

# ELECTRONIC-EXCITATION TRANSFER COLLISIONS IN FLAMES—V. CROSS SECTIONS FOR QUENCHING AND DOUBLET-MIXING OF $K(4^2P)$ -DOUBLET BY $N_2$ , $O_2$ , $H_2$ AND $H_2O$

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**Abstract**—Weighted average cross sections for quenching of the  $K(4^2P)$ -doublet by  $N_2$ ,  $H_2$ ,  $O_2$  and  $H_2O$ , measured in flames, show no significant temperature dependence in the range from 1500 to 2500K. Doublet mixing cross sections for  $K(4^2P_{3/2} \leftrightarrow 4^2P_{1/2})$  transitions were measured at 1720K for  $N_2$ ,  $O_2$ ,  $H_2O$ . The ratios of both mixing cross sections were measured independently and were found to agree with the detailed balance condition within 2 per cent. It is shown that an ionic intermediate-state model cannot explain the large magnitude of  $N_2$ -mixing cross sections.

## 1. INTRODUCTION

MEASUREMENTS are presented on the temperature dependence of effective cross sections for quenching of the  $K(4^2P)$ -doublet by  $N_2$ ,  $O_2$ ,  $H_2$  and  $H_2O$ -molecules in the temperature range from 1500K to 2500K. Quenching of  $K(4^2P)$  has been measured previously by JENKINS,<sup>(6)</sup> at 1400K, and by HOOYMAYERS and ALKEMADE,<sup>(7)</sup> at 1900K, in flames and by COPLEY and KRAUSE in vapor bulbs at 400K.

Until now, doublet mixing cross sections for  $K(4^2P_{3/2} \leftrightarrow 4^2P_{1/2})$  transitions have been measured only at 370K by MCGILLIS and KRAUSE<sup>(9)</sup> for diatomic molecules and by CHAPMAN and KRAUSE for inert-gas atoms.

In order to establish the temperature dependence, we measured mixing cross sections for  $N_2$ ,  $O_2$ , and  $H_2O$  at 1720K.

## 2. EXPERIMENTAL

Quenching and mixing cross sections have been derived from fluorescence efficiencies,  $Y_{i-j}$  as defined in Ref. (3). The experimental method and apparatus used have been described extensively in Refs. (1-4). Weighted-average quenching cross sections, for the doublet as a whole, were obtained for  $N_2$  and  $H_2O$  from  $Y_{12-12}$ -values, measured in series of isothermal, stoichiometric, laminar and shielded  $Ar/N_2/H_2/O_2$ -flames at five temperatures ranging from 1500–2500K, using the method of part I.<sup>(1)</sup> We measured the mixing rate constants,  $k_{21}$ , in six isothermal  $Ar/N_2/H_2/O_2$ -flames, with varying  $Ar/N_2$ -ratios, at 1720K. Since the contribution of Ar to the mixing rate constants cannot a priori be neglected, as can be done for quenching, a computer program was used to calculate the best fit for the mixing cross sections.

Quenching and mixing cross sections for  $O_2$  and  $H_2$  were determined from measurements in  $O_2$ -rich and  $H_2$ -rich flames, respectively.<sup>(2)</sup> In a number of flames,  $Y_{1-12}$  and  $Y_{2-12}$  were found to be equal within experimental error of 3 per cent, which prevented a separate measurement of both quenching rate constants.

### 3. EXPERIMENTAL RESULTS

Results for  $(\sigma_{qu})_{N_2}$  and  $(\sigma_{qu})_{H_2O}$  are given in Fig. 1. The statistical error in  $(\sigma_{qu})_{N_2}$  is estimated to be less than 10 per cent, whereas the error in  $(\sigma_{qu})_{H_2O}$  may be somewhat larger, especially so at the higher temperatures.<sup>(3)</sup> Since  $(\sigma_{qu})_{H_2}$  and  $(\sigma_{qu})_{H_2O}$  appeared to be of comparable magnitude, the uncertainty in the value of  $(\sigma_{qu})_{H_2O}$ , used for calculating  $(\sigma_{qu})_{H_2}$ , introduces a significant systematic error in the values found for  $H_2$ . Figure 2 shows  $(\sigma_{qu})_{H_2}$  in the temperature range from 1500K to 2500K. Our experimental points have been calculated using  $(\sigma_{qu})_{H_2O} = 3.7 \text{ \AA}^2$  in the whole temperature range. The full line gives the best linear fit through these points. We also show, for comparison, the shift in this fit for two other assumed values of  $(\sigma_{qu})_{H_2O}$ .

Results for  $(\sigma_{qu})_{O_2}$  are shown in Fig. 3. Due to the relatively large value of  $(\sigma_{qu})_{O_2}$ , the experimental uncertainty in  $(\sigma_{qu})_{H_2O}$  has only a minor effect on the accuracy of  $(\sigma_{qu})_{O_2}$ , which is thus mainly determined by the statistical error of measurement.

