

NOTE

QUENCHING OF EXCITED STRONTIUM ATOMS MEASURED IN FLAMES

TJ. HOLLANDER, P. L. LIJNSE, L. P. L. FRANKEN, B. J. JANSEN and P. J. TH. ZEEGERS

Fysisch Laboratorium, Rijks Universiteit, Utrecht, Holland

(Received 16 September 1971)

Abstract—The yield factor of resonance fluorescence, Y , of the Sr resonance line ($^1P_1 \rightarrow ^1S_0$ transition) $4607,33 \text{ \AA}$ was measured in hydrogen flames at atmospheric pressure as a function of gas composition (air temperature). From these data, the specific quenching cross sections, σ_{qu} , for Ar, H_2O , H_2 , N_2 , and O_2 were derived; under the assumption that $\sigma_{qu}(\text{Ar}) < 1 \text{ \AA}^2$, the following values were found: $\sigma_{qu}(\text{N}_2) = (21 \pm 2) \text{ \AA}^2$, $\sigma_{qu}(\text{H}_2\text{O}) = (67 \pm 6) \text{ \AA}^2$; $\sigma_{qu}(\text{H}_2) = (22 \pm 5) \text{ \AA}^2$ and $\sigma_{qu}(\text{O}_2) = (400 \pm 80) \text{ \AA}^2$.

Remarkably the σ_{qu} -value for H_2O appeared to be much higher than for N_2 and H_2 in contrast to the result with alkali atoms reported in the literature. Also the high cross section for O_2 should be noted.

INTRODUCTION

OUR INTEREST in determining yield factors for resonance fluorescence stems from our work on line broadening processes in flames.^(1–4) We are particularly interested in the production of two different flames, one of which is a very poor quenching milieu, whereas the second one is a very effective one.⁽⁵⁾

By critical comparison of line profiles measured in these highly differing flames we hope to solve a number of problems concerning the role and relative importance of elastic and inelastic collisions on the line-broadening processes.^(5,6)

In order to make the difference in Y -value ($Y =$ yield factor of resonance fluorescence, see definition in equation 1) as large as possible, we started out with flames with Ar as main diluent gas, as opposed to flames with N_2 as main diluent. Argon is known to be a poor quencher,^(7–9) whereas diatomic molecules like N_2 are much more effective. Stoichiometric hydrogen-oxygen flames were taken, since a further demand for our line profile measurements is that the flames studied should have as few flame-gas components as possible because the interpretation of the collision-broadening processes is more complicated the more different flame-gas molecules and atoms are present. This demand is met in stoichiometric flames.^(7,10,11)

The choice of hydrogen flames was based on the speculation that, since H_2O has been proven to be a poor quencher for the alkali resonance lines,^(7,10,11) it may be suitable for producing flames with relatively high Y -values for the Sr resonance line. This line is suitable for line broadening studies as discussed in detail in Refs. (4) and (5).

Before discussing the cross section values found for Sr, it should be pointed out that no data on Sr and on Ca quenching are available. Only the cross section of Ar for the green B resonance line has been measured in a shock tube.⁽¹²⁾

EXPERIMENTAL

The apparatus used has been described in Ref. (10). The flames were of the usual type, i.e. laminar, premixed, shielded, cylindrical flames produced on a water-cooled Meker burner top and surrounded by a sheath of flowing Ar. In order to get optimal signal-to-noise ratio for the fluorescence signals, the detection frequency of the synchronous rectifier was chosen in the region from 1000 to 4000 Hz (cf. Ref. 13). A Sr high-intensity lamp (Perkin, Elmer, Intensitron lamp, 25 mA max) was used as irradiating source.

The values of the yield factor, Y , for the Sr line ($^1P_1 \rightarrow ^1S_0$ transition) at 4607,33 Å were obtained by measuring the ratio of fluorescence power, E_r , of the line emerging from the flame through a solid angle, ω , to the absorbed primary radiation power, E_a , as a function of alkaline-earth concentration (see Fig. 1).

