experimentally determined physical quantities. When the investigations are performed in the vapour over the pure alkali metal, the atom number density can be determined from the published vapour pressure curves (Nesmeyanov 1963), provided that the temperature of the system is accurately known. However, this is often not the case, so that the uncertainty in the measurement of the temperature as well as the inaccuracies in the vapour pressure curve itself, result in systematic errors.

When the measurements are performed in an alkali vapour mixture the vapour pressure curves for a one-component system are not applicable (Rozwadowski and Lipworth 1966). In that case the partial pressures of the involved elements, which depend on the composition of the mixture (Czajkowski *et al* 1966, Seiwert 1956), have to be determined. One of the methods for accomplishing that is that of Czajkowski *et al* (1966). It requires the measurement of the extinction coefficient both in pure alkali vapour and in the alkali vapour mixture, the accurate measurement of the temperature and the use of the vapour pressure curves for the particular pure element. Another method which can be used in this situation is the method of the curve of growth (Thorne 1974, Huennekens 1982). Its use is convenient only when the spectral

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line is either purely Doppler or purely Lorentz broadened. Otherwise the determination of the actual ratio of the Lorentz to Doppler half-width is necessary in order to apply this method. The accurate data on the temperature of the mixture is required too. The method for the determination of the atom number density which will be assessed in this paper is based on the proportionality of the absorption coefficient in the quasi-static wing of the alkali resonance line with the square of the density of alkali atoms in the vapour. Although it has been used in a number of papers so far (Beuc *et al* 1982, 1984, Vadla *et al* 1992, Beuc and Horvatic 1992) the accuracy of this method has never been systematically tested. To analyse the reliability and the limitations of this method we have performed white-light absorption measurements in the potassium, rubidium and caesium vapours (Huennekens (1982) investigated sodium vapour pressure by the analysis of the impact wing of the line). This simple form of the experiment has been chosen because it can be applied in almost any experimental situation.

In section 2 the unified treatment of both the resonance and foreign gas broadening in the quasistatic region of the spectral line wings is presented. The theoretical expectations that the simple Lorentzian form of the quasistatic wing might not be sufficient for obtaining the correct values for the atom number density have been experimentally verified in section 3. Also, we have tested the applicability of the method in the alkali vapour mixture of an arbitrary composition. In section 4 we present the results of the broadening of the rubidium first resonance lines by collisions with caesium atoms. The atom number densities of both Rb and Cs atoms, needed for the evaluation of the effective $C_6$ constants for Rb–Cs interaction, have been determined in the way elaborated in sections 2 and 3.

## 2. Physical aspects of the method

Generally, the absorption coefficient $k(\nu)$ can be expressed as (Mitchell and Zemansky 1971):

$$k(\nu)=(\pi e^2/mc)f_aN_a\mathcal{P}(\nu) \tag{1}$$

where $\mathcal{P}(\nu)$ is the line profile function normalized to unity, $N_a$ is the absorber number density and $f_a$ is the absorber oscillator strength.

For the difference potential $\Delta V(R)$ of the form $hC_nR^{-n}$ ($n$ is determined by the type of the interaction between absorber and perturber while $R$ denotes their interatomic separation), $\mathcal{P}(\nu)$ in the quasi-static wing of the spectral line is well approximated by the following expression (Sobelman *et al* 1981, Allard and Kielkopf 1982):

$$\mathcal{P}(\nu)=(4\pi/n)N_pC_n^{3/n}(\Delta\nu)^{-(n+3)/n} \tag{2}$$

where $N_p$ is the perturber number density and $C_n$ is the interaction constant.

Equations (1) and (2) yield the expression for the absorption coefficient in the quasi-static line wing:

$$k(\nu)=(4\pi^2e^2/mcn)N_aN_pf_aC_n^{3/n}(\Delta\nu)^{-(n+3)/n}. \tag{3}$$

The above expression for the absorption coefficient is correct when single difference potential contributes to the wing formation. However, there is often more than one difference potential involved, which means that: $h\Delta\nu=\Delta V_i(R)=hC_{ni}R^{-n}$. Here $i$

counts the different optical transitions which contribute to the wing formation, $R$ denotes the interatomic separation for which the former relation has the real solution (real Condon points), $C_{ni}$ is the interaction constant for one particular difference potential. The corresponding expression for the absorption coefficient is then:

$$K(\nu)=(4\pi^2e^2/mcn)N_aN_p\left(\sum_i f_{ai}C_{ni}^{3/n}\right)(\Delta\nu)^{-(n+3)/n} \tag{4}$$

where $f_{ai}$ is the oscillator strength associated with the $i$th optical transition. In expression (4) contributions of different $\Delta V_i(R)$ potentials are simply superimposed, which is not possible in general. However, the adiabaticity of the perturbation assumed within the framework of the used model (Sobelman *et al* 1981), justifies this step.

The above form of the expression for $k(\nu)$ is equally applicable in the case when absorbers and perturbers are dissimilar atoms (foreign gas broadening) as well as in the case when they are identical (resonance broadening). In the latter case it is obviously $N_a=N_p=N$, where $N$ is the atom number density in the system comprising identical particles.

