Measurement of the Natural Lifetimes and Quenching Rate Constants of OH ($^2\Sigma^+$, $v = 0{,}1$) and OD ($^2\Sigma^+$, $v = 0{,}1$) Radicals

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The lifetimes of OH ($^2\Sigma^+$) and OD ($^2\Sigma^+$) radicals were measured by using pulse-photolysis of water and methanol in the vacuum-uv for the production of the electronically excited radicals. From the fluorescence decay measurements the natural lifetimes, as well as the quenching rate constants for several added gases such as H_2O, CH_3OH, H_2, N_2, Ar, and He were determined. In particular, the natural lifetime of OH ($^2\Sigma^+$, $v = 0$), $\tau = (1.00 \pm 0.06) \cdot 10^{-6}$ s, was corrected for rotation-vibration as well as for rotation-electronic interactions resulting in a lifetime of $(0.83 \pm 0.08) \cdot 10^{-6}$ s for the rotationless state. A lifetime of $(0.82 \pm 0.08) \cdot 10^{-6}$ s was derived for the rotationless state of OD ($^2\Sigma^+$, $v = 0$).

Introduction

Numerous experimental investigations have been carried out to determine the spontaneous transition probability or the natural lifetime[1–3] and the f-value[4–10] of the OH ($A^2\Sigma^+ \rightarrow X^2\Pi_i$) (0.0) transition; however, there is still a considerable spread in the published data.

The first published value of the natural lifetime, $\tau = (1.01 \pm 0.05) \cdot 10^{-6}$ s, corresponding to an oscillator strength, $f = (7.25 \pm 0.5) \cdot 10^{-4}$, was measured by Bennett and Dalby[1]. Their method was principally based upon the direct lifetime measurements of OH ($A^2\Sigma^+$) excited by electron pulse bombardment of water or methanol. Recently German and Zare[2] derived a natural lifetime of $(0.77 \pm 0.08) \cdot 10^{-6}$ s for the $\sqrt{N'} = 2$, $J' = 3/2$ rotational level of OH ($A^2\Sigma^+, v' = 0$) from their ORFDOR method (optical radio frequency double resonance) of measuring g-values by using the $g \cdot \tau$ data given by Marshall et al.[11] and German and Zare[12]. This lifetime corresponds to a band oscillator strength of $(9.3 \pm 1.0) \cdot 10^{-4}$.

More recently, Smith[3] has published a lifetime $\tau = (0.85 + 0.13) \cdot 10^{-6}$ s from phase shift measurements using a rf-modulated beam of 200 eV electrons to excite the OH radicals. His lifetime is equivalent to a f-number of $(7.7 \pm 1.1) \cdot 10^{-4}$. Golden et al.[8] determined a f-value of $(7.1 \pm 1.1) \cdot 10^{-4}$ by careful absorption measurements. Their value does not agree with most of the results from former absorption experiments which gave f-value from $5.4 \cdot 10^{-4}$ to $13.0 \cdot 10^{-4}$ [4,5,6,7]. These former absorption measurements had to be corrected by more recent thermodynamic properties of OH as well as by rotational-vibrational interaction and the dependence of the electronic transition moment on the internuclear distance[13,14,15] because of the high temperatures at which these experiments were carried out.

The quenching rate constants for OH ($^2\Sigma^+$) radicals were previously determined by direct lifetime measurements[1] as well as by measuring the quenching of the OH emission under static conditions in photolysis experiments[16,17,18] or in flames[19,20,21].

In the present experiments we have measured the lifetimes of OH ($A^2\Sigma^+$) radicals which were produced by pulse-photolysis of H_2O with the 1236 Å Kr-resonance line. The photolysis of water leads partly to the formation of electronically excited OH radicals[16,22] according to reaction (1) with a characteristic non-thermal rotational energy distribution[23,24,17].

$$H_2O + h\nu\,(1236\ \text{Å}) \rightarrow OH\,(A^2\Sigma^+,\ v' = 0;\,1) + H \quad (1)$$

The photolysis of methanol at 1236 Å has also been used for the formation of electronically excited OH radicals[16].

The formation of excited OH radicals by pulse-photolysis of H_2O or CH_3OH has the advantage of populating well defined quantum states of OH, avoiding any cascading from higher electronic states, which causes difficulties in many electron bombardment experiments.

Similar lifetime measurements on SH ($A^2\Sigma^+$) radicals which were formed by pulse-photolysis of H_2S have been published very recently[25].