In order to check the absence of unknown systematical errors of instrumental origin, Y -values in some flames were also measured with a somewhat different setup⁽¹⁴⁾ (labeled No. 2) described in detail in Ref. (15). A medium Hilger monochromator is used here, whereas in setup No. 1 an interference filter is used for wavelength selection. The detection frequency was again 1000 Hz (see above). After accounting for the fact that the flame volume emitting the fluorescent emission is only a fraction of the irradiated volume (cf. Ref. 16), the Y -values were found.

The temperature of the flames investigated (near-stoichiometric H_2/O_2 flames with Ar and N_2 as main diluent gases) ranged from about 1700 to about 2400 K. The relevant characteristics are presented in Table 1.

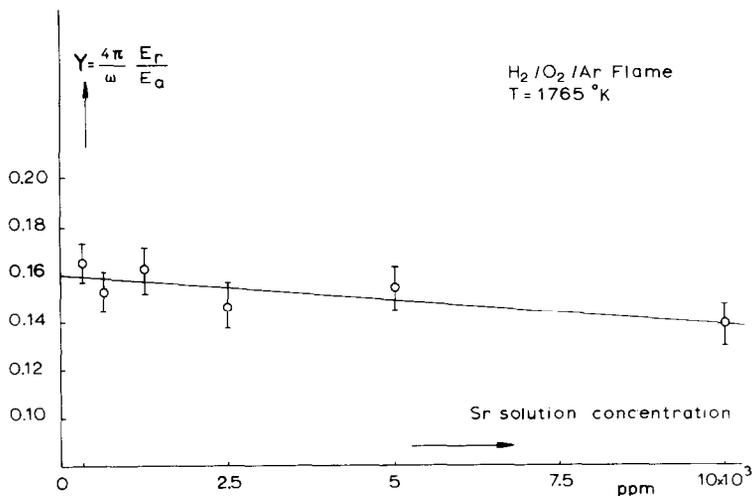


FIG. 1. The yield factor of resonance fluorescence, Y , is given as a function of metal solution concentration for the Sr resonance line in the hydrogen-oxygen-argon flame No. 1. The linear dependence of $4\pi E_r/\omega E_a$ on alkaline-earth concentration found in the low metal content range can be explained by self-absorption.⁽¹⁰⁾ The value of Y obtained by linear extrapolation to zero concentration is the actual Y -value sought and this value is listed in Table 2. This Y -plot was measured with setup No. 1.

TABLE 1. CHARACTERISTICS OF THE FLAMES STUDIED

Flame, No.	Fuel, oxidant and diluent gas	Temperature (K)	Composition of burnt gases* (atm.)				
			N ₂	Ar	H ₂ O	H ₂	O ₂
1	H ₂ /O ₂ /Ar	1765	—	0.818	0.182	—	—
2	H ₂ /O ₂ /Ar	1865	—	0.580	0.312	0.108	—
3	H ₂ /O ₂ /Ar	1950	—	0.705	0.247	0.048	—
4	H ₂ /O ₂ /Ar	1965	—	0.723	0.253	0.024	—
5	H ₂ /O ₂ /Ar	2000	—	0.739	0.256	0.003	0.001
6	H ₂ /O ₂ /N ₂	2000	0.662	—	0.338	—	—
7	H ₂ /O ₂ /N ₂	2000	0.614	—	0.327	0.059	—
8	H ₂ /O ₂ /Ar	2365	—	0.490	0.450	—	0.060

* In this calculation of the equilibrium composition the amount of water sprayed is accounted for.

RESULTS AND DISCUSSION

The Y -values for the Sr line in the various flames were found from the corresponding Y versus solution concentration plots as usual.⁽¹⁰⁾ One of the plots is presented in Fig. 1.

The Y -values derived from the measurements in flames 1–8 are presented in Table 2.

