

QUENCHING OF EXCITED HYDROXYL (${}^2\Sigma^+, v' = 0$) RADICALS IN FLAMES

H. P. HOOYMAYERS and C. TH. J. ALKEMADE

Physical Laboratory, State University of Utrecht, The Netherlands

(Received 14 September 1966)

Abstract—An alternating current photoelectric device (compare the work of BOERS *et al.*,⁽¹⁾ ALKEMADE,⁽²⁾ HOOYMAYERS *et al.*^(3,4) and HOOYMAYERS⁽⁵⁾) has been used for determining the yield factor p of resonance fluorescence for some specific rotational transitions of the (0, 0) band of the hydroxyl ${}^2\Sigma^+ \rightarrow {}^2\Pi$ -band system. Excitation of the selected rotational levels was achieved by irradiating the flame with a hollow cathode bismuth-lamp emitting the 3067.72 Å atomic Bi-line. From the p -values measured in three different hydrogen flames at about 1500–1800°K and 1 atm pressure the specific effective cross-sections^(4,5) S of the excited radical in collision with N_2 , O_2 and H_2O molecules as quenchers could be derived with an accuracy of about 18 per cent. Here the quenching cross section S is defined as π times the square of the distance between the centers of the colliding species. In contrast with the results of our quenching experiments on excited alkali-atoms,^(4,5) it was found that the S -value for H_2O as quencher ($S_{H_2O} = 37 \pm 6 \text{ \AA}^2$) exceeds the values for the other molecules mentioned ($S_{O_2} = 10 \pm 2 \text{ \AA}^2$ and $S_{N_2} = 7 \pm 1 \text{ \AA}^2$) by a factor of at least 4. Combining our results with other data obtained by ZEEGERS^(6–8) at our laboratory in OH-chemiluminescence experiments, it appeared that at our flame conditions,^(4,5) quenching of excited OH(${}^2\Sigma, v' = 0$) radicals by H_2O molecules is partly (≈ 5 per cent) achieved by dissociative quenching according to the reaction $OH^* + H_2O \rightarrow OH + OH + H$.

1. INTRODUCTION

IN ORDER to derive absolute rates of chemiluminescent reactions leading to excited OH(${}^2\Sigma^+$) radicals from the non-thermal intensity of the (0, 0) band of OH at 3064 Å measured in absolute units in flames at our laboratory^(7,8) we need the knowledge of the fluorescence yield factor p , as defined in Refs. 3–5 for this band under flame conditions. Moreover, the study of the quenching rate of the electronic excited state OH(${}^2\Sigma^+$) in flames may contribute to the interpretation of the persistence of the non-equilibrium population of rotational levels of this state, which is observed spectroscopically in certain flames.^(9–12) It was felt that an extension of the scanty data from the literature on the quenching of excited OH-radicals under flame conditions would be useful with respect to the solution of the above problems.^(13–15)

2. THE EXPERIMENTAL SETUP AND CONDITIONS OF MEASURING

With the experimental setup as already described in Refs. 4 and 5, the yield factor p of resonance fluorescence was measured for the rotational transitions of the (0, 0) vibrational band of OH (head at 3064 Å) from the rotational states $K = 11$; $J = 10\frac{1}{2}$ and $K = 10$; $J = 9\frac{1}{2}$ of the excited electronic ${}^2\Sigma^+$ state to the electronic groundstate ${}^2\Pi$ (see Fig. 1).

In these measurements the OH radicals in the flame were irradiated with a periodically chopped (50 c/s) light beam from a bismuth hollow-cathode lamp (15 mA, 3 W). The

