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DETERMINATION OF THE a'-PARAMETER OF RESONANCE LINES IN FLAMES

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Abstract—A method is described for determining experimentally the a'-parameter of resonance lines of Na, K, Li, Cs, Ca and Sr by combining the so-called curves of growth† with duplication curves. Theoretical curves of growth and duplication curves for single lines and doublets (with $f_1 = \frac{1}{3}, f_2 = \frac{2}{3}$) were calculated for a series of thirteen a'-values ranging from 0 to 5·0, by means of a binary electronic computer.

The a'-parameter values for the first resonance lines (and doublets) of the mentioned alkali and alkaline-earth metals were determined experimentally in air–CO and air–C_2H_2 flames at atmospheric pressure with temperatures ranging from 2000 to 2500°K. The corrresponding cross-sections for adiabatic collisions were derived and compared with the available literature data. Additional conclusions were drawn as regards the formation of alkali-and alkaline-earth molecules in these flames.

The possible influence of side-effects, such as (hyper)-fine structure, resonance broadening, broadening due to quenching collisions, radiative disequilibrium and the variation of the index of refraction, will be briefly dealt with.

INTRODUCTION

IN THE DETERMINATION of absolute (atomic) metal contents in flames, in the study of line-shape and in the derivation of optical cross-sections for Lorentz broadening the so-called "a'-parameter" occurs as an important quantity. This parameter is defined as the ratio of damping breadth to Doppler breadth at half intensity.[1] The determination of a' in flames (and vapour bulbs) has been the subject of various publications for a long time. Nevertheless, the values of the a'-parameter derived by different authors, even in flames of the same kind and temperature, still differ considerably from each other. In some cases, these differences may be explained by inaccuracies in the method of measuring or failures in correcting for side-effects. In short, there is still a need of renewed attempts to determine a'-values in flames of known temperature and (qualitative and quantitative) flame gas composition.

In this article, a new combinatory method will be described that allows an accurate determination of the a'- parameter and that avoids *absolute* calibrations of background source or detector sensitivity. This method yields, at the same time, the atomic metal content in the flame, which is an important parameter in our studies of metal oxide dissociation and metal ionisation.[2,3,4,5]

† The "curve of growth" is the (usually double-logarithmic) plot of emission intensity against metal concentration. The "duplication curve" is the (usually double-logarithmic) plot of the "duplication factor" versus the metal concentration; the "duplication factor" is defined, apart from a normalization factor, as the relative increase in flame emission when a mirror is placed behind the flame.

BASIC FORMULAS

It is well known that the spectral shape of an isolated resonance line (considered either in emission or in absorption) in an infinitesimal slab of vapour due to Lorentz damping and Doppler broadening (only), is determined according to classical theory by the frequency dependence of the absorption coefficient $k(\nu)$.[1,6,7,8]

$$k(\nu) = k_0 \frac{a'}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)\,\mathrm{d}t}{(t-x)^2+(a')^2} \tag{1}$$

The quantities appearing in Eq. (1) are defined by

$$k_0 = 2\pi^{\frac{3}{2}} \frac{e^2}{m_e c} \cdot \frac{Nf}{b}, \qquad b = \frac{\pi \Delta\nu_D}{(\ln 2)^{\frac{1}{2}}}$$

$$a' = \frac{\Delta\nu_L}{\Delta\nu_D}(\ln 2)^{\frac{1}{2}}, \tag{1a}$$

$$x = \frac{2(\nu-\nu_0)}{\Delta\nu_D}(\ln 2)^{\frac{1}{2}}.$$

Here e = electronic charge, m_e = electronic mass, c = velocity of light *in vacuo*, N = number of ground state atoms per cm^3, f = oscillator strength of the spectral line considered, ν_0 = frequency of the centre of the line, $\Delta\nu_L$ = the Lorentz half-intensity breadth and $\Delta\nu_D$ = the Doppler half-intensity breadth. Both the latter quantities can be expressed by[1,6]

$$\Delta\nu_L = \frac{2}{\pi} Q_L n \left\{ 2\pi k T \left(\frac{1}{m} + \frac{1}{M} \right) \right\}^{\frac{1}{2}} \tag{1b}$$

and

$$\Delta\nu_D = \frac{\nu_0}{c} \left(\frac{8\pi k T}{m} \right)^{\frac{1}{2}} \left(\ln 2 \right)^{\frac{1}{2}}. \tag{1c}$$

Here Q_L = effective cross-section for Lorentz broadening; m and M are the atomic weights of emitting atoms and perturbing particles (flame molecules), respectively; n = number of perturbing particles per cm^3, k = Boltzmann's constant, and T = absolute temperature.

The definitions given above are in close accord with those used by MITCHELL and ZEMANSKY[1]. Following these authors, we also define the "total absorption", A_G, by

$$A_G = 2\pi \int_0^{\infty} \left\{ 1 - \exp\left[-\int_0^l k(\nu)\,\mathrm{d}s \right] \right\} \mathrm{d}\nu$$

$$= 2\pi \frac{\Delta\nu_D}{(\ln 2)^{\frac{1}{2}}} \int_0^{\infty} \left\{ 1 - \exp\left[-\int_0^l k(x)\,\mathrm{d}s \right] \right\} \mathrm{d}x \tag{2}$$

when l = flame depth.

It should be borne in mind that A_G as defined here is also proportional to the total *line emission,* in thermal equilibrium at a uniform temperature.

In our case of a homogeneous flame from which only a small pencil of light with axis perpendicular to and going through the flame axis is focussed on the photodetector, we may write for

$$\int_0^l k(x)\,\mathrm{d}s = k(x)l$$

with l = depth of colored flame.

The double-logarithmic plot of $Y \equiv A_G/2b$ as a function of Nfl/b represents the theoretic "curve of growth". This curve has two asymptotes given by[9]

$$\log Y = \log\left\{\frac{\pi^2 e^2}{m_e c}\frac{Nfl}{b}\right\}, \text{ when } \frac{Nfl}{b} \to 0,$$

and

$$\log Y = \log\left\{\frac{2\pi^2 e^2}{m_e c} \cdot a' \frac{Nfl}{b}\right\}^{\frac{1}{2}}, \text{ when } \frac{Nfl}{b} \to \infty.$$

According to KOHN and co-workers[9,10] the ordinate Y_s of the intersection point of the asymptotes is given by

$$Y_s = 2a'. \tag{3}$$

We shall further make use of the "duplication factor", D, which has been suggested for the first time by HÜBNER (cf. also the lit. (12)) and was introduced again by ALKEMADE for the determination of a'-parameter and atomic content in flames.[2] Accordingly we have

$$D\left(a', \frac{Nfl}{b}\right) = \left[Y\left(2\frac{Nfl}{b}\right) - Y\left(\frac{Nfl}{b}\right)\right] \Big/ \left[Y\left(\frac{Nfl}{b}\right)\right] \tag{4}$$

From Equation (4) it is clear that the function D (as a function of Nfl/b) has again two asymptotes: $D = 1$ for $Nfl/b \to 0$, and $D = (2)^{\frac{1}{2}} - 1$ for $Nfl/b \to \infty$.