From the Y -values found in the set of flames with different composition and temperature, the specific quenching cross sections, $\sigma_{qu}^{(j)}$ for each of the major flame species were calculated by solving the set of equations⁽¹⁰⁾

$$Y = A(A + k)^{-1}, \quad (1)$$

where A = transition probability [for the Sr line: $A = (1.57 \pm 0.05) \times 10^8 \text{ sec}^{-1}$];⁽¹⁷⁾ k = collisional rate constant, given by

$$k = \sum_{j=1}^m p_j \left(\frac{8}{\pi \mu_j k T} \right)^{1/2} \sigma_{qu}^{(j)}; \quad (2)$$

p_j = partial pressure of the j th flame gas component (in atm), μ_j = reduced mass, k = Boltzmann's constant.

In the derivation of $\sigma_{qu}^{(j)}$ -values, it was assumed that these values do not show a marked temperature dependence in the range considered. This point has not yet been settled, however [cf. Refs. (7), (10), (18) and (19) for more detailed discussion].

It should be noted that the σ_{qu} -values were first derived from Y -values found in flames 2–7 (which flames have about the same temperature) and that these values appeared to agree with those derived from flames 1 and 8 within the experimental scatter. This observation corroborates our assumption about the temperature dependence of $\sigma_{qu}^{(j)}$.

The following specific $\sigma_{qu}^{(j)}$ -values were derived from our experimental Y -values in the various flames, under the supposition that $\sigma_{qu}(\text{Ar}) < 1 \text{ \AA}^2$:

$$\sigma_{qu}(\text{N}_2) = (21 \pm 2) \text{ \AA}^2; \quad \sigma_{qu}(\text{H}_2\text{O}) = (67 \pm 6) \text{ \AA}^2; \quad \sigma_{qu}(\text{H}_2) = (22 \pm 5) \text{ \AA}^2$$

and

$$\sigma_{qu}(\text{O}_2) = (400 \pm 80) \text{ \AA}^2.$$

TABLE 2. *Y*-VALUES MEASURED IN THE VARIOUS FLAMES (CORRECTED FOR SELF-ABSORPTION)

Flame, No.	<i>Y</i> -value, measured with setup No. 1	<i>Y</i> -value, measured with setup No. 2
1	0.16 ± 0.01	—
2	0.084 ± 0.005	—
3	0.09 ± 0.01	0.092 ± 0.015*
4	0.10 ± 0.01	0.11 ± 0.02*
5	0.13 ± 0.01	0.14 ± 0.02*
6	0.070 ± 0.005	—
7	0.07 ± 0.01	—
8	0.050 ± 0.005	—

* Errors mainly due to inaccuracies in flame dimensional factors.

We conclude that these cross sections found for N₂ and H₂ are comparable with the corresponding values found for the alkali metals (cf. Ref. 11). The values for H₂O and, especially, for O₂ are unexpectedly high when compared to alkali results. An explanation for this behavior cannot be given.

It might be interesting to draw some tentative conclusions as to the importance of quenching collisions for the Sr line profile in flames No. 1 and No. 8, showing the largest difference in measured *Y*-value (see Table 2). If we assume that natural and quenching broadening are additive^(1,4,10) and, further, that the relative contributions of elastic and inelastic broadening can be derived from their respective half-intensity widths, we find for flame No. 1 that $Y = 0.16 \rightarrow \Delta\nu_Q = [A(1 - Y)/2\pi Y] = 1.3 \times 10^8 \text{ sec}^{-1}$; from line-broadening experiments,⁽⁴⁾ the total collisional half-width $\Delta\nu_c^* \simeq 3.9 \times 10^9 \text{ sec}^{-1}$ (in the same flame). Here $\Delta\nu_c^*$ is the "combined" half-width for both inelastic and elastic collisions ($\Delta\nu_Q$, $\Delta\nu_e$, respectively). For flame No. 8, $Y = 0.05 \rightarrow \Delta\nu_Q = 4.8 \times 10^8 \text{ sec}^{-1}$; here⁽⁴⁾ we find for the total half-width $\Delta\nu_c^* \simeq 3.4 \times 10^9 \text{ sec}^{-1}$.