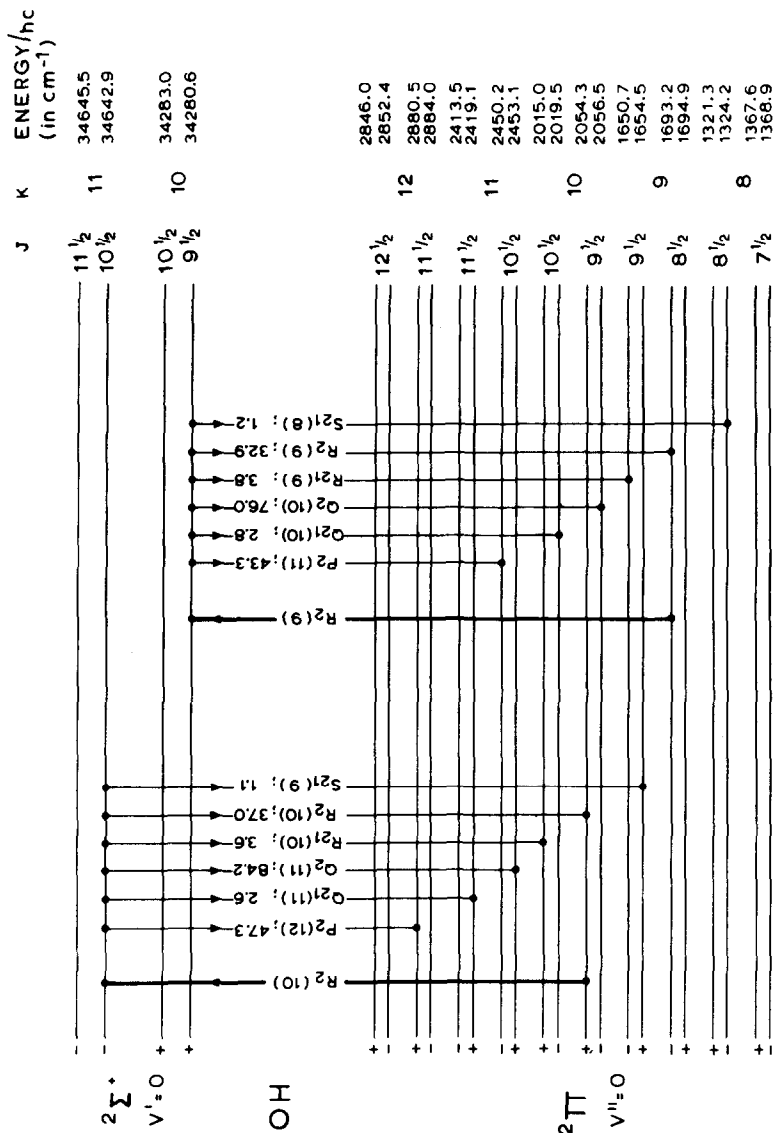


FIG. 1. Energy level diagram for the $(0,0)$ band of the $2\Sigma^+ \rightarrow 2\Pi$ band system of OH. The levels are drawn only for K values that are relevant in our experiments and are arranged according to increasing J values. In the lower electronic state each (J, K) level is split up into two sublevels, because of Λ -type doubling (for clarity the splitting effect is exaggerated and presented by equidistant sub-levels). For each optically allowed transition the branch and relative rotational transition probability ($S_{J,K}$ value) are given in the figure. Data and notation are from DIEKE and CROSSWHITE.^(1,1)

OH flame radicals in their electronic groundstate partly absorb the Bi resonance line at 3067.72 Å. Its total line width at half intensity amounts to at least 0.006 Å, this being the Doppler broadening at room temperature.

The total flame length and total flame diameter of the cylindrical, stoichiometric and oxygen-rich H₂ flames used in our OH-experiments were 15 cm and 4.0 cm, respectively. Experiments have shown that there was a homogeneous temperature distribution and uniform density of the OH radicals in the central part of the flame (with diameter of 1.8 cm), so that we may expect a uniform distribution of the flame gas particles throughout this central part. In our fluorescence measurements a diaphragm was placed in front of the detector to ensure that only fluorescent light from the homogeneous central part of the flame was received by the detector. In comparing the fluorescence signal with the absorbed radiation power from the Bi-lamp we must consequently correct for the absorption of the Bi radiation in the burning flame sheath, which does not contribute to the re-emission light detected. The correction factor for the absorption of the Bi-radiation in the flame sheath was found by measuring the absorption of the narrow Bi-light beam when its distance to the flame axis was so large that it only passed the flame sheath and not the central part of the flame.