With effective interaction constants $C_n^{\mathrm{eff}}$ defined by:

$$C_n^{\mathrm{eff}}=\left\{\sum_i (f_{ai}/f_a)C_{ni}^{3/n}\right\}^{n/3} \tag{5}$$

and the index $J=\frac{1}{2}, \frac{3}{2}$ introduced in order to distinguish between the components of the resonance doublet, one obtains the following expressions:

$$k_J(\nu)=(2\pi^2e^2/3mc)N_aN_pf_J(\Delta\nu)^{-3/2}(C_6^{\mathrm{eff}})^{1/2} \tag{6}$$

$$k_J(\nu)=(4\pi^2e^2/3mc)N^2f_J(\Delta\nu)^{-2}C_3^{\mathrm{eff}} \tag{7}$$

for the quasi-static absorption coefficient in the case of the van der Waals interaction (typical example of foreign gas broadening, $n=6$) and resonance interaction ($n=3$), respectively.

The method for the determination of the atom number density analysed here, relies essentially on expression (7). Namely if $C_3^{\mathrm{eff}}$ are accurately known, $N$ can be determined from the measurement of the absorption coefficient in the quasi-static resonant wing of the spectral line. In the evaluation of the experimental data we have chosen to use the theoretical results for $C_3^{\mathrm{eff}}$ deduced from the calculations of the quasi-static wing profiles for the alkali resonance lines which have been carried out by Movre and Pichler (1980). Their expression for the quasi-static absorption profile, rewritten in the notation that we have adopted here, is the following:

$$k_J(\nu)=(e^4/24m^2c\nu_J)N^2f_{3/2}^2\mathcal{K}_J(\nu) \tag{8}$$

where $\mathcal{K}_J(\nu)$ and $\nu_J$ are the reduced absorption coefficient (which comprises the contributions of all optical transitions which can take part in the line wing formation at given $\Delta\nu$) and the line centre frequency of the particular component of the resonance doublet, respectively.

When the spin–orbital interaction is much larger than the electrostatic one (*coupled approximation*, Fontana 1962), the following expressions for $\mathcal{K}_J(\nu)$ were obtained (Movre and Pichler 1980):

$$\mathcal{K}_J(\nu) = (\Delta\nu)^{-2} \times \begin{cases} (7+2\sqrt{7})/4 & J=\frac{3}{2} \\ 1 & J=\frac{1}{2} \end{cases} \tag{9}$$

for the blue wing of the D2 line and the red wing of the D1 line, respectively. In this limiting case the reduced absorption coefficient $\mathcal{K}_J(\nu)$ exhibits the pure Lorentzian form.

The expressions for $\mathcal{K}_J(\nu)$ corresponding to the case when the spin-orbital and electrostatic interactions are comparable (intermediate case approximation, Movre and Pichler 1980) are:

$$\overline{\mathcal{K}_J}(\nu) = \mathcal{K}_J(\nu)[1+\beta_J|\Delta Y|] \tag{10}$$

where $\beta_J = 2.3$, $0.55$ for $J=\frac{1}{2}$, $\frac{3}{2}$, respectively, $\Delta Y = \Delta\nu/\Delta\nu_{\mathrm{fs}}$, where $\Delta\nu_{\mathrm{fs}}$ is the fine structure splitting and $\Delta\nu$ is measured from the centres of the D2 and D1 lines, respectively. In this case the reduced absorption coefficient exhibits the deviation from the pure Lorentzian form.

The equation (10) holds for the blue wing of the D2 line (numerical accuracy better than 0.5%) and the red wing of the D1 line (numerical accuracy of about 3%) and for $|\Delta Y|$ up to 0.3.

The $\overline{\mathcal{K}_J}(\nu)$ for the inner wings of the resonance doublet are not available in the form of relation (10). These wings are disturbed by the occurrence of the inner satellites and are therefore not convenient for such kind of the analysis. Nevertheless, the corresponding numerical data are tabulated (Movre and Pichler 1980), so that the quantitative analysis can be done if needed.

Comparison of expressions (7) and (8), with relation (9) incorporated, yields $C_3^{\mathrm{eff}}$ in the coupled approximation:

$$(C_3^{\mathrm{eff}})_J = (e^2 f_J / 8\pi^2 m\nu_J) \times \begin{cases} (7+2\sqrt{7})/16 & J=\frac{3}{2} \\ 1 & J=\frac{1}{2} \end{cases} \tag{11}$$

for the D2 and D1 line, respectively.

Also, comparing relations (7) and (8), and taking into account expression (10) one obtains $C_3^{\mathrm{eff}}$ in the intermediate case approximation:

$$(\overline{C_3^{\mathrm{eff}}})_J = (C_3^{\mathrm{eff}})_J[1+\beta_J|\Delta Y|]. \tag{12}$$

As one can see $C_3^{\mathrm{eff}}$ obtained in the intermediate case approximation, in fact, are not constant but depend on $\Delta\nu$. In other words, having chosen to speak of the absorption profile in terms of the effective interaction constants (relation (7)) the deviation of the line profile from the pure Lorentzian form can be expressed through $\Delta\nu$ dependent effective $C_3$ constants.

