# QUENCHING OF EXCITED RUBIDIUM ($5^2P$) ATOMS IN FLAMES

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**Abstract**—An alternating current photoelectric device (compare the work of BOERS,[1] HOOYMAYERS *et al.*[2-4] and HOOYMAYERS[5]) has been used for determining the yield factor $p$ of resonance fluorescence for the infrared rubidium doublet (7800/7947 Å). From the $p$-values measured in five different hydrogen flames at about 2000°K and 1 atm pressure, the specific effective quenching cross-sections[2,5] $S$ of the excited Rb atoms in collision with some molecules could be derived.

The cross section values for these molecules were found to be

$$S_{H_2} = 3.6(\pm 0.4)\,\text{Å}^2, \quad S_{N_2} = 25(\pm 1.5)\,\text{Å}^2, \quad S_{O_2} = 83(\pm 5)\,\text{Å}^2 \quad \text{and} \quad S_{H_2O} = 4.0(\pm 0.8)\,\text{Å}^2$$

respectively. In the derivation of the $S$-values it was assumed that $S_{Ar}$ is negligibly small.

The $S$-values for the diatomic molecules may be considered as valid for a temperature of about 1900°K, whole $S_{H_2O}$ is valid at about 2100°K. The possibility of a resonance effect between the excited Rb-level and the molecular vibrational levels is discussed.

## INTRODUCTION

THE DETERMINATION of the yield factor $p$ of resonance fluorescence has been shown to be a useful method for providing information on the non-adiabatic interaction between excited metal atoms and quenching molecules in flames. Here the yield factor $p$ is defined according to the Voigt–Volmer formula as the fractional probability that an excited atom loses its energy by radiation of a photon. For a survey of the literature and of the major problems involved in the study of (de-)excitation mechanisms we refer to our previous papers in this field.[1-7]

## THE EXPERIMENTAL SET-UP

An alternating-current photoelectric device as described in Ref. 3 has been used for determining the yield factor $p$ for the infrared Rb-doublet (7800/7947 Å). The Rb-atoms, brought into the flame as a spray of RbCl solution, were irradiated with a periodically chopped (50 c/sec) light-beam from a Philips rubidium lamp. The ground state metal atoms in the flame partly absorb this light and the intensity of the resonance fluorescence radiation emitted in a direction perpendicular to the incident beam was measured with a vacuum phototube and a locking device tuned at 50 c/sec. The d.c. component of the unmodulated radiation of the coloured flame was eliminated in this way. A glass filter for selecting the desired radiation was placed at the entrance of the phototube to render the fluctuations caused by the flame-background emission negligible with respect to the noise caused by

the thermal emission of the coloured flame. The flames used had an inner column that was coloured by metal vapour and was shielded by a colourless burning mantle. The diameter of the inner column at 1 cm above the burner head was 1·8 cm and the total flame diameter was 3·5 cm, so that the thickness of the flame mantle was about 1 cm. The total flame length, which ranged from 15 to 20 cm, appeared to depend to some extent on the kind and composition of the entering gases. The characteristics of the burnt gases in the inner column of the flames are listed in Table 1 of Ref. 3. The stoichiometric, oxygen-rich and fuel-rich $H_2$ flames used in the rubidium experiments are presented in this table as nos. 2, 3, 5, 12, and 14, respectively. Flame no. 5 is diluted with nitrogen, the other flames are argon-diluent flames. The flame temperature was measured by the line-reversal method with the use of the accurate photoelectric device developed by Snelleman.[8]

## EXPERIMENTAL RESULTS

Table 1 gives the temperatures of the five flames considered, and it also shows the experimental values of the yield factor $p$ for these flames. The $p$-values were obtained by measuring the ratio of the fluorescence power emerging from the flame to the absorbed primary radiation power as a function of the sprayed Rb concentration. Extrapolation of this ratio to zero concentration, and correction for the solid angle $\omega$ of acceptance of the detector, gives the true $p$-value, free from self-absorption effects.