TABLE 1. CHARACTERISTICS OF FLAMES USED IN OH QUENCHING EXPERIMENTS

Flame number	Supplied gases (l./min)	Calculated equilibrium composition of burnt gases in partial pressures	Measured temperature (°K)
1	H ₂ 1.16	H ₂ O 0.21	1790
	O ₂ 1.42	O ₂ 0.155	
	Ar 3.45	Ar 0.63	
2	H ₂ 1.0	H ₂ O 0.225	1760
	O ₂ 0.5	N ₂ 0.77	
	N ₂ 3.45		
3	H ₂ 1.16	H ₂ O 0.21	1500
	O ₂ 1.42	O ₂ 0.155	
	N ₂ 3.45	N ₂ 0.63	

There is another complication associated with the presence of the flame sheath. The thermal OH emission of the part of the sheath that lies on the optical axis of the detecting system contributes to the 50 c/s noise signal present in the fluorescence measurements (see below). In order to reduce this disturbing effect, the burning mixture of the sheath was chosen oxygen-lean which resulted in a decrease of the OH concentration in the flame sheath, and consequently in its thermal emission noise. It was checked that the resulting difference in gas composition between sheath and central part hardly affected the homogeneous radial temperature distribution and the uniform OH density throughout the central part of the flame viewed by the detector.

The characteristics of the burnt gases in the central part of the flame, containing N₂ or Ar as diluent gas, are listed in Table 1. The equilibrium composition of the burnt gases was calculated by following the computer program drawn up by ZEEGERS⁽⁸⁾ and based

on an iteration procedure described in Ref. 11. Flame gas components contributing partial pressures smaller than 10^{-3} atm have not been entered into the Table, because their influence on the quenching of excited OH radicals is negligible in all cases.

From experiments by ZEEGERS^(6,7) concerning the decay of excess radical concentrations as a function of height above the reaction zone in similar flames, we may infer that the OH radicals in our flames at 1.2 cm above the cones (taking into account the flame speed of 3 m/sec) have equilibrium concentration. It should be noted that the point of maximum temperature, which is a rough indication of the establishment of radical equilibrium lies about 0.6 cm above the cones in our flames.

The flow speed, v , of the flame gases was calculated from the usual relation between v , the gas supply, expansion factor and flame diameter. It was found that v is, virtually, the same for the flames listed in Table 1 and is about 3 m/sec.

In order to enhance the lamp radiation flux absorbed in the flame in our fluorescence measurements, a concave spherical mirror (with aperture = 1) was placed behind the flame in line with the Bi-lamp, so that the exciting light beam focused in the flame by a quartz lens (with aperture 0.8) passes the flame twice. The intensity of the fluorescence radiation emitted in a direction perpendicular to the exciting beam was measured by means of a photomultiplier tube at the entrance of which an interference filter was placed, having its maximum transmission at 3100 Å and a full width at half-peak transmission of 200 Å. Another concave mirror (with aperture = 1) was used to enhance the fraction of the totally emitted fluorescent light detected by the phototube. The mirror was placed behind the flame in line with the quartz lens (with aperture = 1) which focused the fluorescence radiation on the cathode of the photomultiplier (see Ref. 4, Fig. 16, position 1). So the radiation flux of the fluorescent light falling on the detector could be enlarged by a factor $(1.8)^2$, taking into account reflection losses at the mirror and absorption loss in the flame.

The exciting Bi-line (3067.72 Å) fairly well overlaps the rotational $R_2(9)$ and $R_2(10)$ OH-lines⁽¹⁶⁾ of the vibrational (0, 0) band having a wavelength of 3067.66 Å and 3067.77 Å, respectively (see Figs. 1 and 2).

In calculating the expected spectral width of about 0.06 Å at half-peak absorption of the OH absorption lines at flame temperature ($\approx 1800^\circ\text{K}$), we used the average parameter value $a' = 0.3$ of the curve-of-growth (see definition in Ref. 17) for the $^2\Sigma^+ \rightarrow ^2\Pi$ system of OH, as reported by KASKAN.⁽¹⁸⁾ This value of a' was obtained from measurements with atmospheric $\text{H}_2\text{-O}_2$ flames at about 2600°K . Furthermore, in the above estimation of line width it was assumed that the optical density was low anyway. This may be concluded from the negligible self-absorption of the OH emission lines in our flames where OH concentrations are lower than $5 \times 10^{15} \text{ cm}^{-3}$ (cf. Ref. 5). Our measurements of the widths of the Bi-line and OH absorption lines, respectively, as applied in the drawing of Fig. 2, may be examined more closely by calculating from these measurements the expected absorption factor of the Bi-radiation in the flame at a given OH concentration (cf. Ref. 5). We then obtain an absorption factor of 0.045 ± 0.006 for flame No. 1, which is about 30 per cent less than the value actually measured in this flame. This discrepancy points to an actual line width of the Bi-radiation which is larger than the Doppler width at the assumed room temperature. This is not inconsistent with what is generally known about the line width in hollow-cathode discharge lamps.⁽¹⁹⁾ From the estimated spectral widths of the exciting Bi-line and of the flame absorption lines, it may be concluded that only the