Experimental

A schematic diagram of the apparatus is shown in *Figure 1*. Its principal feature is a rotating disc of 24 cm in diameter in which 72 slits of 10 mm length and 1 mm width which were cut at equal distances apart, with high precision. Covered by an evacuated housing the chopper reached a revolving frequency of 500 Hz. Mo-

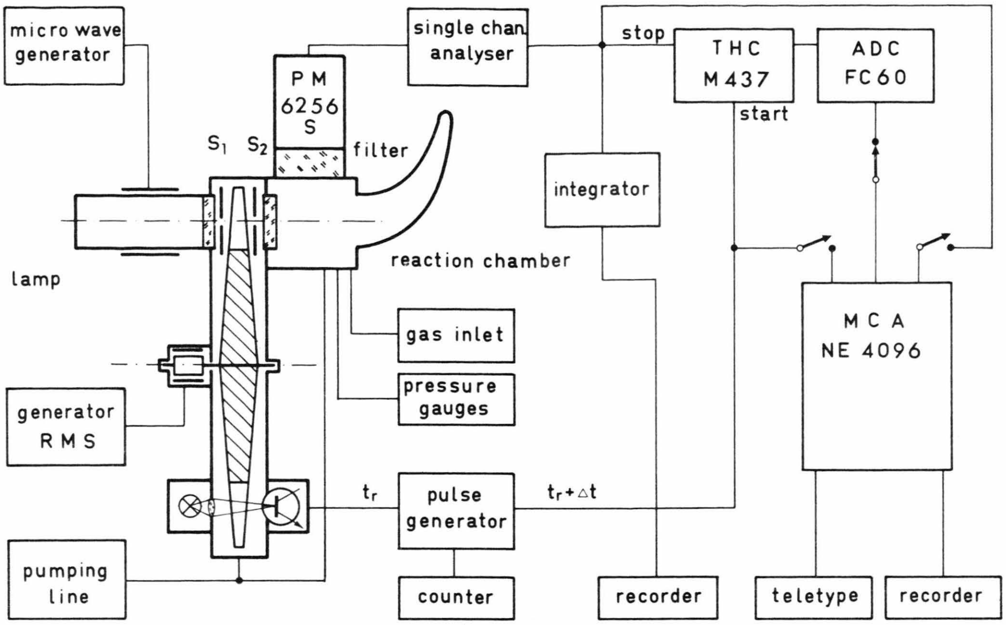

Fig. 1

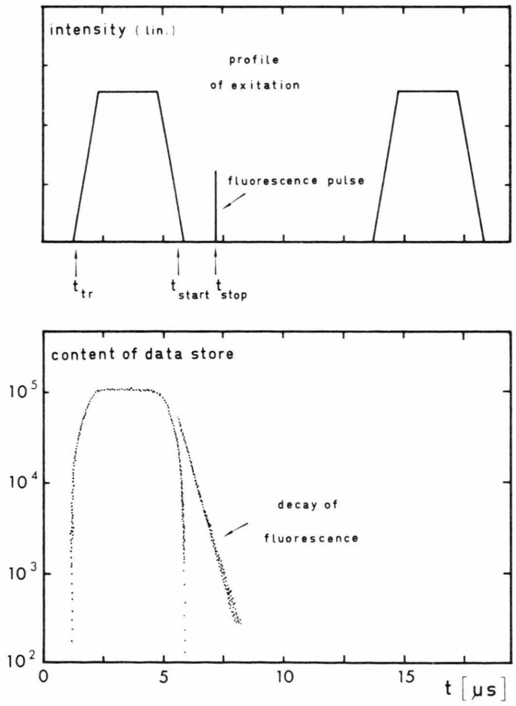

Fig. 2

dulating the light beam from a rare gas resonance lamp by this mechanical chopper gave a trapezoidal time profile as shown in *Figure 2*. The total rise and fall time of the light pulse was about $0.6 \cdot 10^{-6}$ s. A conventional resonance lamp[26, 27] attached to the chopper housing was operated by a microwave discharge in krypton emitting the 1236 Å resonance line. The fluorescence produced by the H_2O photolysis in the fluorescence chamber was detected by means of a cooled EMI 6256-S photomultiplier together with an interference filter. In the case of OH as well as OD, for the (0.0) band a UVR 310 reflection filter Schott und Gen. ($\Delta\lambda = 300$ Å) was used. The (1.0) band was detected by means of a Corion interference filter ($\lambda_0 = 2850$ Å, $\Delta\lambda = 80$ Å).

In order to improve the signal-to-noise ratio the output of the photomultiplier was fed into a single channel analyser[28]. Under steady state conditions the time averaged fluorescence intensity was registered, after proper amplification and integration of the signal pulses, on a strip chart recorder.

The time dependent fluorescence decay was measured by using the "single photon detection method"[29]. For this purpose the experimental set-up consisted of a time-to-pulse-height converter (Ortec Model 437), an analog digital converter (Laben FC-60), and a multi-channel analyser (NE 4096) in which the data were stored over a large number of scans. This arrangement was synchronized with the mechanical chopper by means of a variable delay line by which the "start" point of the time-to-pulse-height converter could be shifted from the beginning of the linear fall-off of the photolysis pulse to its end. A time resolution as short as $50 \cdot 10^{-9}$ s could be obtained by this method. The limitation was mostly caused by the signal-to-noise ratio and by a certain degree of fluctuation in the synchronization. *Figure 3* shows a sectional view of the chopper disc with the housing, the fluorescence chamber, and the rare gas resonance lamp. The experiments were carried out under static as well as under flow conditions. The water vapour pressure in the reaction chamber was measured in the range from 1.0 to 100 mTorr by a thermally stabilized capacitor manometer. Carefully distilled water and 99.9% grade deuterium oxide were used for the fluorescence experiments.