The extension of the theory to the case of *fine structure* doublets has already been outlined by ALKEMADE[2]. A doublet curve of growth and a doublet duplication curve with oscillator strength values f_1 and f_2 for the components are easily computed when the curve of growth for the single line is known, and no overlap occurs between the components.† The asymptotes of the doublet curve of growth, $\bar{Y}$, are found from

$$\log \bar{Y} = \log\left\{\frac{\pi^2 e^2}{m_e c}(f_1 + f_2)\frac{Nl}{b}\right\}$$

† These doublet curves are relevant when both components are measured together in emission which usually occurs in flame photometry. It is implicitly assumed in the following calculations that the a'-parameter values of the components are the same. This assumption is reasonably justified with the Na- and K-doublets in flames at atmospheric pressure as considered here.[10]

and

$$\log \bar{Y} = \log\left\{\frac{2\pi^2 e^2}{m_e c}[(f_1)^{\frac{1}{2}} + (f_2)^{\frac{1}{2}}]^2 \frac{Nl}{b} a'\right\}^{\frac{1}{2}}$$

for $Nl/b \to 0$ and $Nl/b \to \infty$, respectively. The ordinate of the intersection point is now given by

$$\bar{Y}_s = \frac{[(f_1)^{\frac{1}{2}} + (f_2)^{\frac{1}{2}}]^2}{f_1 + f_2} \cdot 2a'$$

In the special case of a doublet with $f_1 = \frac{1}{3}$ and $f_2 = \frac{2}{3}$ the value of $\bar{Y}_s$ is

$$\bar{Y}_s = 3{\cdot}89a'. \tag{5}$$

The doublet duplication curve $\bar{D}(a', Nl/b)$ has obviously the same asymptotes as the singlet duplication curve and is easily evaluated from the singlet curve of growth once f_1 and f_2 are known.

Next we have to take into account the effect of *hyperfine structure* due to nuclear spin and of *isotopic* shift of the spectral lines on the curve of growth and the duplication curves. Several authors have derived expressions for the total absorption, A_G, in the case of a line with hyperfine structure.[12,13,14] In these expressions, partially overlapping lines with equal half-width and the same a'-value are considered. The degree of overlapping is determined by a parameter, γ, according to[12,13,14]: $\gamma = (\Delta\nu)_{hfs}/\delta$. Here $(\Delta\nu)_{hfs}$ is the frequency distance of the hfs-components and δ is the spectral line-width at half-intensity. It is usually assumed that collisional broadening dominates the effect of Doppler broadening. BEHMENBURG[15] has calculated the effect of hyperfine structure on the ordinate value of the intersection point of the asymptotes in the theoretic curve of growth. This author used formulas reported in the lit.(13) and found for the Na D_2-line that $Y_s = 2{\cdot}35a'$ (cf. Equation (3)) under his flame conditions (i.e. $T \approx 2500°K$, $\delta = \Delta\nu_L = 3{\cdot}2 \times 10^9$ sec.$^{-1}$). For Sr Equation (3) applies since hyperfine structure and isotopic shift are absent here.

We checked the possible influence of hyperfine structure and isotopic shift on the theoretical curve of growth, the theoretical duplication curve and on the value of Y_s, c.q. $\bar{Y}_s$, for the first resonance lines of Li (6708 Å); Na (5890/96 Å); K (7665/99 Å) and Cs (8521 Å). For the first resonance lines of Ca and Sr no hyperfine structure and no isotopic shift has been reported in the literature.[15,16,17]

In our flames, the line-shape is due to both Doppler broadening and Lorentz damping, i. e. the corresponding half-intensity breadths are about equal. The wings of the line are mainly determined by Lorentz damping, however. Therefore, we considered in the evaluation of the overlap parameter, γ, the two extreme cases $\delta = \Delta\nu_D + \Delta\nu_L$ and $\delta = \Delta\nu_L$, respectively. It should be noted that the required Lorentz half-breadth follows from the Doppler half-breadth via the a'-parameter (cf. Equation (1a)) which again depends on the assumed value of γ. So we have to apply a method of iteration in order to find the influence of hyperfine structure and isotopic shift on the determination of a' from our experiments. We found in this way, using data from the refs. (16) and (17) for the ordinate value Y_s, i.e. $\bar{Y}_s(T \approx 2000°K)$, the following extreme limits:†

† The limits given refer to $\delta = \Delta\nu_D + \Delta\nu_L$ and $\delta = \Delta\nu_L$, respectively. The lines of Li, Na, K and Cs all show hyperfine structure due to nuclear spin; for K and Li also the isotopic shift has been taken into account.

$$Y_s(\mathrm{Li})/a' = 2{\cdot}10 \text{ to } 2{\cdot}16 \quad \Delta\nu_D = 5{\cdot}5 \times 10^9 \mathrm{sec}^{-1} \text{ and } \Delta\nu_L = 1{\cdot}9 \times 10^9 \mathrm{sec}^{-1}$$
$$Y_s(\mathrm{Na})/a' = 4{\cdot}10 \text{ to } 4{\cdot}56 \quad \Delta\nu_D = 3{\cdot}4 \times 10^9 \mathrm{sec}^{-1} \text{ and } \Delta\nu_L = 1{\cdot}85 \times 10^9 \mathrm{sec}^{-1}$$
$$Y_s(\mathrm{K})/a' = 3{\cdot}92 \text{ to } 4{\cdot}00 \quad \Delta\nu_D = 2{\cdot}0 \times 10^9 \mathrm{sec}^{-1} \text{ and } \Delta\nu_L = 1{\cdot}9 \times 10^9 \mathrm{sec}^{-1}$$
$$Y_s(\mathrm{Cs})/a' = 2{\cdot}60 \text{ to } 2{\cdot}70 \quad \Delta\nu_D = 1{\cdot}0 \times 10^9 \mathrm{sec}^{-1} \text{ and } \Delta\nu_L = 2{\cdot}4 \times 10^9 \mathrm{sec}^{-1}$$

We may remark that the equations introduced above for *fine-stucture* doublets are just a limiting case of line splitting in absence of overlap, which is fully justified in our case.

In our investigations, we need also the direct relation between the cross-section for adiabatic collisions, Q_L, and a'-parameter. One easily sees from the Equations (1a), (1b) and (1c) that

$$Q_L = a'(\pi)^{\frac{1}{2}}\left\{\frac{c}{\nu_0} \cdot n\left(1+\frac{m}{M}\right)^{\frac{1}{2}}\right\}^{-1}. \tag{6}$$

If we account for the presence of the different flame constituents (such as N_2, CO_2, CO and H_2O) by considering their specific $Q_L^{(i)}$-values, masses, M_i, and concentrations n_i, we obtain instead of Equation (6) the result

$$a' = \pi^{-\frac{1}{2}}\frac{c}{\nu_0}\sum_i n_i \cdot Q_L^{(i)}\left(1+\frac{m}{M_i}\right)^{\frac{1}{2}} \tag{7}$$

The dependence of Q_L (and thus of a') on temperature, on kind of metal, on flame gas composition, etc. can be found theoretically according to the Weisskopf–Lindholm theory of impact broadening.[3,10,18,19] If the interaction energy between radiating and perturbing particles is assumed to be proportional to $-Cr^{-6}$ (here C is a positive constant and r represents the inter-particle distance) it follows for the cross-section[3,10]

$$Q_L \propto T^{-1/5} \tag{8}$$

and for the a'-parameter (cf. Equation (7))

$$a' \propto T^{-6/5} \tag{9}$$

if the relative flame gas composition does not change.