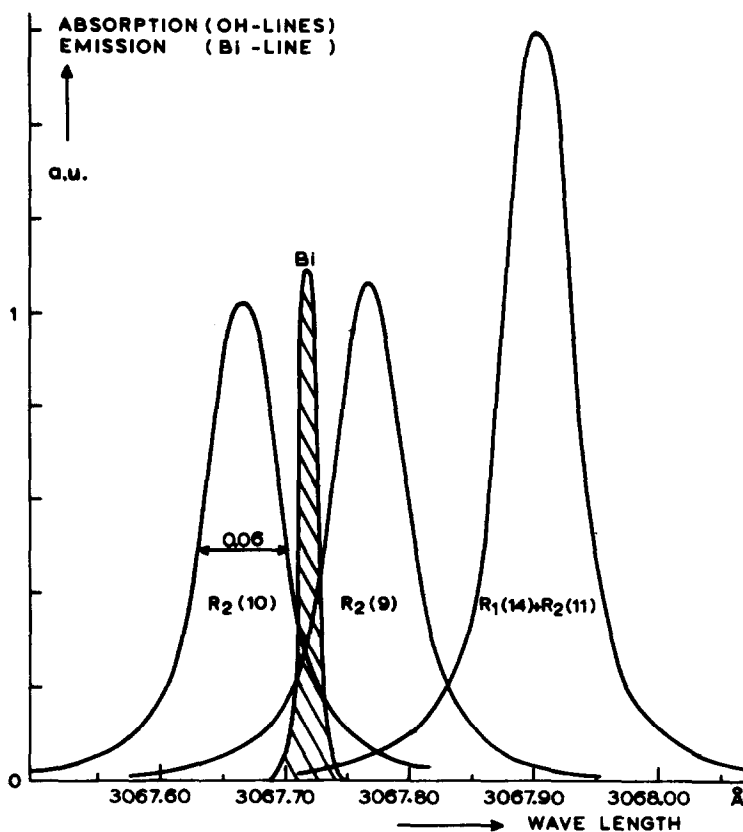


FIG. 2. The spectral positions of the Bi-line from the primary light source and the nearest OH-absorption lines in the flame. The contours of the absorption lines are drawn under the assumption that $a' = 0.3$ (half-peak absorption width $\Delta\lambda = 0.06 \text{ \AA}$, see text) while allowing for their relative oscillator strengths. The (unknown) width of the Bi-line is not drawn on scale, but is expected to be certainly smaller than that of the absorption lines.

rotational levels $K = 11$, $J = 10\frac{1}{2}$, and $K = 10$, $J = 9\frac{1}{2}$ of the vibrational $v' = 0$ level of the $^2\Sigma^+$ state are populated by absorption of the Bi-radiation (see Fig. 2).

The large quenching cross sections and resulting short lifetime of electronically excited OH radicals found in our experiments imply that under our flame conditions the photon emission by an excited radical will, in general, not be preceded by redistribution of the rotational energy (cf. also Refs. 13 and 14). Earlier ultrasonic measurements in N_2 and O_2 ^(20,21) show that the probability per kinetic collision of rotational-translational energy transfer is about 0.1, which is less than the quenching probability of the electronic energy by a factor of at least 10.

Figure 1 shows the optically allowed downward transitions from the rotational levels populated by absorption of Bi-radiation to vibrational levels of the electronic ground state $^2\Pi$. For each transition we give the branch, the K value of the lower state and the relative transition probability (line strength). In the Figure, data and notation are from DIEKE

and CROSSWHITE.⁽¹¹⁾ The selection rule for J in these transitions is: $J \rightarrow J$ and $J \pm 1 \rightarrow J$. It must be strictly satisfied for the free molecule. For K the selection rule $K \rightarrow K$ and $K \pm 1 \rightarrow K$ is valid. Transitions for which $\Delta J = \Delta K$ are strong (main branches), those for which $\Delta J \neq \Delta K$ are weak (satellite branches), except for small values of K . In addition, there is the symmetry selection rule even \rightleftharpoons odd, which is also strict for the free molecule. In the OH radical the electronic spin has the value $\frac{1}{2}$, which produces doublets in the energy level diagram. Moreover, in the ${}^2\Pi$ state both doublet components are double due to the so-called lambda-doubling.^(16,22)