Results

The OH as well as the OD $(A^2\Sigma^+ \rightarrow X^2\Pi_i)$ (0.0) and (1.1) fluorescence spectra obtained by the water photolysis at 1236 Å are shown in Figure 4. The spectra were taken in the third order of a SPEX 1704 grating spectrometer with a resolution of $\Delta\lambda = 0.1$ Å. Most of the

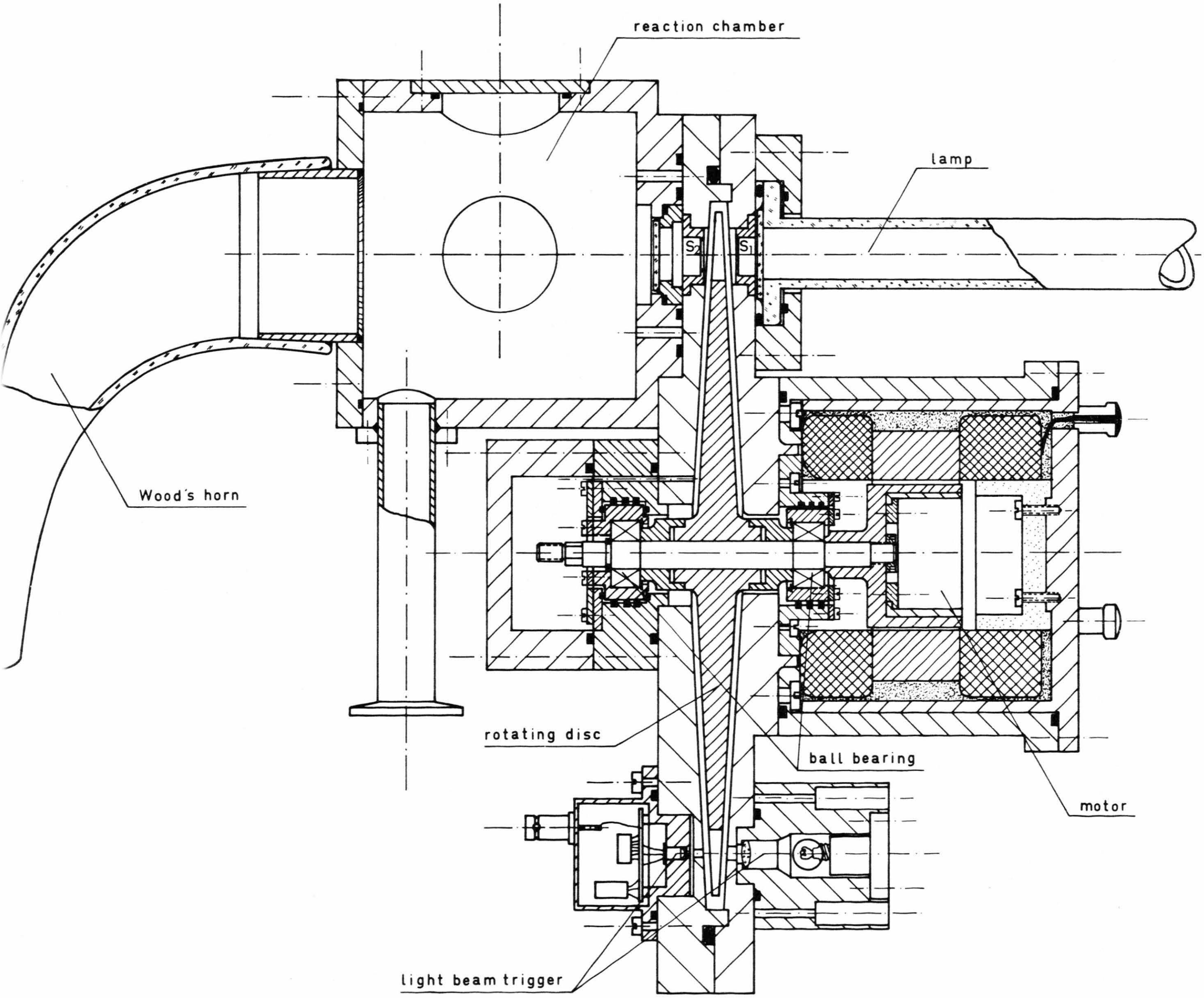

Fig. 3

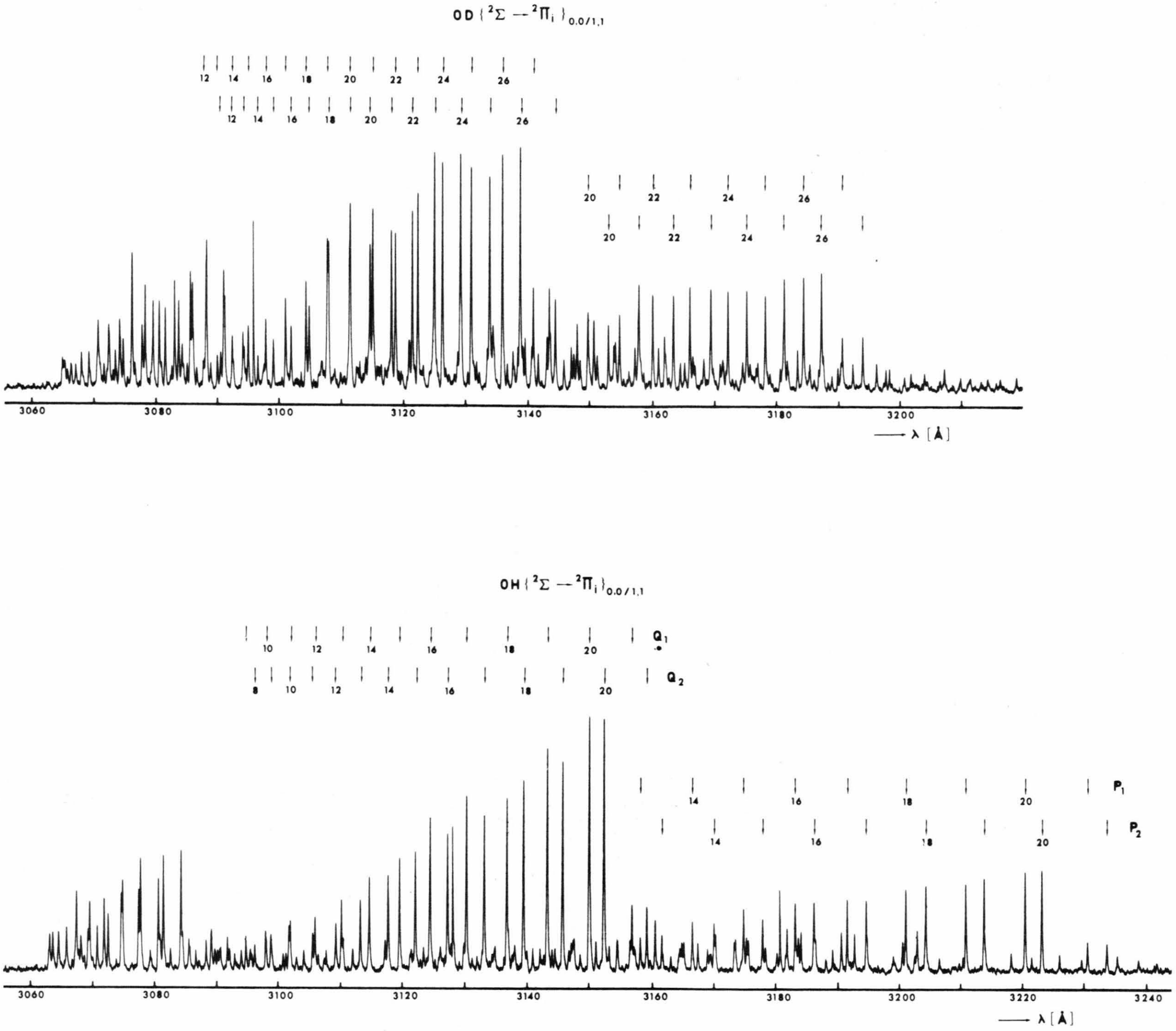

Fig. 4

intensity at 3100 Å is due to the (0.0) band with only about 10% from the (1.1) band. The (1.0) band can be observed at 2850 Å with approximately 1/10 of the (0.0) band intensity.

After pulse photolysis of water with the 1236 Å Kr-resonance line the excited OH or OD radicals can either be deactivated by radiation or by reactive as well as non-reactive bimolecular collisions. The collisional deactivation occurs by H_2O, k_3, and by collision partners M, k_4, which are added to the water. Wall deactivation of excited hydroxyl radicals and deactivation by collisions with H atoms or OH $(^2\Sigma^+)$ radicals can be excluded under the present experimental conditions:

$$\mathrm{OH}\,(^2\Sigma^+) \rightarrow \mathrm{OH}\,(^2\Pi_i) + h\nu; \quad k_2 \qquad (2)$$

$$\mathrm{OH}\,(^2\Sigma^+) + \mathrm{H_2O} \left[\begin{array}{l}\rightarrow \text{products}\\ \rightarrow \mathrm{OH}\,(^2\Pi_i) + \mathrm{H_2O};\end{array}\right. \quad k_3 \qquad (3)$$

$$\mathrm{OH}\,(^2\Sigma^+) + \mathrm{M} \left[\begin{array}{l}\rightarrow \text{products}\\ \rightarrow \mathrm{OH}\,(^2\Pi_i) + \mathrm{M};\end{array}\right. \quad k_4\,. \qquad (4)$$