The listed $p$-values are average values obtained by repeating the measurements at least five times. The major source of error stems from the fluctuations of the thermal emission of the coloured flame at the measurement frequency (50 c/sec). From the measured $p$-values,

TABLE 1. MEASURED YIELD FACTOR FOR RESONANCE FLUORESCENCE

| Flame no. | | $T$ (°K) | $p_{meas.}$ |
|---|---|---|---|
| 1 | (2) | 2210 | 0·33 |
| 2 | (3) | 2070 | 0·32 |
| 3 | (5) | 1940 | 0·036 |
| 4 | (12) | 1850 | 0·19 |
| 5 | (14) | 1885 | 0·088 |

Excited state $Rb(5P_{1/2,3/2})$.
Wavelength 7800/7947 Å.
Optical transition probability $A = 0.36 \, 10^8 \, sec^{-1}$ (cf. Ref. 9).
Relative scatter in $p_{meas}$ : Flame nos. 1, 2 and 4 : 3%
                               Flame nos. 3 and 5 : 6%
Flame numbers in brackets refer to Table 1 in Ref. 3.

we calculated the so-called specific quenching cross-sections $S_{Rb,j}$, defined as $\pi$ times the square of the distance between the centers of the colliding species. Here $j$ indicates the various types of quenching molecules ($N_2$, $O_2$, $H_2$ and $H_2O$). In this derivation, it was assumed that the quenching effect of the argon atoms could be disregarded when compared with the total contribution of the other predominant flame molecules $H_2O$, $O_2$, $H_2$ and $N_2$ (see Discussion). In our calculations, we must make allowance for the unknown temperature dependence of each $S_{Rb,j}$ separately. We solved this problem for oxygen, hydrogen and

water molecules by an iteration procedure. In the derivation of $S_{H_2O}$ we first neglect the quenching effects of all other molecules present in the stoichiometric hydrogen–oxygen–argon flames (nos. 1 and 2 in Table 1). It is seen from the flame characteristics that the burnt gases from these flames consist mainly of water and argon. From the calculated $S_{Rb,H_2O}$ values at 2070 and 2210°K a rough approximation of the dependence of this cross-section on temperature can be deduced ($S \sim T^{-3}$). Next we computed $S_{Rb,H_2}$ and $S_{Rb,O_2}$ in a first approximation (by using the dependence of $S_{Rb,H_2O}$ on temperature that just had been found) from the measurements of $p$ in fuel-rich and oxygen-rich hydrogen–oxygen–argon flames (nos. 4 and 5 in Table 1). The first order approximation for $S_{Rb,H_2}$ and $S_{Rb,O_2}$, in turn, enabled us to derive more reliable values for the quenching cross-section of water molecules that were present in the burnt gases of flames nos. 2 and 3. This procedure was repeated a few times. Assuming in this calculation that the dependence of the cross-sections on temperature for oxygen and hydrogen molecules is not much stronger than $S \sim T^{-1}$, as was found in our previous quenching experiments with sodium and potassium, we may neglect the small differences in temperature of flames nos. 3, 4 and 5. The oxygen and hydrogen quenching contribution in flames nos. 1 and 2 is small so that lack of knowledge about the relationship between $S$ and $T$ for these molecules has only little effect on the accuracy of the determination of $S_{Rb,H_2O}$. The quenching cross-section for rubidium atoms in collision with nitrogen molecules was derived from the $p$-value measured in flame no. 3. In this flame, nitrogen was supplied as "cooling gas" in major concentration.