From the Lindholm theory also absolute values of Q_L can be derived (see later). These theoretic values, however, cannot directly be compared with the experimental values. For this theory considers only adiabatic collisions as was assumed in the earlier Lorentz theory, and not *quenching* collisions. For comparison with this theory we should correct the experimental Q_L values found for the effect of quenching collisions on the spectral line-width. When quenching collisions are also taken into account one may formally write instead of Equation (1a)[20]

$$\Delta\nu_L = a'\Delta\nu_D/(\ln 2)^{\frac{1}{2}} - A/2\pi p \tag{10}$$

Here A is the transition probability involved, and p is the yield-factor of resonance fluorescence,[20] which compares the quenching rate with A.

The $\Delta\nu_L$-values corrected for the effect of quenching collisions can be calculated from Equation (10) when p is known. The value of p follows from the (known) flame gas composition, flame temperature and the specific cross-sections for quenching by the main constituents of the flame.

Finally, the influence of *anomalous dispersion* on the formulas used should be considered too. When absorption or self-absorption of metal vapour in flames is considered the index of refraction, n, is usually assumed to be unity. In fact this holds exactly only at line center, whereas n increases at either side of line center with increasing wavelength, because of anomalous dispersion. The deviation of n from unity reaches a maximum on either side of line center at a distance of about half the line half-breadth. Classical dispersion theory[20a] shows that this maximum deviation is in good approximation given by:

$$\frac{Nfe^2}{4\pi m_e \nu_0 \Delta\nu_L}$$

in the case of a single Lorentz-broadened line. Assuming that the wavelength of line center is less than 1μ, that f is at most unity and $\Delta\nu_L/\nu_0 = 5\cdot 10^{-6}$ (which is a reasonable estimate for metal lines in flames), one calculates that the maximum deviation of n from unity is less than 1 per cent, if N is less than $2\cdot 3 \times 10^{14}$ cm^{-3}. As is shown in Table 2, the highest atomic metal concentration in the flame, when a molar solution is sprayed, amounts to about 10^{14} cm^{-3}. So the neglect of anomalous dispersion in our case seems to be justified. (Doppler broadening is not considered to be essential in the above estimate.)

CALCULATION OF THEORETICAL CURVE OF GROWTH AND DUPLICATION CURVE

The calculation of the singlet curve of growth is laborious. However, it can be shown that[21]

$$\frac{a'}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)\,\mathrm{d}t}{(t-x)^2+(a')^2} = \mathrm{Re}\left[\exp(-z^2)\left\{1+\frac{2i}{(\pi)^{\frac{1}{2}}}\int_0^z \exp(t^2)\,\mathrm{d}t\right\}\right] \tag{11}$$

with $z = x + i\,a'$, and $a' > 0$. The complex function between brackets in the right-hand side of Equation (11) has recently been tabulated by FADDEYEVA and TERENTEV[21] for $0 \leqslant x \leqslant 5$ and $0 \leqslant a' \leqslant 5$. Outside this interval approximating formulas have been given. Making use of these results we have calculated the curve of growth for a single line for different values of a'-parameter as a function of Nfl/b (see Table 1). The corresponding duplication curves and the doublet curves of growth and duplication curves are readily evaluated from the values of the singlet curves of growth according to their definitions in the foregoing Section.

The calculations of the curves of growth were carried out with the aid of an electronic binary computer. Use was made of tabulated values and approximating formulas given by FADDEYEVA and TERENTEV[21]. The errors made in calculating the integral occurring in Equation (2) are due to two causes

(1) Substitution of a finite integration limit instead of an infinite one,
(2) The error made in the application of the Simpson rule which reads

$$\int_0^{2\delta x} f(x)\,\mathrm{d}x = \tfrac{1}{3}\{f(0)+4f(1)+f(2)\}\delta x.$$

TABLE 1. NUMERICAL VALUES OF THE TOTAL ABSORPTION $A_G/2b$, CALCULATED FOR SINGLE LINES AT DIFFERENT a'-VALUES

	$A_G/2b$												
Nfl/b (sec. cm^{-2})	$a' = 0$	$a' = 0{\cdot}10$	$a' = 0{\cdot}20$	$a' = 0{\cdot}30$	$a' = 0{\cdot}40$	$a' = 0{\cdot}50$	$a' = 0{\cdot}60$	$a' = 0{\cdot}70$	$a' = 1{\cdot}00$	$a' = 2{\cdot}00$	$a' = 3{\cdot}00$	$a' = 4{\cdot}00$	$a' = 5{\cdot}00$
2	0·1562	0·1575	0·1585	0·1594	0·1601	0·1607	0·1612	0·1616	0·1625	0·1638	0·1642	0·1644	0·1645
4	0·2933	0·2984	0·3025	0·3059	0·3087	0·3110	0·3130	0·3146	0·3183	0·3241	0·3263	0·3274	0·3280
6	0·4141	0·4248	0·4336	0·4408	0·4468	0·4517	0·4560	0·4595	0·4676	0·4805	0·4858	0·4885	0·4901
8	0·5207	0·5385	0·5531	0·5652	0·5752	0·5837	0·5908	0·5969	0·6108	0·6333	0·6426	0·6475	0·6505
12	0·6990	0·7339	0·7627	0·7867	0·8069	0·8240	0·8386	0·8511	0·8800	0·9281	0·9486	0·9597	0·9665
25	1·069	1·168	1·252	1·324	1·386	1·440	1·486	1·527	1·625	1·798	1·878	1·923	1·951
35	1·233	1·380	1·506	1·615	1·711	1·794	1·868	1·934	2·093	2·389	2·532	2·614	2·667
50	1·388	1·599	1·782	1·942	2·084	2·210	2·322	2·424	2·675	3·173	3·427	3·578	3·679
70	1·516	1·802	2·049	2·267	2·461	2·635	2·793	2·937	3·301	4·068	4·487	4·748	4·924
100	1·637	2·020	2·351	2·638	2·896	3·130	3·343	3·539	4·046	5·179	5·853	6·295	6·604
200	1·845	2·501	3·045	3·515	3·931	4·306	4·650	4·967	5·802	7·832	9·226	10·25	11·04
400	2·029	3·139	4·010	4·740	5·375	5·944	6·462	6·939	8·198	11·34	13·66	15·52	17·06
800	2·196	4·061	5·414	6·509	7·449	8·282	9·039	9·736	11·57	16·19	19·65	22·54	25·04
1600	2·350	5·435	7·467	9·066	10·41	11·62	12·71	13·71	16·34	22·99	28·04	32·27	35·97
3200	2·495	7·474	10·43	12·73	14·67	16·38	17·93	19·35	23·09	32·57	39·80	45·88	51·23
6400	2·631	10·44	14·67	17·94	20·69	23·12	25·31	27·33	32·64	46·09	56·38	—	—
9600	2·708	12·73	17·95	21·94	25·32	28·30	30·99	33·45	39·96	—	—	—	—

Both errors are very difficult to estimate analytically. Therefore a method often used in numerical analysis was applied. The length of the finite integration interval chosen is determined by the computer itself: if the relative contribution of the next interval to which the Simpson rule can be applied, appeared to be less than $0{\cdot}5 \times 10^{-5}$ the integration was broken off (it should be noted that the integration interval thus defined is different for different values of Nfl/b and of a'). As a check we found that, when the integration was continued until the relative contribution of the next interval was less than $0{\cdot}5 \times 10^{-6}$ or $0{\cdot}5 \times 10^{-7}$, the variation in the final result was indeed less than 0·1 per cent.