For higher vibrational levels in the $^2\Sigma^+$ state relaxation processes have be included in reaction (4). Because of the excess of H_2O and M the decay of excited OH radicals or the fluorescence intersity, $I = K_2 \cdot (\mathrm{OH}(^2\Sigma^+))$, follows first order kinetics:

$$I_t = I_o \cdot \exp\{-K \cdot t\}$$

with $$K = K_2 + k_3\,(\mathrm{H_2O}) + k_4\,(\mathrm{M}).$$

The value of the first-order rate constant K can determined from the fluorescence decay curve.

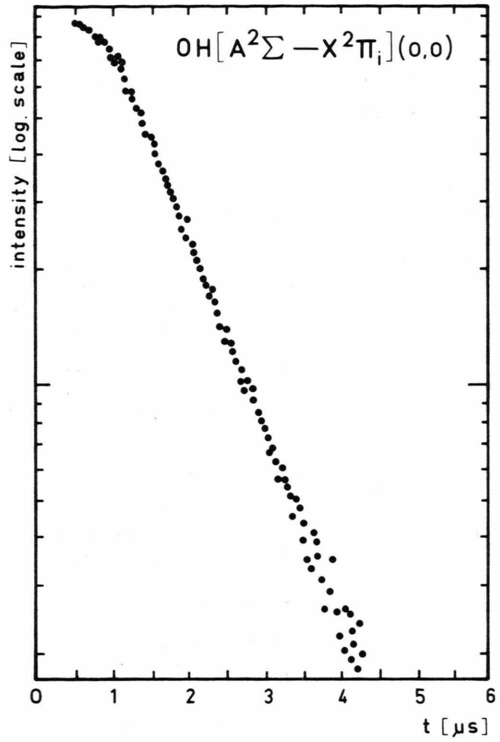

Fig. 5

In Figure 5 a typical decay curve of the OH fluorescence is shown using a semi-logarithmic scale. In Figure 6 (I) a plot of K versus the H_2O pressure is shown for OH ($^2\Sigma^+$, $v' = 0$). From the extrapolation to zero total pressure, $(\mathrm{H_2O}) = (\mathrm{M}) = 0$, the transition probability K_2 or the natural lifetime $\tau = 1/K_2$ of the excited state can be determined on the ordinate axis. The slope of K as a function of the partial pressure (H_2O) and (M) gives k_3 and k_4, respectively. These values were calculated by a least square fit of the experimental data.

Figure 6 (II) shows the dependence in the case of the methanol photolysis. In both cases a natural lifetime of $\tau = (1.00 \pm 0.06) \cdot 10^{-6}$ s was obtained.

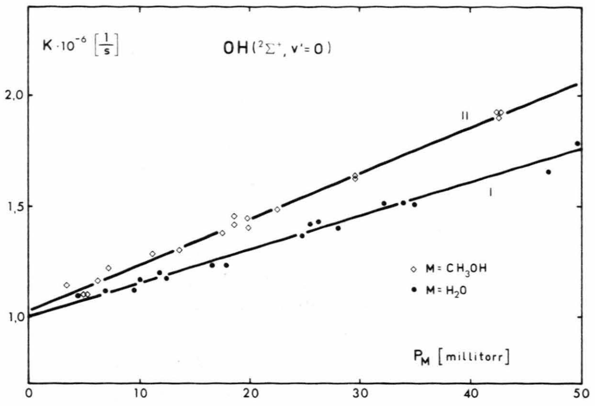

Fig. 6

Using the Franck-Condon factors $q_{ov''}$ calculated by LEARNER[14] and ANKETELL et al.[15] from Eq. (5) and making the assumption that $\sum |Re(r)|^2$ is constant,

$$f(0.0) = \frac{1}{\tau} \cdot \frac{g_{v'}}{g_{v''}} \cdot \frac{m\,c}{8\,\pi^2\,e^2}\,\frac{\nu_o\,q_{oo}}{\sum\limits_{v''} \tau^3_{o\,v''}\,q_{ov''}} \tag{5}$$

an uncorrected band oscillator strength of $f(0.0) = (7.2 \pm 0.6) \cdot 10^{-4}$ was derived. In Eq. (5) $g_{v'}$ and $g_{v''}$ are the statistical weights of degenerated supper and lower electronic states, respectively. $\nu_{J'J''}$ are the wavenumbers of particular (o. v'') bands.