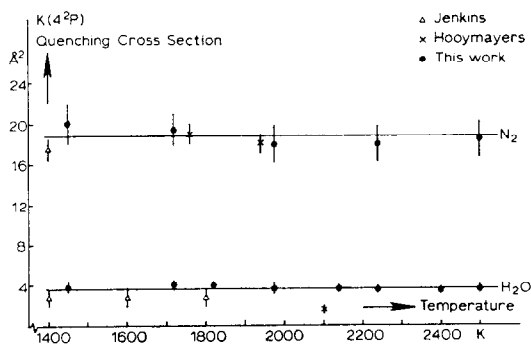


Fig. 1. Experimental cross-sections for quenching of  $K(4^2P)$ -doublet by  $N_2$ - and  $H_2O$ -molecules, as a function of temperature. Literature-data of HOYMAIERS and ALKEMADE<sup>(7)</sup> and JENKINS<sup>(6)</sup> are shown in the figure.

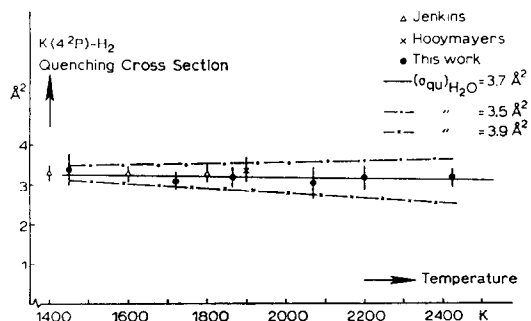


Fig. 2. Experimental cross sections for quenching of  $K(4^2P)$ -doublet by  $H_2$ -molecules as a function of temperature. The full-line gives the best fit through the experimental points for  $\sigma_{H_2O} = 3.7 \text{ \AA}^2$ . The broken lines show the shift in this fit for different values of  $\sigma_{H_2O}$ . Literature-data of JENKINS<sup>(6)</sup> and HOYMAIERS and LIJNSE<sup>(14)</sup> are shown in the figure.

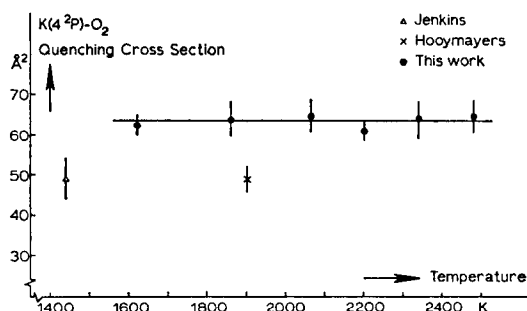


Fig. 3. Experimental cross sections for quenching of  $K(4^2P)$ -doublet by  $O_2$ -molecules, as a function of temperature. Literature-data of JENKINS<sup>(6)</sup> and HOOYMAYERS and LIJNSE<sup>(14)</sup> are shown in the figure.

Doublet-mixing cross sections were measured in eight flames at 1720K only, as the rather large statistical error did not warrant the determination of their probably small variation with temperature (see Table 1). In each flame, the measurement of the ratio  $Y_{2-2}/Y_{2-1}$  was repeated about 10 times. In one flame, in which  $Y_{12-12} \ll 1$ , the ratio  $Y_{1-2}/Y_{2-1}$  was found to equal its detailed balance value within 2 per cent.<sup>(3)</sup> The same conclusion must, therefore, hold for the cross section ratio  $\sigma_{12}/\sigma_{21}$ . The ratio of the Einstein-emission probabilities for the doublet components was taken to be unity, within 1 per cent, according to LINK<sup>(12)</sup> and HEAVENS.<sup>(13)</sup> Mixing cross sections for  $N_2$ ,  $O_2$  and  $H_2O$ , at 1720K, are given in Table 1.

Table 1. Doublet mixing and quenching cross sections of  $K(4^2P_{1/2, 3/2})$  in  $\text{\AA}^2$

Collision partner	$\sigma_{qu}$	$\sigma_{12}$	$\sigma_{21}$	$\sigma_{12}/\sigma_{21}$		Temperature (K)	Ref.
				exp.	theor.		
$N_2$	$34 \pm 2$	$100 \pm 8$	$66 \pm 6$	$1.51 \pm 0.16$	1.62	400	8, 9
$N_2$	$19 \pm 1.5$	$190 \pm 25$	$100 \pm 15$	$1.91 \pm 0.04$	1.91	1720	this work
$O_2$	$63 \pm 3$	$75 \pm 25$	$40 \pm 12$	$1.91 \pm 0.04$	1.91	1720	this work
$H_2$	$9.4 \pm 1.3$	$76 \pm 7$	$53 \pm 4$	$1.43 \pm 0.20$	1.62	400	8, 9
$H_2$	$3.3 \pm 0.5$	—	—	—	—	1720	this work
$H_2O$	$3.6 \pm 0.4$	$100 \pm 30$	$50 \pm 15$	$1.91 \pm 0.04$	1.91	1720	this work