From these approximate calculations, it appears that flame No. 1 provides for the Sr line studied a milieu with practically negligible influence of quenching on the line profile. In flame No. 8, the relative contribution of quenching is roughly 15 per cent. In order to produce a flame in which the contribution of quenching collisions is at least equal to that of the elastic ones, we must search for more efficient quenching species as diluent gas to replace (partially) N₂. The production of flames with less N₂ and relatively higher H₂O concentrations, i.e. H₂/N₂O flames, is in progress. Furthermore, we will try out flames with H₂O and/or CO₂ and CO as main diluent gases, i.e. CO/H₂/O₂ and CO/N₂O/CO₂ flames, since it is expected that CO₂ is an efficient quencher.^(7,10)

Although O₂ appears to be highly efficient in quenching the Sr line, it is not feasible to produce flames with O₂ as main quenching molecule. First of all, it is practically impossible to burn flames with such a high partial pressure of molecular oxygen that the contribution of oxygen to the quenching is greater than that of water molecules. Furthermore, the content of atomic Sr in this flame would be too low (due to molecule formation) to allow line-profile measurements.^(20,21) This objection against the use of O₂ as main diluent holds also for the use of undiluted O₂-rich hydrogen-oxygen flames.

Acknowledgement—The authors wish to thank Prof. Dr. C. Th. J. ALKEMADE for valuable discussions and his interest.

REFERENCES

1. C. H. P. VAN TRIGT, T.J. HOLLANDER and C. TH. J. ALKEMADE, *JQSRT* **5**, 813 (1965).
2. T.J. HOLLANDER and H. P. BROIDA, *JQSRT* **7**, 965 (1967).
3. T.J. HOLLANDER and H. P. BROIDA, *Combust. Flame* **13**, 63 (1969).
4. T.J. HOLLANDER, B. J. JANSEN, J. J. PLAAT and C. TH. J. ALKEMADE, *JQSRT* **10**, 1301 (1970).
5. B. J. JANSEN, T.J. HOLLANDER and C. TH. J. ALKEMADE, to be published.
6. W. BEHMENBURG and H. KOHN, *JQSRT* **4**, 163 (1964); *ibid* p. 177; W. BEHMENBURG, *Z. Astrophys.* **69**, 368 (1968).
7. D. R. JENKINS, *Proc. R. Soc. (Lond.)* **A293**, 493 (1966); *ibid* **306**, 413 (1968); cf. also *Proc. R. Soc. (Lond.)* **A303**, 453 (1968).
8. G. COPLY, B. P. KIHLE and H. KRAUSE, *Phys. Rev.* **163**, 34 (1967).
9. J. N. DODD, E. ENEMARK and A. GALLAGHER, *J. chem. Phys.* **50**, 4838 (1969).
10. H. P. HOOYMAYERS and C. TH. J. ALKEMADE, *JQSRT* **6**, 501, 847 (1966).
11. C. TH. J. ALKEMADE and P. J. TH. ZEEGERS, Excitation and De-excitation processes in flames, in *Spectrochemical methods of analysis: Quantitative analysis of atoms and molecules*, (Ed. Dr. J. D. WINEFORDNER). Wiley, N.Y., (1971).
12. F. NAUMANN and K. W. MICHEL, 8th Int. Shock Tube Symp., London (1971).
13. C. TH. J. ALKEMADE, H. P. HOOYMAYERS, P. L. LIJNSE and TH. J. M. VIERBERGEN, in press.
14. H. P. HOOYMAYERS, *Spectrochim. Acta* **23B**, 267 (1968).
15. P. J. TH. ZEEGERS and J. D. WINEFORDNER, *Spectrochim. Acta* **26B**, 161 (1971).
16. S. J. PEARCE, L. DE GALAN and J. D. WINEFORDNER, *Spectrochim. Acta* **23B**, 793 (1968).
17. V. LETFERS, *Opt. Spectrosc.* **21**, 371 (1966); N. P. PENKIN, *JQSRT* **4**, 41 (1964).
18. H. P. HOOYMAYERS and P. L. LIJNSE, *JQSRT* **9**, 995 (1969).
19. P. L. LIJNSE and R. J. ELSENAAR, to be published.
20. P. J. KALFF, Ph.D. Thesis, Utrecht 1971.
21. J. VAN DER HURK, private communication.