The equation (7) expressed in terms of the wavelength separation $\Delta\lambda$ from the line centre has the form:

$$k_J(\lambda) = (4\pi^2 e^2 f_J \lambda_J^3 C_3^{\mathrm{eff}} / 3\mathrm{mc}^3)\mathrm{N}^2(\lambda/\Delta\lambda)^2 \tag{13}$$

where $\lambda_J$ is the wavelength of the centre of the particular component of the resonance

**Table 1.** The values of the multiplicative constants appearing in the expression (16) used for the determination of the atom number density $N$.

| | $J$ | $\alpha(10^{19}\,\mathrm{cm}^{-5/2})$ | $\gamma$ |
|---|---|---|---|
| K | 1/2 | 3.801 | 518.508 |
| | 3/2 | 2.169 | 124.542 |
| Rb | 1/2 | 3.645 | 122.044 |
| | 3/2 | 2.136 | 29.736 |
| Cs | 1/2 | 2.915 | 46.223 |
| | 3/2 | 1.768 | 11.601 |

doublet.

The expression for $N$ deduced from relation (13) is:

$$N = \alpha_J (k_J(\lambda))^{1/2} (\Delta\lambda/\lambda) \tag{14}$$

where

$$\alpha_J = (mc^2\sqrt{6}/e^2 f_J \lambda_J^{3/2}) \times \begin{cases} [16/(7+2\sqrt{7})]^{1/2} & J=\frac{3}{2} \\ 1 & J=\frac{1}{2} \end{cases} \tag{15}$$

Taking into account the values for the effective $C_3$ constants obtained in the intermediate case approximation, one obtains the following analogues of expression (14):

$$N = \alpha_J (k_J(\lambda))^{1/2} (\Delta\lambda/\lambda)[1+\gamma_J(\Delta\lambda/\lambda)]^{-1/2} \tag{16}$$

where $\gamma_J = \beta_J[(\lambda_J/\Delta\lambda_{\mathrm{fs}}) + (-1)^{J+1/2}]$.

The values of the multiplicative constants $\alpha_J$ and $\gamma_J$ for K, Rb and Cs are given in table 1. As for the values of the oscillator strengths $f_J$ needed in the evaluation of the $\alpha_J$, we have used the data of Wiese *et al* (1969) for the potassium and the data of Link (1966) for the rubidium and caesium.

The term $\gamma_J(\Delta\lambda/\lambda)$ appearing in the denominator of relation (16) can be regarded as the correction, reflecting the fact that the line wing does not have pure Lorentzian form. The correction is more pronounced in the red wing of the D1 line than in the blue wing of the D2 line for one particular alkali element. The value of the square root in the denominator of relation (16) corresponding to the D1 line is roughly 10% greater than the analogous one for the D2 line taken at the same detuning $\Delta\lambda$ from the line centre. With regard to the one particular component of the resonance doublet the value of the correction is less pronounced at the certain detuning $\Delta\lambda$ in the case of heavier alkali elements due to larger fine-structure splitting $\Delta\lambda_{\mathrm{fs}}$. For instance, in the blue wing of the D2 line the correction is $\approx 3\%$ when the ration $\Delta\lambda/\Delta\lambda_{\mathrm{fs}}$ equals 0.1. Hence, one should expect that, regarding the correction, the wing of the potassium line at $\Delta\lambda \approx 0.3$ nm, will be equivalent to the caesium line wing at $\Delta\lambda \approx 4.3$ nm.

However, it is yet to be proved whether the difference in the predictions of expressions (14) and (16) for the atom number density $N$, can be experimentally observed or not. That will depend on the statistical accuracy of the absorption coefficient data. The extent to which the correction, if observable, can be neglected will coincide with the experimental error bar for the absorption coefficient data.