#### 4. DISCUSSION

Our values for  $(\sigma_{qu})_{N_2}$  are in good agreement with previous flame results of JENKINS<sup>(6)</sup> and HOOYMAYERS and ALKEMADE<sup>(7)</sup> (see Fig. 1). Lifetime measurements of COPLEY and KRAUSE,<sup>(8)</sup> in vapour bulbs at 400K, have yielded  $(\sigma_{qu})_{N_2} = (34 \pm 2)\text{\AA}^2$ . Thus, the temperature dependence of  $(\sigma_{qu})_{N_2}$  for  $K(4^2P)$  is similar to that observed for other alkalis,<sup>(5)</sup> i.e. a gradual decrease of about a factor 2, going from 400K to flame temperatures. Within error limits, our  $(\sigma_{qu})_{H_2O}$  agrees with JENKINS'-value, but an unexplained discrepancy exists between our  $(\sigma_{qu})_{H_2O}$  and HOOYMAYERS'-value.

The agreement of our  $(\sigma_{qu})_{H_2}$ -values, calculated with  $(\sigma_{qu})_{H_2O} = 3.7\text{\AA}^2$ , with previous flame results is good. Note that JENKINS'- $(\sigma_{qu})_{H_2}$  is only little influenced by his  $(\sigma_{qu})_{H_2O}$ -value used. Low-temperature data<sup>(8)</sup> for  $(\sigma_{qu})_{H_2}$  are significantly larger, by about a factor 3.

Our  $(\sigma_{qu})_{O_2}$ -values are by about 20 per cent larger than the incidental values, reported in Refs. (6) and (14). Therefore, we carefully checked our entire experimental set-up, but we could find no explanation for this difference. In contrast to previous results for Na( $3^2P$ )- $O_2$  quenching<sup>(2)</sup>  $(\sigma_{qu})_{O_2}$  for K( $4^2P$ ) appears to be temperature-independent, within 5 per cent, in the T-range from 1600K to 2500K. Comparing the  $(\sigma_{qu})_{O_2}$ -values for K, with those for the other alkalis, no evidence is found for an electronic-energy exchange resonance-effect between the K( $4P$ )-doublet and the near-resonant  $O_2(^1\Sigma_g^+)$ -state ( $\Delta E \approx 0.01$  eV).

Comparison of our  $(\sigma_{21})_{N_2}$  with the value measured by MCGILLIS and KRAUSE<sup>(9)</sup> at 370K suggests that  $(\sigma_{21})_{N_2}$  is weakly temperature dependent, as has been found previously for Rb<sup>(3)</sup> and Cs.<sup>(4)</sup>

ANDREEV and VORONIN<sup>(15)</sup> have argued that transitions through an ionic intermediate-state, which are commonly accepted in the explanation for large diatomic quenching cross sections, would also provide a likely mechanism for mixing collisions. If this ionic model explains both the quenching and mixing process, the corresponding cross sections might be interrelated. Only those collisions that lead to an ionic state but do not end up in a quenching collision, can contribute to mixing. Thus, an upper limit to the sum,  $(\sigma_{10} + \sigma_{12})$ , of quenching and mixing cross sections, can be found from the value of  $\pi R_c^2$ . Here  $R_c$  is the maximal crossing distance of the initial potential energy curves with the ionic curves. The quantity  $R_c$  can be estimated from the equation<sup>(16)</sup>  $IP - EA = e^2/R_c - e^2\alpha/2R_c^4$ , where  $IP$  is the alkali-ionization potential,  $EA$  is the electron affinity of the diatomic molecule,  $e$  is the electronic charge and  $\alpha$  is the ionic-complex polarizability, which was taken to be  $40 \text{ \AA}^3$ .<sup>(16)</sup> In this way, a value  $\pi R_c^2 \approx 55 \text{ \AA}^2$  is estimated for  $N_2$ -alkali collisions. However, experimental values for  $(\sigma_{10} + \sigma_{12})$ , as measured at 1720K, are  $210 \pm 25$ ,  $118 \pm 20$  and  $105 \pm 20 \text{ \AA}^2$  for K-, Rb- and Cs- $N_2$  collisions, respectively.<sup>(3,4)</sup> As outlined in Refs. (5) and (17), inclusion of an attractive potential in the ionic curve-crossing model may enhance the cross section for collisions leading to an ionic state. At flame-temperatures, however, its effect can be estimated to be at most about 40 per cent, giving an estimated upper limit to  $(\sigma_{10} + \sigma_{12})$  of about  $75 \text{ \AA}^2$ . Comparing our estimated value with the experiments we can conclude that for  $N_2$  the ionic curve-crossing model cannot explain the large magnitude of mixing cross sections, contrary to ANDREEV and VORONIN's suggestion. The well-known mechanism, which is responsible for the occurrence of large inert-gas mixing cross sections<sup>(18)</sup> for K and Na and which may lead to upper limits of about  $180 \text{ \AA}^2$ , might explain the occurrence of K- $N_2$  mixing collisions at impact parameters exceeding  $R_c$ . However, since the Cs- and Rb-inert gas mixing cross sections are very small, this latter mechanism is not expected to be significant for Cs- and Rb- $N_2$  collisions. More theoretical work on molecular mixing cross sections, including rotational effects, is urgently needed.

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