The rate constants k_3 for the deactivation of OH ($^2\Sigma^+$, $v' = $ o) radicals by H_2O and CH_3OH were determined as

$$k^{v'=0}_{\mathrm{H_2O}} = (4.5 \pm 0.9) \cdot 10^{-10}\ \mathrm{cm^3 \cdot molecule^{-1}\,s^{-1}},$$

$$k^{v'=0}_{\mathrm{CH_3OH}} = (6.4 \pm 1.1) \cdot 10^{-10}\ \mathrm{cm^3 \cdot molecule^{-1}\,s^{-1}}.$$

Accordingly, the quenching cross-sections for H_2O and CH_3OH respectively, using the relation $k = \sigma \cdot \bar{v}$ with $\bar{v}$ as mean gas kinetic velocity have the values:

$$\sigma^{v'=0}_{\mathrm{H_2O}} = (53 \pm 10)\ \text{Å}^2, \quad \sigma^{v'=0}_{\mathrm{CH_3OH}} = (86 \pm 15)\ \text{Å}^2.$$

In the case of OH ($^2\Sigma^+$, $v' = 1$), a natural lifetime of $\tau = (0.92 \pm 0.07) \cdot 10^{-7}$ s was measured resulting in a band oscillator strength of $f_{10} = (2.7 \pm 0.5) \cdot 10^{-4}$ if Learner's Franck-Condon factors are used.

For the quenching rate constant and quenching cross-section with H_2O the following values were determined:

$$k^{v'=1}_{\mathrm{H_2O}} = (4.0 \pm 0.9) \cdot 10^{-10}\ \mathrm{cm^3 \cdot molecule^{-1} \cdot s^{-1}},$$

$$\sigma^{v'=1}_{\mathrm{H_2O}} = (47 \pm 10)\ \text{Å}^2.$$

In the pulse-photolysis experiment with D_2O the corresponding values for OD ($A^2\Sigma^+$) were also determined.

Table 2. Oscillator strength f_{oo} and $f_{oo}{}^o$ of the transition ($^2\Sigma^+ - {}^2\Pi_i$).

band	methode	$f_{oo} \cdot 10^4$	$f_{oo}{}^o$	reference
OH (0.0)	absorption measuremtens on $H_2O_2 + O_2$, 1473 °K	(12.3 ± 1.8)	(9.5 ± 1.4)	(4)
	absorption measurements on $H_2 + O_2$, 1360–1460 °K	(6.4 ± 1.3)	(5.4 ± 1.0)	(5)
	absorption measurements on $H_2 + O_2$-flames, 2660 °K	(13.0 ± 5.2)	(10.7 ± 4.3)	(6)
	shock-tube 3300–3900 °K	(9.0 ± 5.0)	(10.0 ± 6.0)	(7)
	absorption measurements on $H + NO_2$, 320 °K	(7.1 ± 1.1)	(7.1 ± 1.1)	(8)
	shock-tube	(39 ± 9)	—	(9)
	hook-methode	(14.8 ± 1.3)	—	(10)
	Hanle-effect	(9.3 ± 1.0)	(9.3 ± 1.0)	(2)
	lifetimes measurements $H_2O + e^-$	(7.25 ± 0.6)	(8.0 ± 0.8)	(1)
	lifetimes measurements $H_2O + e^-$	(7.7 ± 1.1)	—	(3)
	lifetimes measurements $H_2O + hr$ (1236 Å)	(7.2 ± 0.6)	(8.6 ± 0.8)	this work
OH (1.0)	hook-methode	(8.9 ± 1.7)	—	(10)
	lifetime measurements $H_2O + hr$ (1236 Å)	(2.7 ± 0.9)	—	this work
OD (0.0)	lifetime measurements $D_2O + hr$ (1236 Å)	(7.2 ± 0.6)	(8.6 ± 0.8)	this work

Table 3. Quenching rate constants and cross sections of the reaction OH ($^2\Sigma^+$; $v' = 0$) + M
k: [10^{-10} cm^3 molecule^{-1} s^{-1}] (first number) σ: [Å^2] (second number).

H_2O	CH_3OH	H_2	D_2	N_2	CO	CO_2	O_2	He	Ar	reference
—	—	0.06	—	0.005	0.12	—	—	—	0.002	(16)
—	—	0.3	—	0.06	1.6	—	—	—	0.03	(16)
3.0	—	—	—	—	—	1.1	0.46	—	0.14	(19)
35	—	—	—	—	—	16	7	—	2	(19)
6	8	—	—	—	—	—	—	—	—	(1)
(70 ± 15)	(110 ± 45)	—	—	—	—	—	—	—	—	
3.2	—	—	—	0.53	—	—	0.66	—	—	(20)
(37 ± 6)	—	—	—	(7 ± 1)	—	—	(10 ± 2)	—	—	
5.0	—	0.6	0.4	0.4	3.0	—	—	0.1	—	(18)
57	—	3	3	5	36	—	—	0.8	—	
2.5	—	—	—	0.05	—	—	—	<0.002	<0.002	
33.5	—	—	—	0.66	—	—	—	<0.01	<0.01	(17)
—	—	1.0	—	—	1.7	—	—	—	—	(27)
—	—	5.3	—	—	27	—	—	—	—	
4.5	6.4	0.65	—	0.1	—	—	—	<0.01	0.01	this work
(53 ± 10)	(86 ± 15)	(3.4 ± 0.5)	—	(1.3 ± 0.6)	—	—	—	<0.07	0.05	

Table 1. Natural lifetimes and quenching rate constants for electronically exited OH and OD radicals by parent molecules.