The second error mentioned can be estimated by comparing the results of integration with a chosen value of δx and $\frac{1}{2}\delta x$, respectively. When $\delta x = 0{\cdot}5$ the deviation from the results obtained with $\delta x = 0{\cdot}25$ was again less than 0·1 per cent. In Table 1 values calculated with $\delta x = 0{\cdot}25$ are given. Moreover, for very high or very low values of Nfl/b the correctness of the calculated curve of growth can be checked by calculating from it the corresponding values of the duplication curve. It is known that the latter curve has a horizontal low- and high-density asymptote with D-value equal to 1·0 and $[(2)^{\frac{1}{2}}-1]$, respectively (see the above). Errors in both extremities of the calculated curve of growth would show up in the value of these asymptotes. The agreement found was again satisfactory (within 0·1 per cent.).

Values of Y (singlet line) in the range $Nfl/b = 2, \ldots, 9600$ sec cm^{-2} for a'-parameter ranging from 0·0 to 5·0 are presented in Table 1.

It should be remarked that our data concerning singlet curves of growth with a'-parameter equal to 0·20; 0·30; 0·40; 0·60; 0·70; 3·0 and 4·0 have not yet been published in the literature. Our calculated data may supplement and check the available data in the literature as regards theoretic curves of growth and duplication curves[3].

There is good agreement (within the error limit) with corresponding results used and/or calculated by VAN DER HELD[22]; PENNER and KAVANAGH[23]; ALKEMADE[2]; and HOFMANN and KOHN[10], as far as they go.

Some theoretical curves of growth for singlet lines with different a'-parameter are given in Fig. 1.

The (corresponding) singlet duplication curves are shown in Fig. 2.

THE EXPERIMENTAL DETERMINATION OF a'-PARAMETER AND ATOMIC METAL CONTENT

For an extensive discussion of current methods the reader is referred to the literature.[2,3,6,9,10] The determination of the a'-parameter of a resonance line in a flame can be performed by a shift of the *experimental* curve of growth, c.q. the duplication curve, parallel to the axes of plotting, so that it superposes completely one of the theoretic curves of growth, c.q. duplication curves.[2,3] (The *experimental* curve of growth and experimental duplication curve have already been defined in terms of metal concentration in the solution that is sprayed into the flame.) This superposition yields immediately the a'-value and the actual atomic flame content for a given metal concentration in the sprayed solution. However, as can be seen from Figs. 1 and 2, the differences in shape between the curves for different a'-values are not very pronounced (especially for $a' > 1$) so that an accurate determination of the a'-parameter is hardly possible in this way.[3]

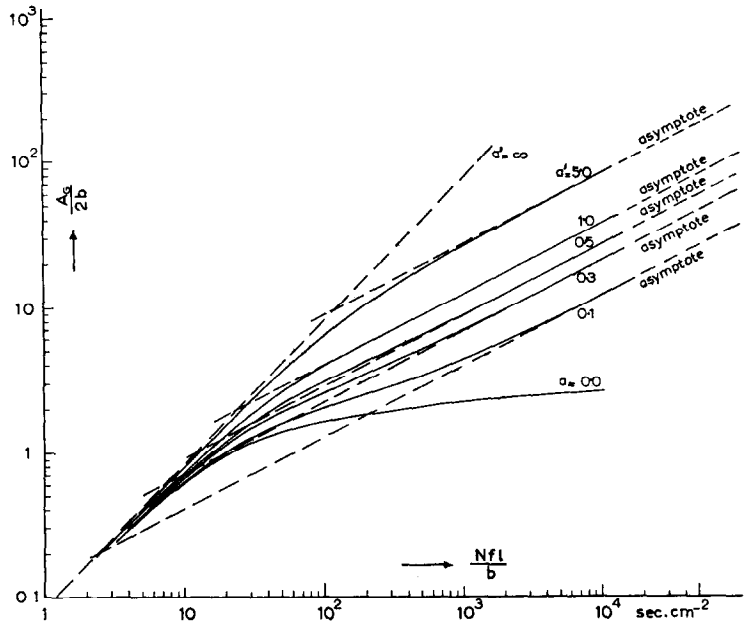

FIG. 1. Some theoretic curves of growth for a single spectral line with a'-parameter values ranging from 0·0 to 5·0.

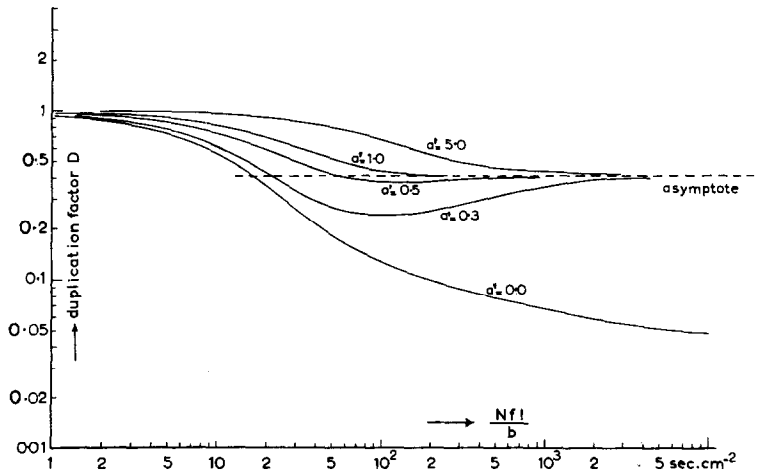

FIG. 2. Some theoretic duplication curves for a single spectral line with a'-parameter values ranging from 0·0 to 5·0.

It should be realized that difficulties may arise in the accurate experimental determination of the curve of growth which may cover a concentration range of $1:10^4$ and an intensity range of $1:10^3$. Ionisation, self-reversal and deviations in the sprayer performance at high concentration may cause deviations from the expected low- and high-density

asymptotes, respectively.[24] The difficulties caused by ionization and deviations in sprayer performance, but *not* by self-reversal, are eliminated when the duplication curve[2,3] is used. However, here the required correction for reflection losses, etc. may cause errors.[2,3]

In order to circumvent the necessity of absolute calibration of the properties of the monochromator and of a background light source, as occurs in the method proposed by HINNOV[9,10], and in order to reduce the ambiguities of the duplication curve method (especially for $a' > 1$) followed by ALKEMADE[2], we developed a method which is essentially a combination of both methods.

With our method both the curve of growth and the corresponding duplication curve for (singlet or doublet) lines of the metals investigated have to be measured. The duplication factor measured has to be corrected for reflection losses, etc.[2] In practice *both* asymptotes of the experimental D-curve are measured and it is first checked that the ratio of their ordinate values has the expected value $1[/(2)^{\frac{1}{2}} - 1]$. Then the logarithmic plot of D is shifted along the ordinate axis until both asymptotes attain their theoretically expected position. In this way the experimental D-values are easily normalized. Further, one should have at hand a series of theoretic curves of growth and corresponding duplication curves for singlets or doublets at different a'-values. Self-reversal and ionization should not occur in the experimental curves, the spray performance must be strictly independent of solution concentration and the photometer should be strictly proportional in the range intensity $1:10^3$.