In the radiative depopulation of the two rotational states mentioned, only transitions to the $v'' = 0$ vibrational state need to be considered, because the intensity of the rotational transitions of the vibrational (0, 0) band exceeds the intensity of the rotational lines of the (0, v'') bands ($v'' \neq 0$) of the ${}^2\Sigma^+ \rightarrow {}^2\Pi$ band system by a factor of at least 10^2 (see Refs. 11 and 18).

The fluorescent rotational lines corresponding to the (0, 0) band transitions shown in Fig. 1 are all transmitted through the interference filter used. A small correction should be made, however, for the difference in filter transmission of the fluorescent lines and the exciting Bi-radiation, respectively.

The major source of accidental error in our measurements is connected with the fluctuations of the non-modulated thermal OH emission in the flame in the 50 c/s frequency band of measuring. The interference filter placed at the entrance of the photomultiplier resulted in the interfering noise being solely due to thermal (0, 0) band transitions of OH because the other vibrational bands of ${}^2\Sigma \rightarrow {}^2\Pi$ band system (1, 0; 1, 1; etc.), are not transmitted through the filter. In order to reduce this noise, flames with low temperatures (i.e. about 1800°K) were chosen. Moreover, the diaphragm which is placed between flame and photomultiplier (see above) ensures that only the part of the central flame irradiated by the Bi-lamp will contribute to the background noise. This finally resulted in a value of 1.5 for the signal to noise ratio, defined as the ratio of the signal to the root mean square value of the meter fluctuations.

In each fluorescence measurement the galvanometer deflection due to the re-emission signal was recorded for a period of 20 sec, while every measurement was repeated at least fifteen times.

3. MEASUREMENTS OF FLUORESCENCE YIELD FACTOR

The fluorescence yield factor p can be determined by the radiation flux E_a absorbed from the exciting light beam and the radiation flux E_r of the fluorescent light observed in a direction perpendicular to the incident beam.^(4,5)

The recorder deflection corresponding to the re-emitted radiation power was obtained by subtracting the spurious signal due to stray light from the total signal measured in re-emission position (the detector observed the flame at right angles to the exciting beam and with the Bi-lamp on and off, respectively). This stray-light signal, the magnitude of which could be reduced after some effort to one-fourth of the magnitude of the average re-emission signal, was solely due to random scattering of the radiation of the exciting lamp, which was determined by measuring the spurious signal with the flame off and the lamp on. It was established that the observed fluorescence radiation was not due to scattering in the flame itself or to other spurious effects. This result was established by checking

the absence of any absorption and re-emission signal when the flame was irradiated by a mercury discharge lamp, emitting various lines of similar strength as the Bi-line, which were transmitted by the interference filter.

TABLE 2. MEASURED YIELD FACTOR p OF RESONANCE FLUORESCENCE OF OH RADICALS IN FLAMES

Excited fluorescent states (see Fig. 1)		OH(${}^2\Sigma, v' = 0$) $\left\{ \begin{array}{l} K = 11 \\ J = 10\frac{1}{2} \end{array} \right.$ and $\left\{ \begin{array}{l} K = 10 \\ J = 9\frac{1}{2} \end{array} \right.$	
Optical transition probability A (in sec^{-1})		1.05 10^6	
Relative error in p		18%	
Flame number	$p \cdot 10^3$	$A^{-1}k_{-1} \cdot 10^{-2}$	$pA^{-1} \cdot 10^9$ (sec)
1	1.3	7.8	1.3
2	0.9	11.5	0.9
3	0.75	13.3	0.75

k_{-1} describes the probability per sec that the excited atom loses its energy in a quenching collision with a flame particle.

$A^{-1}k_{-1}$ is the number of quenching collisions during the natural lifetime of the excited state.

pA^{-1} is the actual lifetime of the excited state.

Moreover, it was checked that the corrected re-emission radiation was indeed due to flame fluorescence because it did decrease when the argon in the flame was replaced by N_2 as diluent gas, which has a much larger quenching efficiency (see below).