	τ: [10^{-6} s]	parent molecule	k_M: [10^{-10} cm^3 molecule^{-1} s^{-1}]	σ_M: [Å^2]	reference	
OH ($^2\Sigma^+$, $v' + 0$)	1.01 ± 0.05	H_2O	—	70 ± 15	Benett et al.	(1)
	1.01 ± 0.05	CH_3OH	—	110 ± 45		
	0.85 ± 0.13	H_2O		—	Smith	(3)
	0.77 ± 0.08	—	—	—	Zare et al.	(2)
	1.00 ± 0.06	H_2O	4.5 ± 0.9	53 ± 10	this work	
	0.97 ± 0.06	CH_3OH	6.4 ± 1.1	86 ± 15		
OH ($^2\Sigma^+$, $v' = 1$)	0.75 ± 0.12	H_2O	—	—	Smith	(3)
	0.92 ± 0.07	H_2O	4.0 ± 0.9	47 ± 10	this work	
OD ($^2\Sigma^+$, $v' = 1$)	1.00 ± 0.06	D_2O	4.1 ± 0.9	50 ± 10	this work	
OD ($^2\Sigma^+$, $v' = 1$)	1.04 ± 0.08	D_2O	3.8 ± 0.8	47 ± 10	this work	

Our results are summarized in Table 1, Table 2, and Table 3, together with the data previously published by other authors.

Discussion

The natural lifetime of OH ($^2\Sigma^+, v = o$) obtained by the present measurements is in good agreement with the results of BENNETT and DALBY[1]; but our results are somewhat different from these of SMITH[3] and GERMAN and ZARE[2].

In contrast to our findings, SMITH[3] did not observe any pressure dependence of the first order rate constant K in the region of 0.5 to 5 mTorr. If the lifetime value measured by SMITH[3] is corrected for quenching, applying our quenching rate constant for H_2O at a water pressure of 5 mTorr, a value of $\tau = 0.92\ 10^{-6}$ s is obtained. With this correction both lifetime values agree within the experimental error limits. The lifetime measured by GERMAN and ZARE[2] lies definitely outside the error limit of the present results. This lifetime was determined for the rotational level $N' = 2$, $J' = 3/2$, a rather low rotational quantum state. In contrast, our value was measured for rotationally "hot" OH (Σ^+, $v = o$) radicals integrated over all J' levels which are shown in the spectra of Figure 4.

As was recently shown[14], in molecules such as OH the Born-Oppenheimer approximation is not regidly valid because the electronic transition moment $\sum |Re|^2$ and the Franck-Condon factors $q_{v'v''}$ are not independent of the internuclear distance It was pointed out by LEARNER[14] and by ANKETELL et al.[15], and more recently by CHAKRABORTY et al.[31] that for hydrides or deuterides such as OH and OD, rotation vibration interaction has also to be taken into account.

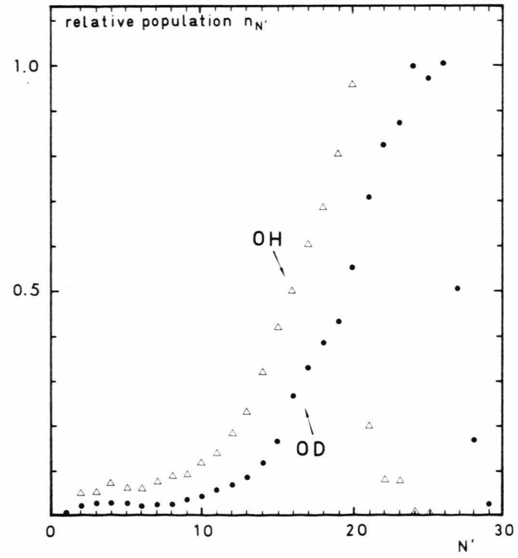

Fig. 7

Accordingly, the electronic transition moment and the Franck-Condon factors depend on the rotational quantum number of the radical. As a consequence, the transition probability decreases with increasing quantum numbers N' or J'. If the lifetime of an excited state is measured, the result depends on the rotational energy distribution and on the spectral sensitivity of the detection system. In our case, the detection sensitivity is constant over the spectral region of 3050 to 3220 Å within 5%.

Our experimentally determined lifetime had to be corrected by a certain factor Z to obtain the lifetime of a rotationless state.