Corrections for ionization and deviations of spray performance can easily be made in the case of alkaline-earth metals by plotting the atomic emission as a function of the (corresponding) molecular band emission, instead of solution concentration. It should be kept in mind that the atomic concentration and the oxide concentration are lowered by the same factor by both effects if oxygen is present in relatively large concentration (as was the case in our flames).[3,5,24] When we measured Na, K, Li and Cs, the flame temperature was chosen so low, that ionization did not play a part (see below). With Na-measurements at higher temperatures an excess of Cs was simultaneously sprayed into the flame as electron donor element in order to suppress the ionization of Na.[3,24]

From the *experimental* curve of growth for a certain element the ordinate, y_s, of the intersection point of the asymptotes is read in relative emission measure. For a particular solution concentration, c_i, chosen in the environment of the experimental intersection point, the relative emission value, y_i, and the normalized duplication factor, D_i, were determined. One now considers for that particular solution concentration the ratio y_i/y_s and chooses as a trial a rather arbitrary value of a'-parameter. From the theoretic curve of growth with this a'-value we now derive the value of Nfl/b such, that the corresponding ordinate Y_i is in proportion to Y_s (being the ordinate value of the intersection point in the theoretic curve of growth) as y_i to y_s. It should be borne in mind that Y_s directly follows from a' through Equation (3), so that one need not actually draw the asymptotes of the theoretic curve.

The above procedure was repeated for a set of different a'-parameters, for which theoretic curves of growth are available. In this way one gets a plot of calculated Nfl/b-values versus *assumed* a'-parameter values for this particular solution concentration, c_i.

We also derive from the one-parametric family of theoretic duplication curves for each tentatively assumed value of a' the value of Nfl/b, which corresponds to the D_i-value experimentally found for the above solution concentration, c_i. In this way another curve

of calculated Nfl/b-values against assumed a'-parameter is obtained. One now immediately finds from the intersection of both curves the *true* a'-parameter and the *true* value of Nfl/b corresponding to the solution concentration c_1 sprayed (see Fig. 5). The atomic flame content N follows directly from the known values of f, l and b (see the above).

This procedure may be repeated for different solution concentrations chosen on either side of the concentration at the intersection point. Since the a'-parameter should be essentially independent of the solution concentration considered, a measure for the accuracy of the a'- (and N-) values derived in this way can be obtained (see Fig. 5). The N-values thus found should be proportional to the concentrations in the corresponding metal solutions sprayed if certain conditions are fulfilled (see the above). This again yields a check of the consistency of the method applied.

With doublets (with $f_1 = \frac{1}{3}$ and $f_2 = \frac{2}{3}$) essentially the same procedure can be followed, if we replace y_1, y_s, D_1, etc. by the corresponding values $\bar{y}_1$, $\bar{y}_s$, $\bar{D}_1$, etc., for doublets and if we apply Equation (5) instead of (3). The results obtained are shown in Table 2.

For the application of our "combinatory method" only *relative* intensity measurements are needed. As opposed to the method of HINNOV[9] we need a set of *full* theoretic curves of growth and D-curves with a'-parameter varying from e.g. 0·1 to 5·0. Just as with the method of Hinnov an accurate experimental determination of the mutual position of the asymptotes of the curves of growth is required. Our method requires, moreover, the measurement of normalized D-factors.

Our combinatory method has the following advantages apart from those already mentioned:

(1) the shape of the experimental D-curve, in particular the depth of the minimum, if present, gives a rough information about the order of magnitude of the a'-value involved (see also Fig. 2).

(2) One may use the additional information given by the experimental duplication curve for checking the constancy of spray performance. With high solution concentrations such that D fairly well approaches its final horizontal asymptote, the experimental curve of growth should approximate a $(N)^{\frac{1}{2}}$–relationship. A deviation from this relationship may indicate that the spray performance depends on the solution concentration. It should be kept in mind that the spray performance does *not* affect the D-values measured.[3] In a similar way the duplication curve may help us to decide which points in the experimental curve of growth can be used to fix the high-density asymptote.

Our method is more suitable than the duplication method, in particular when $a' > 1$, in which case the shape of the D-curve does not depend critically on the a'-value (i.e. a minimum does not occur, see Fig. 2).

It was verified that the experimental a'-value found from our combinatory method, when disregarding any hyperfine structure splitting (due to nuclear spin) or isotopic shift, is incorrect by only 2–3 per cent in the worst case of complete splitting of the components. The application of the *other* methods (i.e. comparison of curves of growth or duplication curves separately, or Hinnov's method) yields strongly deviating a'-values when hyperfine structures are neglected. It can be estimated (see the above) that with the latter methods the a'-values of Li, Na, K and Cs are found to be too high by 5–8, 5–17, 1–3 and 30–35 per cent respectively. The error limits correspond to the two extreme cases of expected spectral overlap, respectively. For Ca and Sr the a'-values do not deviate, since hyperfine structure and isotopy are absent here (see the above).

The determination of N, however, is affected by hyperfine structure (and isotopic shift) to the same extent with our combinatory method as with the other methods. When hyperfine structure and isotopy are neglected, the *same* relative errors as mentioned above in the determination of the a'-parameter by the other methods are to be expected here.

In our flame where the observed lines are partly overlapping, the error in a' with our method can thus be fully disregarded. The N-values, however, are too high by some per cents (see the above).

EXPERIMENTAL CONDITIONS

Curves of growth and corresponding D-curves were measured with Li, Na, K, Cs, Ca and Sr in CO–air, CO–air with additional N_2, CO–enriched air and C_2H_2–air flames, with temperatures of about 2200, 2000, 2460 and 2470°K, respectively. The flames were laminar, premixed cylindrical flames surrounded by a burning colourless flame mantle of the same gas composition. The metals were introduced as chlorides dissolved in distilled water into the central flame column by means of a liquid sprayer.[2,24] The salt concentrations ranged from 5 to 80,000 ppm (1 ppm = 1 mg/l). The burner used was of the Mékèr type.

A small pencil of flame light with axis perpendicular to the flame axis and going through the centre of the coloured flame was focused on the photomultiplier window. The thickness of the coloured flame part amounted to 13–16 mm depending on the flame gas composition. For the measuring of duplication curves a combination of convex lens and plane mirror was placed behind the flame with optical axis perpendicular to and going through the flame axis.[2,3]

The flame light was selected by a relatively simple single-pass monochromator with mirror optics and the intensity was measured by means of a photometer involving synchronous a.c. detection.[2,3]

The measurements were carried out at distances ranging from 1·0 to 7·3 cm above the blue cones. The flame temperatures at these heights were determined with the visual sodium D-line reversal method.

Several demands have to be imposed on the measuring device and conditions of measuring. The most important of these are (i) elimination of ionization effects (ii) constancy of spray performance and linearity of measuring device.