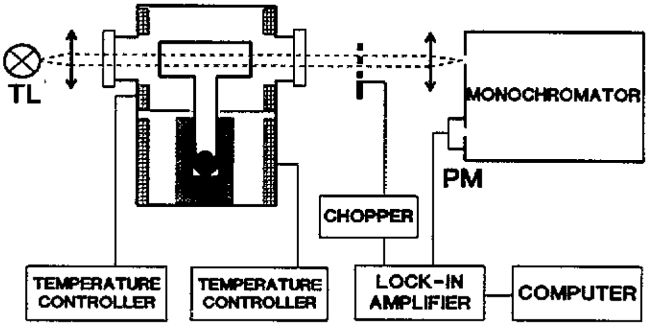

**Figure 1.** Experimental set-up: TL, tungsten lamp; PM, photomultiplier.

## 3. Experiment and results

A schematic diagram of the experimental arrangement is shown in figure 1. The Pyrex glass cell (2.8 cm in diameter, typical length 13 cm) containing high-purity alkali metal (K, Rb or Cs) in its side-arm, was situated in a two-chamber oven with separate heating systems. The temperature in both chambers was controlled by Haake (type 24 and 32) temperature controllers. The feed-back information was supplied by Pt resistance thermometers attached to the walls of the oven. The temperature of the bath ($T_b$) as well as of the cell ($T_c$) was measured by calibrated Fe–constantan thermocouples, glued to the glass walls with high temperature cement (Astroceram) of good thermal conductivity. To minimize temperature gradients along the side-arm of the cell and ensure temperature stability of the bath, it was enclosed in a massive metal block. The temperature stability of the bath and the cell was ±0.1 K and ±0.2 K, respectively. The depositing of alkali atoms on the cell windows was prevented by keeping the temperature of the absorption cell about 30 K higher than that of the bath. The absorption measurements were carried out in the temperature range from 500 K to 600 K. The white-light absorption measurements were done using the tungsten lamp as a continuous light source. The parallel beam was passed through the absorption cell and focused on the 10 μm entrance slit of the monochromator (1 m McPherson model 2051, instrumental profile 0.02 nm). The transmitted light beam was chopped by a chopper (SR 540) operated at 1 kHz frequency. The output of the photomultiplier (RCA S-20) was fed to the lock-in amplifier (SR 510) connected to the computer via an IEEE488 interface. The absorption spectra were collected automatically with an average rate of 75 points/nm. The spectrum of the tungsten lamp was measured at room temperature both prior to and after completing the measurement at elevated temperature, in order to control and account for possible alteration of the intensity of the continuum $I_0$.

The absorption coefficient was determined according to the relation:

$$k(\lambda) = (1/L)\ln(I_0(\lambda)/I(\lambda)) \tag{17}$$

where $L$ is the length of the column of absorbing media and $I$ is the transmitted intensity.

The results of the determination of the atom number density in the potassium vapour are shown in figure 2. Using the experimental data for the absorption coefficient across the blue wing of the potassium D2 line, the set of values for the atom number density in the absorption cell ($N_c$) has been obtained using relation (14) and

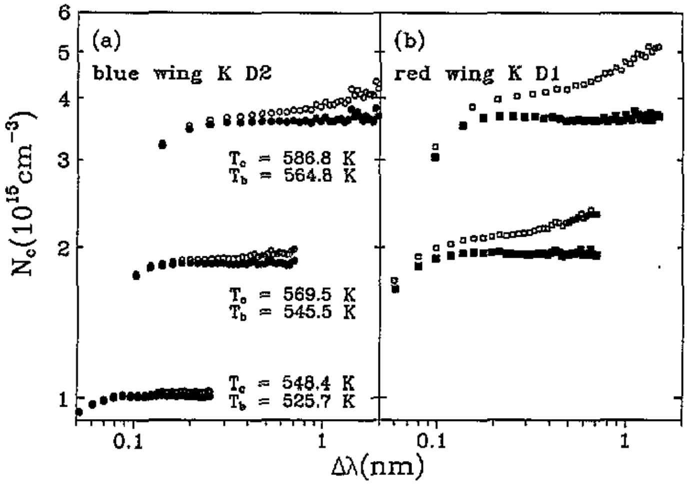

**Figure 2.** The number density of potassium atoms in the absorption cell ($N_c$) determined from the blue wing of the K D2 line (*a*) and the red wing of the K D1 line (*b*) and plotted against wavelength separation $\Delta\lambda$ from the centre of the corresponding line. Results for $N_c$, obtained using equation (14) and (16), are represented with the open and full symbols, respectively. $T_b$ and $T_c$ denote bath and cell temperature respectively.

plotted against the corresponding separation $\Delta\lambda$ from the line centre (figure 2(a)). The results are given for three representative temperatures covering the investigated temperature range. The obtained atom number density exhibits the dependence on the wavelength separation $\Delta\lambda$, rather than a constant value which should be expected if the line profile is purely Lorentzian. However, if one takes into account the correction due to the line wing deviation from the pure Lorentzian form (relation (16)), the $N_c$ against $\Delta\lambda$ plot (figure 2a)) exhibits clearly displayed plateau. This plot

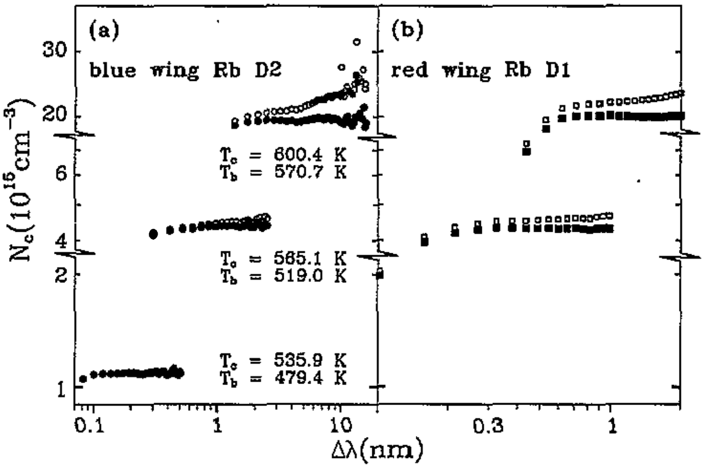

**Figure 3.** The number density of rubidium atoms in the absorption cell ($N_c$) determined from the blue wing of the Rb D2 line (*a*) and the red wing of the Rb D1 line (*b*) and plotted against wavelength separation $\Delta\lambda$ from the centre of the corresponding line. Results for $N_c$, obtained using equation (14) and (16) are represented with the open and full symbols, respectively. $T_b$ and $T_c$ denote bath and cell temperature respectively.