The average transition probability A_1 from a state with a given rotational distribution is expressed by relation (6)[32]:

$$\bar{A}_1 = \frac{1}{\tau} \tag{6}$$

$$= \frac{\displaystyle\sum_{v''} \sum_{J'J''} \frac{64\,\pi^4 \nu^3 q^{J'J''}_{v'v''} \sum |Re\,(r^{J'J''}_{v'v''})|^2\, S_{J'J''}\, n_{J'}}{3\,h\,c^3\,(2J'+1)\,(2-\delta_{o,\Lambda'})\,(2S+1)}}{\displaystyle\sum_{J'} n_J{}'}$$

$q^{J'J''}_{v'v''}$ and $Re\,(\bar{r}^{J'J''}_{v'v''})$ are the Franck-Condon factors and the electronic part of the transition moment. Both are dependent on J.

The product $q^{J'J''}_{v'v''} \cdot \sum |Re\,(\bar{r}^{J'J''}_{v'v''})|^2$ is usually defined as $p^{J'J''}_{v'v''}$ the relative transition probability[14]. Relative values of $p^{J'J''}_{v'v''}$ for OH and OD were taken from Learner[14]. $S_{J'J''}$ is the so-called rotational line strength taken from SCHADEE[32] and SCHULZ and LE CERF[33], and $n_{J'}$ the relative rotational population of the states with the quantum number J'. Their populations were calculated from our OH spectra using Eq. (7).

$$n_{J'} = I^{J'J''}_{oo} \frac{(2J'+1)}{\nu^3 p^{J'J''}_{oo} \cdot S_{J'J''}}. \tag{7}$$

The results are shown in Fig. 7 for OH ($^2\Sigma^+, v' = 0$) and OD ($^2\Sigma^+\ v' = 0$), but with notation of the quantum number N' as commonly used for the rotational state of the coupling case b not considering the spin component.

In the case of OH and OD, the sum of all relative transition probabilities $p^{J'J''}_{v'v''}$ of the $v' = 0, v'' \neq 0$ progression is only about 2% of the (0.0) transition probability. Thus Eq. (7) can be simplified to:

$$\bar{A}_1 = \frac{\sum\limits_{J'J''} \dfrac{64\,\pi^4\,\nu^3\,p_{\mathrm{o,o}}^{J'J''}\,S_{J'J''}\,n_{J'}}{3\,h\,c^3\,(2\,J'+1)\,(2-\delta_{\mathrm{o},\,\Lambda'})\,(2\,S+1)}}{\sum\limits_{J'} n_{J'}} \tag{8}$$

Disregarding the dependence of $p_{\mathrm{o,o}}^{J'J''}$ on rotational quantum number J', one can define a band transition propability $\bar{A}_2$:

$$\bar{A}_2 = \frac{\sum\limits_{J'J''} \dfrac{64\,\pi\,\nu^3\,S_{J'J''}\,n_{J'}}{3\,h\,c^3\,(2\,J'+1)\,(2-\delta_{\mathrm{o},\,\Lambda'})\,(2\,S+1)}}{\sum\limits_{J'} n_{J'}}\,. \tag{9}$$

The ratio of $\bar{A}_1$ and $\bar{A}_2$ is the correcting factor Z by which the lifetime has to be multiplied in order to obtain the lifetime of a rotationless state of OH ($^2\Sigma^+$, $v' = \mathrm{o}$). This factor Z was calculated for the $v' = 0$ level of electronically excited OH and OD radicals using a 370–165 IBM computer; values of $Z_{\mathrm{OH}} = 0.83$ and $Z_{\mathrm{OD}} = 0.82$ were obtained. The correction of our experimentally determined OH ($^2\Sigma^+$, $v = \mathrm{o}$) lifetime leads to a lifetime of $(0.83 \pm 0.08) \cdot 10^{-6}$ s and a corresponding oscillator strength of $(8.5 \pm 0.8) \cdot 10^{-4}$ for the rotationless state in excellent agreement with the results of GERMAN and ZARE[2]. In the case of OD ($^2\Sigma^+$, $v = 0$) for the rotationless state a lifetime of $(0.82 \pm 0.08) \cdot 10^{-6}$ s and an oscillator strenght of $(8.5 \pm 0.8) \cdot 10^{-4}$ were derived.

The OH excitation by bombardement of H_2O with 20–60 eV electrons produces a rotational distribution similar to that from the H_2O photolysis at 1236 Å[34]. Accordingly, the agreement of our uncorrected OH lifetime with that from BENNET and DALBY's experiment had to be expected.

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Note added in proof:

Our calculated lifetime of OH ($^2\Sigma^+$, $v' = 0$), $\tau = (0.83 \pm 0.08)\ 10^{-6}$ s, for low N' values agrees very well with recent results of SUTHERLAND and ANDERSON[35] and ELMENGREEN and SMITH[36]. Recently we obtained in our laboratory an experimental value of $\tau = (0.82 \pm 0.06)\ 10^{-6}$ s for the $N' = 2$ state[37].