(i) The influence of ionization on the curve of growth and D-curve can be avoided by choosing the flame temperature sufficiently low, as is the case in the cool CO-flame with temperature of about 2000°K, so that practically no ionization occurs in the concentration range considered of the elements under investigation (see the above). Ionization can also be suppressed at higher flame temperature by adding through a second sprayer in parallel an excess amount of an electron donor element, i.e. Cs.[3,10,24] This method was applied to Na. In the case of alkaline-earth metals the measurements were corrected for ionization by making use of the fact that ionization affects the concentration of metal oxide molecules in the flame to the same relative extent as the atomic concentration. So the intensity of the oxide bands (which is not disturbed by self-absorption) is a good measure for the true atomic content.[3,5,24]

(ii) Since the metal solution concentrations ranged from about 10 to 10^5 ppm, the detection device should be linear for a wide range of emission intensities. Photomultipliers were used, the linearity of which, was carefully checked.[3] The same holds for the amplifier and the synchronous rectifier used. If necessary, the radiation falling on the photocathode could be weakened in calibrated steps by placing grey filters (of known transmission factor) into the light-path.

We may mention that according to a variant proposed by *van Willigen* at our laboratory duplication factors can be determined accurately by placing a light-chopper *between* flame and duplicating mirror, so that the reflected flame light is measured directly. By placing next the chopper between flame and photometer (without mirror) the *direct* flame emission is measured as a function of solution concentration. After division and normalization (see the above) the D-curve is found.

EXPERIMENTAL RESULTS

Sodium was measured in all four flames. Ca and Sr were studied in the CO-flames with maximum temperatures of 2218 and 2458°K. Li, K and Cs were observed merely in the coolest CO-flame.

Some of the measured curves of growth and corresponding D-curves are presented in Figs. 3 and 4.

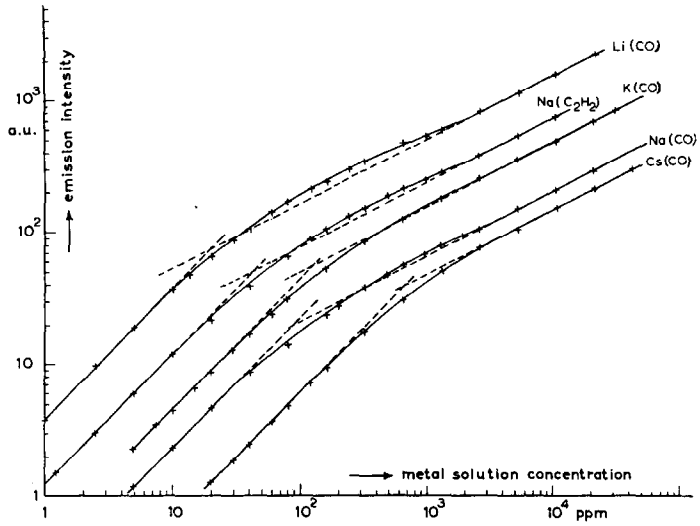

FIG. 3. Experimental curves of growth are shown for Na (at 5890/96Å), Li (at 6708Å), K (at 7665/99Å) and Cs (at 8521Å) in the coolest CO–air flame (T = 1964°K) and for Na (at 5890/96Å) also in the air–C_2H_2 flame (T = 2389°K). The initial and final asymptotes are indicated by dotted lines with slope equal to tan α = 1 and $\frac{1}{2}$, respectively.

From the experimental curves of growth and duplication curves we derived the a'-value for three different concentrations of metal under investigation as described earlier (see Fig. 5).

The relevant heights in the different flames, the corresponding temperatures, the derived a'-parameter values, number of metal atoms (in cm^{-3}) corresponding to molar solution concentration and Q_L-values are listed in Table 2.

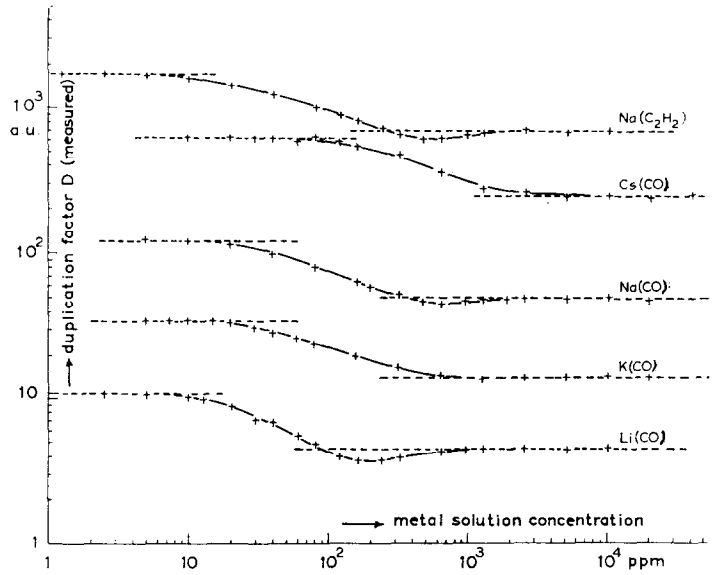

FIG. 4. Experimental duplication curves are shown for Na, Li, K and Cs under the same conditions as mentioned in Fig. 4. The duplication factors are expressed in arbitrary units and the initial and final asymptotes are indicated by dotted horizontal lines.

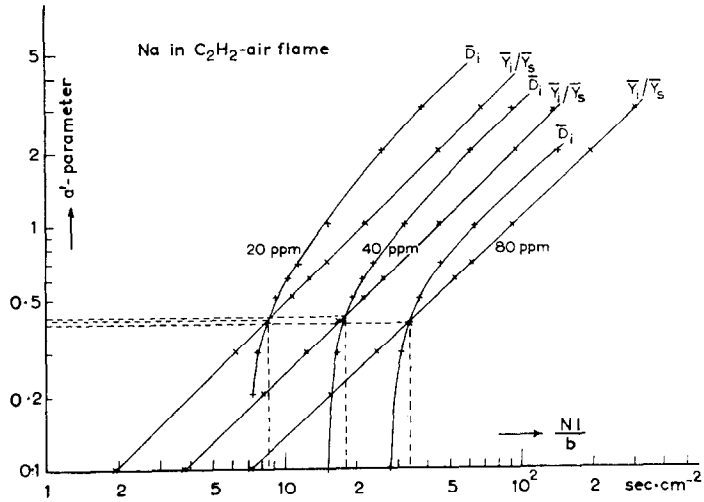

FIG. 5. This figure illustrates the graphical interpolation procedure of deriving the a'-parameter and the absolute atomic metal content N in the flame by combining the curve of growth with the duplication curve. As indicated in the figure the a'-parameter and the atomic content were derived for Na (at 5890/96Å) in the C_2H_2–air flame (T = 2389°K) (see text).