The rather strong dependence of $S_{Rb,H_2O}$ on temperature, as deduced from flames nos. 1 and 2, agrees with the results of our previous quenching experiments on sodium, provided that the argon quenching contribution is neglected in comparison with the contribution of the other flame particles (see Ref. 3). In oxygen-rich and nitrogen-rich flames, the quenching rate is determined mainly by collisions with oxygen and nitrogen molecules, respectively. The quenching due to water molecules is relatively small, so that the rather large uncertainty in the value for $S_{Rb,H_2O}$ expected at 1900°K does not critically influence the $S$-values of these diatomic molecules. Our calculations finally led to the cross-section values: $S_{H_2} = 3.6$ ($\pm 0.4$) $Å^2$, $S_{N_2} = 25$ ($\pm 1.5$) $Å^2$, $S_{O_2} = 83$ ($\pm 5$) $Å^2$ and $S_{H_2O} = 4.0$ ($\pm 0.8$) $Å^2$. The $S$-values for the diatomic molecules may be considered as valid for a flame temperature of about 1900°K, while $S_{H_2O}$ is valid for about 2100°K.

The error limits given for $S$-values of hydrogen, oxygen, and nitrogen molecules allow also for the uncertainty in the dependence of $S_{Rb,H_2O}$ on temperature.

As extreme cases we considered $S_{H_2O}$ independent of temperature or else varying as $T^{-3}$.

## DISCUSSION

In the derivation of $S$ from the $p$-values we have neglected the contribution of the argon-atoms to the quenching effect compared with the total contribution of the other species present in the flame gases. (This assumption is based on the results of argon-quenching experiments by TSUCHIYA,[10] JENKINS,[11] HURLE[12] and recent experiments on sensitized fluorescence in sodium, potassium, rubidium and cesium induced by argon at low pressures.[13–16]) In the latter experiments, alkali atoms in an atmosphere of argon atoms are irradiated by only one of the two components of the doublet lines investigated. From the resonance fluorescence radiation observed with both doublet lines, it follows that the cross-section for collisions accomplishing transfer of energy between the doublet levels

decreases from $100 \text{ Å}^2$ to $5 \times 10^{-4} \text{ Å}^2$. when the energy difference between these levels increases from 0·002 eV for argon in collision with excited sodium atoms $(3^2P_{3/2})$ to 0·070 eV for $Ar–Cs(6^2P_{3/2})$ collisions. In view of these findings we may expect that argon atoms are also inefficient quenchers for the quenching process studied in our experiments where excited Rb-atoms return to their ground state by giving up their total excitation energy ($\approx 1.5$ eV).

As was done before for sodium and potassium, we investigated for rubidium atoms the correlation between the specific quenching cross section and the resonance defect $|\Delta E|$. The latter is defined as the energy difference between the atomic excitation level and the nearest vibrational level of the quenching molecule.

TABLE 2. COMPARISON OF RESONANCE DEFECT $\Delta E$ WITH MEASURED SPECIFIC QUENCHING CROSS SECTION $S$

| Quenching molecule | Atomic excitation level and excitation energy (eV) | | Vibrational quantum number $r$, and energy $E$ of nearest molecular level (eV) | | $\Delta E$ (eV) | $S \times 10^{10}$ at 1900°K (cm²) |
|---|---|---|---|---|---|---|
| | | | $r$ | $E$ | | |
| $H_2$ | $Rb(5P_{1/2})$ | 1·561 | 3 | 1·461 | −0·100 | 3·6 |
| | | | 4 | 1·890 | +0·329 | |
| | $Rb(5P_{3/2})$ | 1·589 | 3 | 1·461 | −0·128 | |
| | | | 4 | 1·890 | +0·301 | |
| $O_2(^3\Sigma)$ | $Rb(5P_{1/2})$ | 1·561 | 8 | 1·464 | −0·097 | 8·3 |
| | | | 9 | 1·634 | +0·073 | |
| | $Rb(5P_{3/2})$ | 1·589 | 8 | 1·464 | −0·125 | |
| | | | 9 | 1·634 | +0·045 | |
| $N_2$ | $Rb(5P_{1/2})$ | 1·561 | 5 | 1·409 | −0·152 | 25 |
| | | | 6 | 1·681 | +0·120 | |
| | $Rb(5P_{3/2})$ | 1·589 | 5 | 1·409 | −0·180 | |
| | | | 6 | 1·681 | +0·092 | |