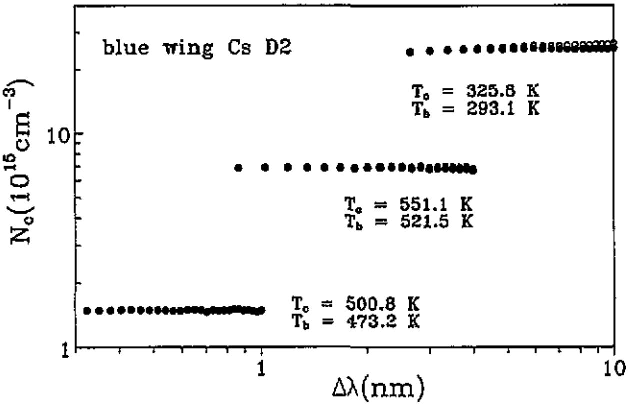

**Figure 4.** The number density of caesium atoms in the absorption cell ($N_c$) determined from the blue wing of the Cs D2 line and plotted against wavelength separation $\Delta\lambda$ from the centre of the line. Results for $N_c$, obtained using equation (14) and (16) are represented with the open and full symbols, respectively. $T_b$ and $T_c$ denote bath and cell temperature respectively.

visualizes very well the statistical dispersion of the obtained data and enables $N_c$ to be simply read off from the figure with the accuracy of ±3%. Figure 2(b) shows the results of the analogous analysis of the red wing of the potassium D1 line. The agreement between the values for $N_c$ obtained from the D1 and D2 components, respectively, is within the declared accuracy. The determination of $N_c$ from the red wing of the D1 line at the lowest temperature shown, was not possible because of the insufficiently pronounced quasi-static wing.

The results of the analogous analysis for the atom number density in the rubidium and caesium vapours are shown in figure 3 and 4, respectively. The explanations given for figure 2 are valid for these figures too. The casesium D1 line was not included in the analysis because the spectral response of the system in the region of the corresponding wavelengths yielded the appreciably lowered signal to noise ratio. Comparison of figures 2, 3 and 4 shows that, when going towards heavier alkali element, the effect of the $\Delta\lambda$ dependence of the effective $C_3$ constant becomes less pronouced at the same $\Delta\lambda$, for both components of the resonance doublet.

The presented results show that the theoretical quasi-static line profile obtained in the coupled approximation (relation (14)) is not sufficient for the description of the entire quasi-static resonance wing of the line. Namely, the $\Delta\lambda$ dependence of $C_3^{\mathrm{eff}}$ has been clearly observed. When the D2 line is concerned, its influence overcomes the experimental dispersion of the data (i.e., relation (14) becomes inadequate for the determiantion of $N_c$) when $\Delta\lambda/\Delta\lambda_{\mathrm{fs}}$; reaches the value of ≈0.06. When the quasistatic resonance wing of the D1 line is just grown enough as to enable the use of the method, the deviation of the $N_c$ against $\Delta\lambda$ plot from the expected plateau is already far outside the error bar of the experimental data. Therefore expression (14) is not at all applicable for the determination of the atom number density from the outer wing of the D1 line. However, using relation (16), which accounts for the $\Delta\lambda$ dependence of $C_3^{\mathrm{eff}}$, one always obtains the plateau-like $N_c$ against $\Delta\lambda$ curve from which the corresponding value of the atom number density can be read off.

The different choice for the oscillator strengths needed for the evaluation of the results does not significantly influence the absolute value of the determined atom number densities. For instance, using more recent values for $f$, which can be found in the paper of Hansen (1984), one would obtain 3% higher results for K, 2.5% lower for Rb and 1% higher for Cs. All differences fall within the declared atom number density error bar.

The shape of the $N_c$ against $\Delta\lambda$ curves can be affected by the continuum level intensity $I_0$. In the evaluation of the presented results we have used the mean value of $I_0$ measurements carried prior to and after the absorption measurements at elevated temperature, the difference between them being less than 0.5%. In the range of the wing used for the determination of $N_c$, $\ln(I_0/I)$ was typically greater than 0.1, so that the change in the slope of $N_c$ against $\Delta\lambda$ curves induced by the alteration of $I_0$ in the course of the aborption measurement falls within the error bar already stated.

All presented $N_c$ against $\Delta\lambda$ curves exhibit the decrease towards the line centre. Such a behaviour is due to the finite width of the instrumental profile. A simple numerical simulation of the convolution of the particular wing profile with the instrumental one yields the observed shape of the curves. The effect was experimentally checked using the monochromator slits ten times wider, which resulted with ten times wider $\Delta\lambda$ range in which the decrease of $N_c$ towards the line centre was obtained.