The accidental errors listed in this Table have been estimated from the scattering of the values obtained when the measurements were repeated with different solution concentrations. The extent of this scattering corresponds to what is expected on account of the experimental sources of error involved. The accidental error in the atomic metal

TABLE 2. VALUES OF a'-PARAMETER, CROSS-SECTION FOR LORENTZ BROADENING (Q_L) AND ABSOLUTE ATOMIC CONTENT AS FOUND IN THIS WORK FROM SELF-ABSORPTION

Metal	Wave length of line(s) (Å)	Oscillator-strength used	Flame	Temperature (°K)	Height above cones (cm)	Flame thick-ness (cm)	a'	Q_L (Å^2)	$N \times 10^{-13}$ for molar solution (cm^{-3})
Li	6708	0·75					0·29 ± 0·02	18	5·1
Na	5890/96	($\frac{1}{3}$ + $\frac{2}{3}$)	CO–O_2–N_2	1964	1·0	1·40	0·45 ± 0·03	27	5·2
K	7665/99	($\frac{1}{3}$ + $\frac{2}{3}$)					0·78 ± 0·04	31	5·3
Cs	8521	$\frac{2}{3}$					2·0 ± 0·1	47	4·8
Na	5890/96	($\frac{1}{3}$ + $\frac{2}{3}$)					0·38 ± 0·02	26	11·7
Ca	4227	1·6	CO–O_2–N_2	2200	4·3	1·45	0·46 ± 0·03	37	0·85
Sr	4608	1·8					0·96 ± 0·05	53	0·51
Na	5890/96	($\frac{1}{3}$ + $\frac{2}{3}$)					0·33 ± 0·02	25	12·6
Ca	4227	1·6	CO–O_2–N_2	2450	4·3	1·55	0·41 ± 0·03	37	1·1
Sr	4608	1·8					0·85 ± 0·04	53	0·60
Na	5890/96	($\frac{1}{3}$ + $\frac{2}{3}$)	C_2H_2–O_2–N_2	2389	7·3	1·35	0·41 ± 0·02	30	10·1

content amounts, on the average, to 10 per cent. The calculation of the Q_L-values was based on the assumption that in first approximation the flames consist merely of nitrogen molecules. The f-values were taken from the present literature and should be considered as weighted values.[3] Any error in f will result in an equal error in N of the opposite sign. For the alkali metals only small differences in reported f-values are found.[3] It should be remarked that the uncertainty in f is of the order of the experimental error in our determination of Nfl/b.

The factor of discrepancy of about 2 between the Na-content in the coolest CO-flame and that in the other CO-flame (see Table 2) for equal solution concentrations, is to be explained by the use of solution pick-up capillaries with different inner diameter (causing a different spray yield and different rate of liquid intake.[24]

DISCUSSION AND CONCLUSIONS

(i) *Dependence of experimental Q_L-value on flame gas composition*

The Q_L-values listed in Table 2 were calculated from a'-values under assumption that the flame gases consist only of N_2 molecules. This assumption is reasonable since the partial pressure of nitrogen exceeds 60 per cent for all flames investigated, and no very great differences between $Q_L^{(i)}$-values for N_2, and the other major flame constituents are expected.

In next order approximation we may account for the presence of the main flame constituents (such as N_2, CO_2, CO, H_2O, H_2) according to Equation (7), in which the mass and specific cross-section $Q_L^{(i)}$ of each particle occurs. It can easily be shown that the differences in mass in itself do not lead to errors larger than 10 per cent, when Equation (6) for a pure N_2-atmosphere is used instead of Equation (7).

The discrepancy of about 20 per cent found between the Q_L-values of Na in the CO-flames and in the air–C_2H_2 flame (converted to equal temperatures), respectively, can thus not be explained by mass effects only (see Table 2). Most probably this difference has to be reduced to a noticeable difference in $Q_L^{(i)}$-values for the relevant flame molecules.

BEHMENBURG[15] has determined a'-values for Na and Sr (at 5890 and 4608 Å respectively) in C_2H_2-flames with N_2, He, Ar and CO_2 as main diluent gases. From his results we have tried to derive the specific Q_L-values for Na of the major flame constituents: N_2 and CO_2, using also data from earlier experiments with Na and Hg resonance lines in vapour bulb with different foreign gases.[1] We found that Q_L (Na, N_2) and Q_L(Na, CO_2) amounted to about 53 and 68 Å^2, respectively. Specific $Q_L^{(i)}$-values of CO, H_2O and H_2 could not be derived from the data in the Lit.(15) and these species may still contribute to the a'-value measured.

Assuming the *ratio* of the above values of $Q_L^{(i)}$ for N_2 and CO_2 in collision with Na to be correct, and considering the actual N_2- and CO_2-concentrations in our flames, we derive $Q_L = 29{\cdot}6$ Å^2 and $= 24$ Å^2 for N_2 from the a'-values found in our C_2H_2- and CO-flames of comparable temperature, respectively. The discrepancy between these values might suggest that the (unknown) $Q_L^{(i)}$-values of other flame molecules (such as CO, H_2O† and H_2) should be taken into account too.

† BEHMENBURG[15] has proved that Stark broadening caused by interaction with H_2O dipoles can be fully neglected. Its contribution to the line-width amounts to less than 1 per cent under flame conditions.

(ii) *Dependence of experimental a'-values on temperature*

a'- and Q_L-values are available for Na in three CO-flames of different temperature (see Table 2). Considering the experimental error in the a'-value we may conclude that a' for Na varies with temperature as $T^{-\alpha}$ with $1{\cdot}1 < \alpha < 1{\cdot}3$. This outcome suggests a small increase of Q_L for Na with decreasing temperature, as expected from theory. Regarding the discrepancy noted sub(i) this conclusion should be considered with some restriction, however. The dependence of Q_L for Ca and Sr on temperature, as derived from Table 2, is less conclusive.

(iii) *Comparison of our results with the literature data*

Considering our results obtained in the coolest CO-flame the Q_L-values for the alkali metals are seen to be increasing in the sequence Li–Na–K–Cs, corresponding to an increase in atomic radius. The same result has been found by HOFMANN and KOHN[10] (see Table 3). It can be predicted theoretically from the similarity of the alkali spectra and from the increase of corresponding wavelengths in the order Na–K–Rb–Cs, that the Q_L-values should likewise exhibit a moderate increase in that order.[6] For Li in this respect no data are available.

After accounting for the differences in temperature (according to Equation (8)) a rather large discrepancy appears to remain between our values and those of some other authors. The agreement of our values with those of VAN DER HELD[22] and ALKEMADE[2] is for Na, however, very satisfactory. It should be kept in mind, however, that the results obtained in vapour bulbs (see Table 3) can hardly be converted to temperatures comparable with those of our flames. The Q_L-values found by SOBOLEV *et al.*[28] from interferometric measurements of spectral line profiles might be somewhat too high, if the limited resolving power of the apparatus used is not properly accounted for.[2]

We want to consider in more detail the results of HOFMANN, KOHN[10] and of BEHMENBURG *et al.*[15] in comparison with ours. Their measurements have recently been performed under flame conditions similar to ours.

When the Q_L-values of Li, Na, etc. as found by HOFMANN[10], BEHMENBURG[15] and us, were corrected for the effect of different temperature and for the differences in flame gas composition as far as possible (see the above), a discrepancy between our Q_L-values and those of Hofmann and Behmenburg of about a factor 2 appeared to remain. This holds for the alkali metals and to a less extent also for Ca, but not for Sr for which metal the agreement is satisfactory (see Table 3). An explanation for these discrepancies cannot be given (cf. also the discrepancy between our values for Na in CO– and C_2H_2-flames at the same temperature).

HOFMANN and KOHN[10] have computed theoretic Q_L-values of Na (at 5896 Å) and K (at 7699 Å) at 2500°K in N_2-milieu from the Lindholm theory (see the above) and have found 54 and 65 Å^2, respectively. Our experimental results show a rather great discrepancy with respect to these theoretic values, though the predicted increase in Q_L in the sequence of Na to K is in our case clearly confirmed.