Table 2 lists the measured experimental values of the fluorescence yield factor p ; the calculated number of quenching collisions during the natural lifetime of the excited state, k_{-1}/A ; and the actual lifetime, p/A , of excited OH radicals in the flame investigated. The p values listed are average values obtained by repeating the measurements at least 15 times.

The value of the radiative transition probability of the considered fluorescent rotational lines, $A = 1.05 \cdot 10^6 \text{ sec}^{-1}$, used in the evaluation of our experimental data has been determined by BENNETT and DALBY⁽¹⁵⁾ from measurements on excited OH radicals produced by electron bombardment, allowing for the effect of vibration-rotation interaction according to LEARNER's data⁽²³⁾ (see Appendix to Ref. 5).

4. DERIVATION OF SPECIFIC QUENCHING CROSS SECTIONS

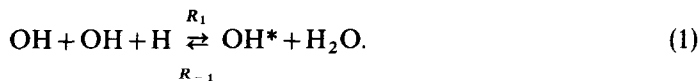
From the linear expressions that express p as a function of the partial pressure of the relevant flame particles, and from our knowledge of the p values as listed in Table 2, we have derived the so-called effective quenching cross section S (cf. Refs. 4 and 5) of excited OH (${}^2\Sigma$) molecules in collision with N_2 , H_2O and O_2 molecules. Each flame with known composition yields one equation of this type. The values of specific cross sections that provide a best fit for all flames investigated are, for O_2 : $(10 \pm 2) \text{ \AA}^2$; for H_2O : $(37 \pm 6) \text{ \AA}^2$; for N_2 : $(7 \pm 1) \text{ \AA}^2$, and are valid for a flame temperature of about 1500–1800°K (see Table 1). It was supposed that the contribution of the Argon atoms to k_{-1} could be disregarded when compared with the total contribution of the other, predominant flame molecules H_2O , O_2 and N_2 (cf. Ref. 14).

5. COMPARISON WITH LITERATURE DATA AND CONCLUSIONS

Very little written data is available concerning the values of quenching cross sections of excited OH ($^2\Sigma$) molecules in collision with O₂ and H₂O molecules and Ar atoms, whereas for N₂ no quenching cross section is available at all. CARRINGTON reported values for the quenching of OH ($^2\Sigma$) radicals by O₂, CO₂ and H₂O molecules obtained from his investigations on an acetylene-oxygen flame at a pressure of 3.5 mm Hg. These values appeared (after correction for the difference in the value of $A = 1.7 \cdot 10^6 \text{ sec}^{-1}$ used by CARRINGTON⁽¹⁴⁾ and the recent value $A = 1.05 \cdot 10^6 \text{ sec}^{-1}$ used by us) to be less than our quenching cross sections for O₂ and H₂O by about a factor of 2.5. CARRINGTON's specific cross sections for O₂, CO₂ and H₂O were deduced by linear extrapolation of the reciprocal p -values (measured with different pressure and composition of supplied gases) to zero partial pressure of acetylene in acetylene flames rich in O₂, (O₂+H₂O) and (O₂+CO₂), respectively. The validity of this method might be doubted, however, because it neglects any T -dependence of these cross sections in the large range of flame temperatures used in this extrapolation (800–1500°K). Moreover, Carrington's S -values for O₂, CO₂ and H₂O seem to contradict the value $p = 0.08$ actually measured by him in an oxygen-rich acetylene flame (ratio O₂/C₂H₂ = 8; $T = 1500^\circ\text{K}$; for flame characteristics see Ref. 14). Using his S -values for this flame and disregarding the contribution of the minor flame species such as CO, H₂, O, H, OH), we calculated a value $p = 0.4$. In order to bring this value into agreement with his experimental p -value, one would have to assume an average effective cross section for all the other minor flame species of the order 170 \AA^2 which seems rather high. This may suggest that the S -values found by Carrington for H₂O, O₂ and CO₂ are too low, which is also suggested by the results of our experiments for H₂ and O₂. So it seems that the procedure of extrapolating to zero acetylene pressure should be applied with caution.

It is noted that the quenching effect of H₂O is about 4–5 times as large as that of O₂ and N₂, which is in sharp contrast with the very low efficiency of H₂O in the quenching of excited alkali-atoms. Also recent experiments⁽¹⁵⁾ on the quenching of excited OH ($^2\Sigma$) radicals by H₂O molecules at 315°K point to a comparatively large quenching cross section value $S = (70 \pm 15) \text{ \AA}^2$. In these experiments the OH radicals are produced by bombardment of H₂O molecules with 200 eV electrons at various low pressures ($\approx 10 \mu\text{Hg}$).