The vapour pressure $p$ over the liquid alkali in our system is $p = N_b k T_b$, where $N_b$ is the atom number density over the bath and $k$ is the Baltzman constant. In the systems where the mean free path of atoms in the vapour is much smaller than the diameter of the tube connecting two reservoirs at different temperatures (in our experiment the ratio was of the order of $10^{-5}$) the atom number densities and temperatures of the reservoirs are related by $T_c N_c = T_b N_b$ (Huennekens 1982). Therefore we have calculated the vapour pressure according to $p = N_c k T_c$.

The results obtained for the potassium vapour pressure are plotted against inverse bath temperature (index b is omitted for simplicity) in figure 5(*a*). The agreement with the vapour pressure curve of Nesmeyanov (1963) is within the error bar declared for the atom number density data, i.e. ±3%. The agreement with the previously reported experimental data in the same temperature range (Weiler 1929, Honig 1962, Shirinzadeh and Wang 1983, Hultgren *et al* 1973) is also very good.

The vapour pressure data for caesium are also shown in figure 5(a). In the whole investigated temperature range they lie about 10% under the vapour pressure curve of Nesmeyanov (1963), but the same holds for various previous experimental data (Hackspill 1913, Kronter 1913, Fuchtbauer and Berteis 1921) in the same temperature interval. The available experimental results for the caesium vapour pressure at these temperatures (see Nesmeyanov 1963 for the extensive list) show tendency to group around the vapour pressure curve of Taylor and Langmuir (1937) rather than Nesmeyanov (1963) one. The latter one represents weighted statistical average through the data covering temperatures of both solid and liquid caesium. The data obtained by Taylor and Langmuir (1937) can be, according to Nesmeyanov (1963), considered the most reliable ones. The agreement of our results with the plot of Taylor and Langmuir (1937) is within ±3%.

The results for the rubidium vapour pressure are shown in figure 5(*b*). Up to our knowledge there are no experimental results for the Rb vapour pressure in the temperature range that we have investigated. Therefore we have shown the data available in the adjacent temperature regions (Hackspill 1913, Killian 1926, Scott 1924, Gallagher and Lewis 1973) together with the plots of Nesmeyanov (1963) and Ditchburn and Gilmour (1941). Our results are roughly 10% higher than the

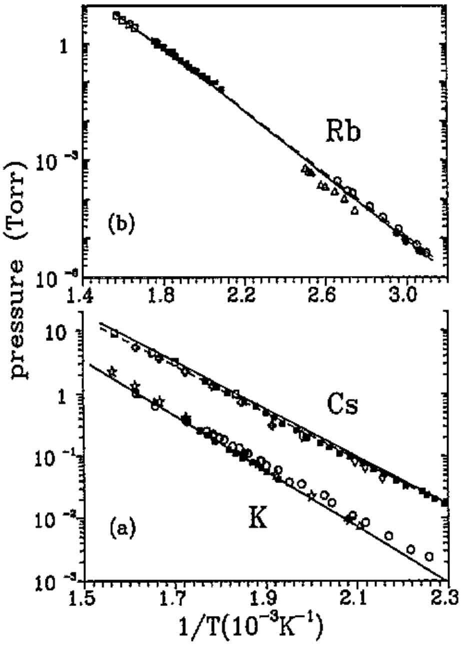

**Figure 5.** (a) The potassium and caesium vapour pressure plotted against $1/T$: ■, present results; full curves, Nesmeyanov (1963); broken curve, Taylor and Langmuir (1937); ○, Weiler (1929); ▲, Honig (1962); ☆, Shirinzadeh and Wang (1983); △, Hultgren *et al* (1973): □, Hackspill (1913); ✣, Kroner (1913); ◇, Fuchtbauer and Berteis (1921). (*b*) The rubidium vapour pressure plotted against $I/T$; ■, present results; full curve, Nesmeyanov (1963); broken curve, Ditchburn and Gilmour (1941); □, Hackspill (1913); ○, Killian (1926); △, Scott (1924); ●, Gallagher and Lewis (1973).

prediction of both plots. Since these fits are based on the assembly of the results which involves quite a wide temperature interval uncovered with the experimental data, such a difference is not a worrying one.

The obtained results for the vapour pressure for all three investigated elements show that the absolute value of the atom number density evaluated according to relation (16) is at most 10% in error with respect to the corresponding Nesmeyanov (1963) vapour pressure curve. The presented results show that the atom number density can be reliably determined from the wing region extending up to $\Delta\lambda_{\max} \approx 0.3\,\Delta\lambda_{\mathrm{fs}}$. From the side closer to the line centre this region is limited by the width of the impact profile. The method is not applicable for $\Delta\lambda \geqslant \Delta\lambda_{\max}$. In this region, the line wing is influenced either by higher order terms in the interaction potential (e.g., van der Waals interaction), by the Boltzman factor or by the overlapping with the molecular bands, so that the model within which the line profile has been obtained is no more adequate.