As stated above, these theoretic values as such cannot directly be compared with the experimental values: the latter should be corrected for the effect of quenching collisions. Using Equation (10) we corrected the experimental $\Delta\nu_L$-values by computing the p-value for Na (at 5890/96 Å) and K (at 7665/99 Å) for the air–C_2H_2 flame of Hofmann as well as for some of our CO- and C_2H_2-flames, from the known flame gas composition, using

TABLE 3. CROSS-SECTIONS FOR LORENTZ BROADENING (Å²) FROM THE LITERATURE COMPARED WITH OUR RESULTS†

Author(s)	Milieu	Temperature (°K)	Li	Na	K	Cs	Ca	Sr	Ba	Reference
MINKOWSKY	vapour bulb	<1000	—	59	—	—	—	—	—	(25)‡
SCHÜTZ	vapour bulb	<1000	—	69	—	—	—	—	—	(26)‡
V.D. HELD	air-city gas flame	2080	—	33	—	—	—	—	—	(22)
MARGENAU AND WATSON	vapour bulb	<1000	—	42	—	—	—	—	—	(27)‡
SOBOLEV AND MAZHERICHER	air–C_2H_2 flame	~2500	53	85	—	—	132	—	—	(28)
JAMES AND SUGDEN	H_2–O_2–N_2 flame	2200–2400	(22)	(68)	(125)	(164)	—	—	—	(29)§
ALKEMADE	air–C_3H_8 flame	2180	—	34	—	—	—	—	—	(2)
HOFMANN AND KOHN	air–C_2H_2 flame	2500	46·5	59·3	59	87	56·6	66·0	37·3	(10)
BEHMENBURG	air–C_2H_2 flame	2500	—	53·5	—	—	—	65·0	—	(15)‖
This study	air–CO flame	1964	18	27	31	47	—	—	—	—
This study	air–CO flame	2450	—	25	—	—	37	53	—	—
This study	air–C_2H_2 flame	2389	—	30	—	—	—	—	—	—

† The Q_L values are calculated for a homogeneous N_2-milieu.

‡ Absorption measurements of pressure broadening of the Na *D*-lines in vapour bulbs at low temperature and in pure N_2-milieu.

§ These values are derived under the assumption that a'(Na) equals 1·0. These absolute values are thus not mutually independent and only their mutual ratios should be compared.

‖ In the case of the 5890Å Na-line corrections were made for hyperfine structure.

the specific cross-sections for quenching by N_2, CO, CO_2, H_2O, O_2 and H_2 which HOOYMAYERS at our laboratory has found in flames.[20] The corrected Q_L^*-values refer again to N_2-atmosphere. BEHMENBURG[15] has already corrected his experimental Q_L-values of Na for the effect of quenching collisions. The corrected Q_L^*-values thus found are collected in Table 4.

TABLE 4. VALUES OF CROSS-SECTION FOR LORENTZ BROADENING Q_L^* IN N_2–ENVIRONMENT, CORRECTED FOR QUENCHING COLLISIONS

Flame	Temperature (°K)	Q_L^* (Na) (Å^2)	Q_L^* (K) (Å^2)	Reference
air–C_2H_2	2500	53	56	(10)
air–C_2H_2	2500	47	—	(15)
air–C_2H_2	2400	25	—	This work
air–CO	2450	18	—	This work
air–CO	2000	20	28	This work

From the above data it is seen that the agreement between the corrected experimental Q_L^*-value for Na as derived by Hofmann and Kohn and the theoretic value turns out to become better. The corrected experimental value of Behmenburg and Kohn is also in good agreement with the theoretically predicted value (see the above). For K the agreement is less satisfactory. On the other hand, the discrepancy between our experimental values for Na and K and that of Hofmann and Kohn, and Behmenburg and Kohn becomes larger after correction for quenching effects.

It may be noted that the position of the final asymptote of the curve of growth determines critically the a'-values derived according to the method applied by the latter authors.[10,15] Especially for a'-values < 1 the final asymptote of the experimental curve of growth might easily be drawn in too high (vertical) position, if the investigated concentration range does not extend to sufficiently high concentrations. Remarkably, the discrepancies between a'-values found according to HINNOV's[9,10,15] method and ours are, indeed, larger for $a' < 1$ than for higher a'-values (compare the a'-values of Na, K, Li, (Ca) on the one hand, and those of Sr and Cs on the other).

We may remark that the corrections for quenching effects are only applicable in the case of Na and K. For the other metals investigated the relevant cross-sections for quenching are not yet known.

BEHMENBURG[15] reported also a'-values of the Na- and Sr first resonance lines measured in C_2H_2–Ar–O_2 flames at 2500°K. A special difficulty arises in flames where the diluent gas consists for the major part of noble gas atoms that have a low quenching and excitation efficiency. In such flames the apparent excitation temperature is generally lower than the vibrational temperature of the flame molecules which latter practically equals the flame temperature.[3,20] This deviation is caused by a lack of radiative equilibrium, which affects notably the occupation of the excited metal state when the rate of excitation by collisions with flame particles is comparatively low. This deviation is more pronounced

at lower metal concentrations in the flame at which the radiation density at line-centre is virtually negligible; at high metal concentrations, however, the excitation temperature (measured according to the line-reversal method) is practically equal to the vibrational temperature.

Consequently the line intensity at low metal concentrations in the flame is relatively more depressed by this disequilibrium effect than at high concentrations. This effect leads to a downward, parallel shift of the initial asymptote in the experimental curve of growth. This again results into a too *high* value of a'-parameter as determined when HINNOV's method is used.[15]

We calculated this deficiency in excitation temperature for Behmenburg's argon flame, using the specific quenching cross-sections measured by HOOYMAYERS[20], and found that the maximum deficiency amounted to only 16°K. This value does not lead to a measurable effect in the Na-curve of growth, however.

Finally we may remark that *resonance* broadening due to interaction between the emitting atoms in the flame may have some influence on the line-width. BEHMENBURG[15] has made plausible that this contribution can be disregarded even at the highest salt solutions sprayed into the flame. Additional evidence can be derived from the outcome of our experiments: the experimental curves of growth fit very well one and the same theoretic curve (with *fixed* a'-parameter value) and are not distorted as would be the case if resonance broadening plays a part, and a' would increase with increasing N-value. When resonance broadening dominates, the final asymptote should read then (see the above) $Y \propto N$ (instead of $Y \propto N^{\frac{1}{2}}$) in contrast with our experimental curves of growth (see Fig. 3).

(iv) As regards the *formation* of *alkali* and *alkaline-earth molecules* some interesting conclusions may be drawn from a comparison of the results in Table 3. It should be noted that the depression of the atomic metal content in the flame by ionization was eliminated either by adding excess amounts of an electron donor element, or by choosing sufficiently low flame temperature, or by correcting the atomic fraction by means of the (simultaneously measured) band emission (see the above). So any difference in atomic flame content for solutions of the same molarity must be ascribed to differences in molecular formation.

The atomic content of Li, Na, K and Cs in the coolest CO-flame appear, indeed, to be equal (within the limits of experimental error) for solutions with the same molarity. Under assumption that Na does not form molecules in this flame[3,29] this result proves that hydroxide formation in this flame is negligible for the alkali metals considered.

For Ca and Sr it is clear that the atomic metal content is only a small fraction of the total metal content present in the flame. This result indicates that in the case of alkaline-earth metals a considerable molecular formation occurs in the flame. A further discussion of this subject in connection with the determination of dissociation energies of alkaline-earth oxides is given elsewhere.[3,4,5]

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