Table 2 shows the excitation energies of the relevant atomic and molecular vibrational levels, together with the specific quenching cross-sections at 1900°K. In Fig. 1, $S_{Rb,j}$ is plotted as a function of $|\Delta E|$. For comparison we added the corresponding plots found in our previous work[3] for the excited alkali atoms Na(3P), K(4P) and K(5P) in collisions with the same diatomic molecules. Since the experiments described in this paper are not made with each doublet component separately, allowance should be made for the difference in $\Delta E$-values that exist for each doublet component. This difference in resonance defect may amount to 0·028 eV ($\approx 0.15$ kT). The values of $|\Delta E|$ plotted in Fig. 1 refer to the smallest defect in energy between a given vibrational level and either doublet levels. Incidentally, the $5P_{3/2}$ levels of Rb having the smallest resonance defect (see Table 2) with respect to the molecular vibrational levels of nitrogen, and hydrogen also has the larger statistical weight. Starting from the relationship given in Fig. 1, as a first approximation, it follows that the quenching cross section for excited Rb $(5P_{1/2})$ atoms in collision with both these molecules is very small.

If we assume, in view of investigations on cesium by McGILLIS et al.,[17] that the molecules present in the flame will establish an equilibrium distribution between the levels of

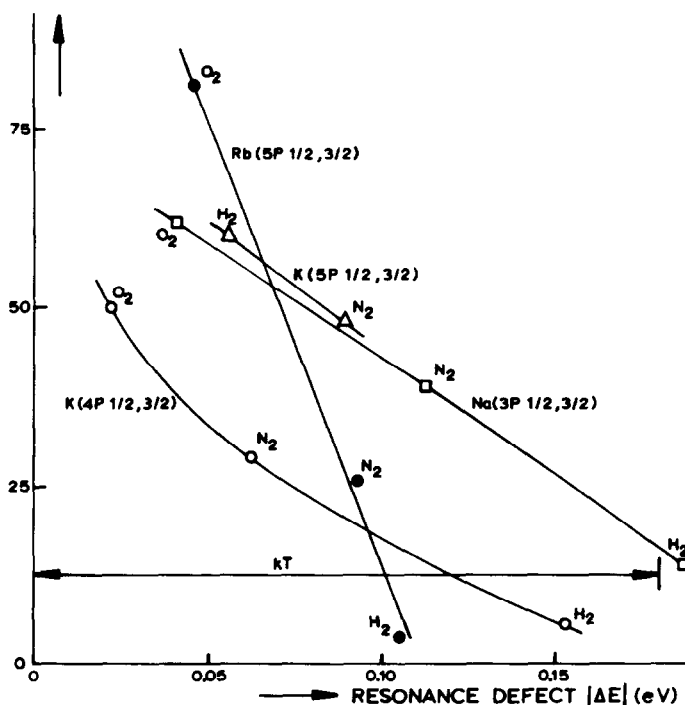FIG. 1. The effective specific quenching cross-section $S$ for some diatomic molecules ($O_2$, $N_2$ and $H_2$) in collision with excited sodium atoms in the $3P_{1/2,3/2}$ state, excited potassium atoms in the $4P_{1/2,3/2}$ and $5P_{1/2,3/2}$ states, and excited rubidium atoms in the $5P_{1/2,3/2}$ states, are plotted as functions of the absolute resonance defect $|\Delta E|$.