It may be interesting to investigate how far this large cross section of H₂O as quencher of OH is related to possible dissociative quenching processes. Zeegers has determined experimentally the formation of excited OH* ($^2\Sigma$) in flames similar to ours, according to the reaction:



The value p of the fluorescence yield factor found by us and the value of pR_1 found experimentally in Zeegers' investigations, where R_1 represents the absolute rate constant of the formation of OH from reaction (1), enables us to compute the relative contribution of dissociative quenching to the total (dissociative + collisional) quenching of OH* by H₂O.

Denoting the rate constant of the reverse reaction (1) by R_{-1} we have, applying detailed balancing,

$$R_{-1}/R_1 = K_1 \cdot Z_{\text{tot}}/Z_0 \quad (2)$$

where

$$K_1 = \frac{[\text{H}]_{\text{eq}}[\text{OH}]_{\text{eq}}}{[\text{H}_2\text{O}]_{\text{eq}}}$$

stands for the dissociation constant of the equilibrium $\text{H} + \text{OH} \rightleftharpoons \text{H}_2\text{O}$.

Z_{tot} is the total state sum of the OH radical at flame temperature which can be approximated by^(22,24)

$$Z_{\text{tot}} = [kTg_0/hcB_0] \{1 - \exp(-hc\omega_0/kT)\}^{-1} \quad (3)$$

where B_0 and ω_0 are the rotational and vibrational constants, respectively, and g_0 is the statistical weight of the electronic ground state ${}^2\Pi$. Z_0 is the rotational state sum for the lowest vibrational level $v' = 0$ of the ${}^2\Sigma$ state. For sufficiently large T values this sum can be replaced by^(22,24)

$$Z_0 = [kTg_1/hcB_1] \exp(-E_0/kT).$$

where g_1 is the statistical weight of the excited state ${}^2\Sigma$, and B_1 is the rotational constant of this state. E_0 is the energy of the lowest rotational level of the (${}^2\Sigma$, $v' = 0$) state.

Inserting in equation (2) the value R_1 , which can be deduced[†] from the measured values of p and of pR_1 (see above), we find R_{-1} from K_1 , Z_{tot} and Z_0 . Hence we obtain for the relative contribution of dissociative quenching $R_{-1}[\text{H}_2\text{O}]$ ($[\text{H}_2\text{O}]$ stands for the H_2O concentration in the flame) to the total quenching of OH^* by H_2O molecules.

$$\frac{R_{-1}[\text{H}_2\text{O}]}{k_{-1}^{\text{H}_2\text{O}}} = 0.05,$$

where $k_{-1}^{\text{H}_2\text{O}}$ is the collisional plus dissociative quenching rate by H_2O , which is directly connected to the specific quenching cross section $S_{\text{H}_2\text{O}}$ measured by us and mentioned above. It should be noted that R_{-1} is expected to increase markedly with increasing flame temperature according to the above relation for R_{-1}/R_1 , the right hand side of which involves two exponential temperature factors which combine to $\exp(-(D-E_0)/kT)$. Here $(D-E_0) = 1.12$ eV is the difference between the dissociation energy D of the H_2O molecule into $\text{H} + \text{OH}$ and the energy E_0 of the excited OH state considered. Since all other factors as well as the contribution of inelastic collisions with H_2O molecules to the OH quenching rate are not expected to depend critically on flame temperature, the ratio of the dissociative quenching rate to the collisional quenching rate by H_2O molecules involves an activation energy of about 1.1 eV. This ratio is therefore expected to double whenever the flame temperature is raised by 200°K.

Another possibility of chemical quenching of OH^* by H_2O has been suggested by Carrington. Thus OH (${}^2\Sigma$) is reported to be quenched by the following reaction involving oxygen abstraction, which is exothermic by about 1.5 eV and is not forbidden by spin conservation rules, viz.



[†] In the calculation of R_{-1} it is implicitly assumed that the value of the fluorescence yield factor found in our study hardly differs from the effective p -value occurring in the product $R_{-1}p$ measured by Zeegers, though this product refers to the (0, 0) band as a whole, whereas our p -values refer to some specific rotational transitions.