## 4. Effective $C_6$ constants for rubidium–caesium interaction

The effective $C_6$ constants for Rb*–Cs interaction were determined from the absorption coefficient measurements, which were carried out in the way described in section 3, for both the rubidium and caesium resonance lines.

Since the rubidium resonance lines in the mixture are disturbed by the caesium molecular B–X band, the temperature of the cell was always maintained some 60 K above the temperature of the bath, in order to improve the degree of the dissociation of the Cs molecules. This consequently suppressed the caesium B–X band to an extent sufficient to provide the undisturbed part of the wing 0.3–0.4 nm wide, from which $C_6^{\mathrm{eff}}$ could be reliably determined. The temperature was varied between 520 K and 540 K in the bath, and 580 K and 600 K in the cell. At lower temperatures the wings of the Rb D lines were not sufficiently grown for the purpose of our investigation. At higher temperatures the increased range of the total absorption reduced the available part of the wing on the side closer to the line centre, while grown wings at larger detuning were not quite a benefit since in that region the Cs molecular band could not be satisfactorily suppressed (this concerns especially the blue wing of the Rb D2 line). In the case of Rb–Cs mixture one should expect that both Rb D lines will exhibit blue asymmetry, due to the repulsive van der Waals interaction of the Rb*–Cs pair (Movre and Beuc 1985). The total absorption coefficient in the blue wings of the Rb D lines comprises two contributions. The first one is due to the resonant interaction between Rb atoms and the second one reflects the repulsive long-range interaction of the Rb*–Cs pair. Since the former is proportional to $N_{\mathrm{Rb}}^2$ and the latter depends on $N_{\mathrm{Rb}}N_{\mathrm{Cs}}$ (relations (7) and (6)), it is to expect that in the case when the Cs vapour pressure overrules the total vapour pressure, the blue wings of the Rb D lines will be dominated by Rb*–Cs interaction. The total measured absorption coefficient in the blue wings of the Rb D lines can be expressed as:

$$k_{\exp}(\lambda) = k_3(\lambda) + k_6(\lambda) \tag{18}$$

where $k_3(\lambda)$ and $k_6(\lambda)$ are the contributions arising from the resonance interaction between Rb atoms and Rb*–Cs interaction, respectively. The superimposing of the partial contributions to the total absorption coefficient is justified within the model described in section 2.

The caesium and rubidium atom number densities in the vapour mixture were determined according to relation (16). The atom number density of caesium was determined from the blue wing of the Cs D2 line. The rubidium atom number density was determined from the red wing of the Rb D1 line which is not disturbed by Rb*–Cs interaction and reflects pure resonance interaction between Rb atoms.

The $k_3(\lambda)$ contribution to the total absorption coefficient in the blue wing of the Rb D2 line was calculated according to relation (7), using experimentally determined values for $N_{\mathrm{Rb}}$ and corresponding $C_3^{\mathrm{eff}}$ obtained in the intermediate case approximation (relation (12)).

For the determination of the $k_3(\lambda)$ contribution in the blue wing of the Rb D1 line it was necessary to analyse the listed numerical values for the corresponding reduced absorption coefficient $\mathcal{K}_{1/2}(\nu)$ given in the paper of Movre and Pichler (1980). It was found that for the present need (i.e., in the range of $\Delta Y$ up to 0.02 from the centre of the D1 line), $\mathcal{K}_{1/2}(\nu)$ in the blue wing of the D1 line coincides with the one obtained for the red wing of the same line in the coupled approximation (relation (9)). Therefore the $k_3(\lambda)$ contribution in the blue wing of the Rb D1 line was calculated according to relation (7), using corresponding $C_3^{\mathrm{eff}}$ obtained in the coupled approximation (relation (11)).

The $k_6(\lambda)$ contribution was extracted from the measured $k_{\exp}(\lambda)$ according to relation (18). The results obtained for $k_{\exp}(\lambda)$ and $k_6(\lambda)$ for the blue wings of the Rb D lines are displayed in figures 6(*a*) and 6(*b*), respectively.