The cross-sections for the rubidium doublet may be considered as valid for $1900°K$. The other cross section values are valid for $2000°K$. The value of $kT$ at $2000°K$ is indicated by an arrow drawn parallel to the abscissa.

the Rb-doublet, we can treat $O_2$ and $H_2$ as quenchers on the basis of the $\Delta E$-values corresponding to the $5P_{3/2}$ state of rubidium. Using the relationship between $S$ and $\Delta E$ plotted in Fig. 1, it is possible to find the weighted average of both the $\Delta E$-values belonging to oxygen as quenching molecule by applying a sort of iteration procedure, taking into account the difference in statistical weight and in resonance defect for the two doublet lines. This only results in a small shift to the right ($\approx 0.01$ eV) of the oxygen–rubidium point in Fig. 1. In these plots, no correction was made for the existence of an activation factor in the case of endothermic quenching (i.e., $E_{mol} > E_{exc.\ atom}$). For a discussion about the small correction which should be applied, we may refer to our previous paper. The small value for $S_{Rb,H_2O}$ and the course of the $S$ vs. $\Delta E$ curve found in this work agree qualitatively with our earlier findings on sodium and potassium.

Finally, it should be realized that our conclusion concerning the pronounced dependence of $S$ on resonance defect may be somewhat disputable because, for all alkali doublet lines investigated except for K ($4044/47$ Å), the $\Delta E$-value corresponding to $O_2$ as quenching molecule is the smallest one and that of $H_2$ the largest one. An apparent resonance effect, therefore, might be induced by the different chemical properties of the diatomic molecules

considered. However, the relatively large cross-section of $H_2$ molecules in collision with excited $K(5P_{1/2,3/2})$ atoms supports our conclusion. In order to establish this conclusion, it is necessary to eliminate the difference in chemical properties between the molecules compared. For this reason, fluorescence experiments on sodium have been started in deuterium–oxygen argon flames in order to compare the $S$-values for deuterium and hydrogen. The $\Delta E$-value for hydrogen molecules colliding with excited sodium atoms exceeds that of deuterium by a factor of about three, so that a large difference in true $\Delta E$ effect, if present, may be expected.

## REFERENCES

1. A. L. BOERS, C.TH.J. ALKEMADE and J. A. SMIT, *Physica* **22**, 358 (1956).
2. H. P. HOOYMAYERS and C.TH.J. ALKEMADE, *JQSRT* **6**, 510 (1966).
3. H. P. HOOYMAYERS and C.TH.J. ALKEMADE, *JQSRT* **6**, 847 (1966).
4. H. P. HOOYMAYERS and C.TH.J. ALKEMADE, *JQSRT* **7**, 495 (1967).
5. H. P. HOOYMAYERS, Thesis, University of Utrecht (1966).
6. C.TH.J. ALKEMADE, *Proceedings of the Xth Colloquium Spectroscopicum internationale*. Spartan Books, Washington (1963).
7. C.TH.J. ALKEMADE and H. P. HOOYMAYERS, *Combustion and Flame* **10**, no. 3, 306 (1966).
8. W. SNELLEMAN, Thesis, University of Utrecht (1965).
9. J. K. LINK, *J.O.S.A.* **56**, 1195 (1966).
10. S. TSUCHIYA, *J. Chem. Soc. Japan* **37**, 6 (1964).
11. D. R. JENKINS, *Chem. Comm.* **6**, 171 (1966).
12. A. G. GAYDON and I. R. HURLE, *Proc. Roy. Soc. (Lond.)* **A262**, 38 (1961).
13. R. SEIWERT, *Ann. Phys.* **18**, 54 (1956).
14. G. D. CHAPMAN and L. KRAUSE, *Can. J. Phys.* **44**, 753 (1966).
15. F. S. C. BRUCE PITRE, A. G. A. RAE and L. KRAUSE, *Can. J. Phys.* **44**, 731 (1966).
16. M. CZAJKONSKI, D. A. McGILLIS and L. KRAUSE, *Can. J. Phys.* **44**, 91 (1966).
17. D. A. McGILLIS and L. KRAUSE, *Phys. Rev.* **153**, 1 (1967).