However, from the analysis of the chemiluminescent OH-excitation mentioned above, and by applying detailed balancing, it follows that the latter quenching reaction is certainly not predominant in our flames, when compared to the above discussed dissociative quenching reaction (1). Because of these considerations we may conclude that under our flame conditions the quenching of OH radicals by O₂, N₂ and H₂O molecules is mainly governed by collisional quenching in which the quenching molecule carries off the excitation energy without chemical reaction.

Finally, we note that the large quenching cross sections and the resultant short lifetime of excited OH (²Σ) radicals in flames of 1 atm pressure (see Table 2) explain the spectroscopically observed persistence of the initial non-equilibrium rotational distribution produced during the formation of the excited OH radicals without having to assume an unusually slow rotational relaxation on the part of excited OH radicals. The probability that a photon is emitted after rotational-translational energy transfer has taken place under our flame conditions, will be at most of the order of 0.1 since this is the ratio of the actual radiative lifetime to the rotational relaxation time. In view of the high efficiency of quenching collisions (which are about as frequent as "kinetical" collisions), this probability might even be considerably lower than 0.1, because the probability of a collision leading only to rotational-translational energy transfer without simultaneous quenching is expected to be small.

Acknowledgement—The authors are indebted to Mr. W. van Dijk for his valuable assistance in the experimental work.

REFERENCES

1. A. L. BOERS, C. TH. J. ALKEMADE and J. A. SMIT, *Physica*, **22**, 358 (1956).
2. C. TH. J. ALKEMADE, *Proceedings of the Xth Coll. Spectr. In.*, Spartan Books, Washington, 143 (1963).
3. H. P. HOOYMAYERS and C. TH. J. ALKEMADE, *JRSRT* **6**, 501 (1966).
4. H. P. HOOYMAYERS and C. TH. J. ALKEMADE, *JQSRT* **6**, 847 (1966).
5. H. P. HOOYMAYERS, Thesis, University of Utrecht (1966).
6. P. J. TH. ZEEGERS and C. TH. J. ALKEMADE, *Combust. Flame* **9**, No. 3 (1965).
7. P. J. TH. ZEEGERS and C. TH. J. ALKEMADE, *Tenth Symposium (International) on Combustion*, p. 33, Combustion Institute, Pittsburgh (1965).
8. P. J. TH. ZEEGERS, Thesis, University of Utrecht (1966).
9. H. P. BROIDA and D. F. HEATH, *J. Chem. Phys.* **2**, 6, 223 (1957).
10. A. G. GAYDON and H. G. WOLFARD, *Proc. R. Soc. A* **194**, 169 (1948).
11. W. R. KANE and H. P. BROIDA, *J. Chem. Phys.* **21**, 347 (1953).
12. H. P. BROIDA and H. J. HOSTKOWSKI, *J. Chem. Phys.* **25**, 676 (1956).
13. H. P. BROIDA and T. CARRINGTON, *J. Chem. Phys.* **23**, 2202 (1955).
14. T. CARRINGTON, *J.C.P.* **30**, 1087 (1959).
15. R. G. BENNET and F. W. DALBY, *J. Chem. Phys.* **40**, 1414 (1964).
16. S. H. DIEKE and H. M. CROSSWHITE, *JQSRT* **2**, 97 (1961); first published as Bumblebee Series Report, No. 87 (1948).
17. A. C. G. MITCHELL and M. W. ZEMANSKY, *Resonance Radiation and Excited Atoms*, 2nd edn., Cambridge University Press (1961).
18. W. E. KASKAN, *J. Chem. Phys.* **29**, 1420 (1958).
19. R. HERRMANN and C. TH. J. ALKEMADE, *Flammenphotometrie*, 2nd edn., Springer, Göttingen, 1960; translated into English by P. T. Gilbert, Interscience, New York (1963).
20. A. B. CALLEAR, *Appl. Opt. Suppl. on Chem. Lasers*, 145 (1965).
21. G. C. COWAN and D. F. HORNIG, *J. Chem. Phys.* **18**, 1008 (1950).
22. G. HERZBERG, *Spectra of Diatomic Molecules*, 2nd edn., van Nostrand, New York (1950).
23. R. C. M. LEARNER, *Proc. R. Soc. A* **269**, 311 (1962).
24. J. A. SMIT, Thesis, University of Utrecht (1950).