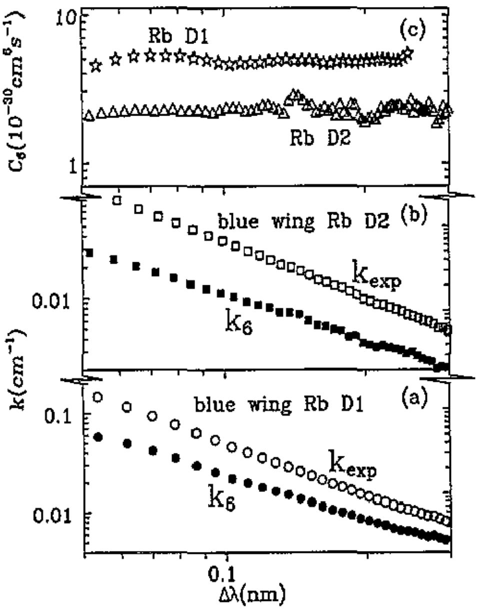

**Figure 6.** (*a*) and (*b*) The absorption coefficient in the blue wings of the Rb D lines broadened by collisions with Cs atoms against the wavelength separation from the centre of the corresponding line; open symbols, the total measured absorption coefficients; full symbols, the part of the absorption coefficient due to Rb*–Cs interaction only. (*a*) $T_b=534.3$ K, $T_c=590.3$ K, $N_{Rb}=7.3\times10^{14}$ cm$^{-3}$, $N_{Cs}=8.1\times10^{15}$ cm$^{-3}$. (*b*) $T_b=519.9$ K, $T_c=573.3$ K, $N_{Rb}=4.3\times10^{14}$ cm$^{-3}$, $N_{Cs}=4.9\times10^{15}$ cm$^{-3}$. (*c*) The effective $C_6$ constants for Rb*-Cs interaction for the Rb D1 (☆) and Rb D2 (△) line plotted against wavelength separation $\Delta\lambda$ from the centre of the corresponding line.

Supposing that Rb*–Cs long-range interaction is pure van der Waals type we have equated $k_6(\lambda)$ with expression (6), which in consequence allowed determination of the effective $C_6$ constants for Rb*–Cs interaction. The results for $C_6^{\rm eff}$, for the both Rb D lines are shown in figure 6(*c*). The obtained values are the following: $C_6^{\rm eff}=(4.9\pm0.3)\times10^{-30}$ cm$^6$ s$^{-1}$ for the Rb D1 line and $C_6^{\rm eff}=(2.4\pm0.3)\times10^{-30}$ cm$^6$ s$^{-1}$ for D2 line. With the use of the calculated values (Movre and Beuc 1985) for $f_{ai}$ and $C_{6i}$, expression (5) yields the following theoretical results for the effective $C_6$ constants: $C_6^{\rm eff}=4.95\times10^{-30}$ cm$^6$ s$^{-1}$ for D1 line and $C_6^{\rm eff}=2.37\times10^{-30}$ cm$^6$ s$^{-1}$ for D2 line. These theoretical calculations of $C_6^{\rm eff}$ had already been experimentally verified in a couple of different systems (K*–Cs (Beuc *et al* 1982), K*–Rb (Beuc *et al* 1984)).

As in the case of the resonance broadening where $\Delta\lambda$ dependence of $C_3^{\rm eff}$ was observed further in the wings of the line (figures 2, 3 and 4), one can expect the similar behaviour for $C_6^{\rm eff}$ (see Beuc *et al* 1982). Due to the reasons mentioned before, the region of the wing studied, was obviously not that far one, in which the contributions to the absorption coefficient arising from such a short internuclear separations for which the interatomic potential would not be of the pure van der Waals type, could be observed.

As can be seen, the agreement between experimental and theoretical values for $C_6^{\rm eff}$ is really good. Since the applied procedure for the determination of $C_6^{\rm eff}$ essentially depends on the reliability of the determined values for $N_{Rb}$ and $N_{Cs}$, we can conclude that the presented method can be successfully used for the determination of the atom number densities in the binary alkali vapour mixture too.

## 5. Conclusion

The presented method for the determination of the atom number densities in the alkali vapours utilizes the proportionality of the absorption coefficient in the quasi-static wings of the alkali first resonance lines with the square of the corresponding atom number density. It has been tested by the white-light absorption measurements in the vapours of K, Rb and Cs. It has been found that the atom number density can be determined with the statistical accuracy of ±3%. The vapour pressures determined from the experimental values for the temperature and the atom number density agree with the corresponding values given by Nesmeyanov (1963) vapour pressure curves within at least 10%. In order to test the validity of the method for the determination of the atom number densities in the alkali binary vapour mixture as well, it has been applied in the measurements of the effective $C_6$ constants for Rb*–Cs interaction. The major error in their experimental values arises from the uncertainty in the determination of the rubidium and caesium atom number densities. The excellent agreement of the experimentally obtained values with the theoretical calculations qualifies the use of the method in the case of alkali binary mixture as well.

The presented method has the advantage of the methods which involve the use of the vapour pressure curves or curve of growth, because it does not require the data on the temperature of the vapour in order to determine the atom number density.

Using the described method one can determine the atom number density in the vapours over alkali binary mixture of an arbitrary composition (one-component alkali vapour can be considered as trivial case) in any situation when the quasi-static resonant wings of a spectral line can be observed. The method is applicable in the region of the wing which extends from the impact region limit up to the wavelength separation from the line centre $\Delta\lambda_{\mathrm{max}} \approx 0.3\,\Delta\lambda_{\mathrm{fs}}$($\Delta\lambda_{\mathrm{fs}}$ is the fine-structure splitting). In that case the atom number density of the particular element in the vapour mixture can be determined from the measurement of the absorption coefficient using the simple formula given by expression (16) and the multiplicative constants listed in table 1, with an overall accuracy of at least 10%.

### *Acknowledgments*

We would like to thank the Ministry of Science (Republic of Croatia) and NIST/NBS (USA) for financial support.

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