

OH LIFETIME MEASUREMENTS OF SEVERAL K LEVELS IN THE $\nu' = 1$ MANIFOLD OF THE $A^2\Sigma^+$ ELECTRONIC STATE: EXCITATION VIA A TUNABLE UV LASER

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Reported are OH lifetime measurements of several different K' levels in the $\nu' = 1$ manifold of the $A^2\Sigma^+$ electronic state. These measurements are the first to be reported using an excitation source which populated only single K' levels in the $\nu' = 1$ manifold. The excitation source in this case consisted of a frequency doubled tunable dye laser with a 0.25 Å line width at ≈ 2825 Å. The dye laser itself was driven by a Q -switched frequency doubled neodymium glass laser, having a nominal output energy of 250 mJ per pulse. The average lifetime found for the K' levels, 0, 1, 2, and 4 was 687 ± 24 ns. When corrected for quenching by H_2 and Ar, the average value becomes 765 ± 34 ns.

1. Introduction

The natural lifetime of OH in the electronically excited $A^2\Sigma^+$ state has been the subject of several investigations over the last 15 years [1-8]. These studies, which have concentrated primarily on the lifetime of the $\nu' = 0$ vibrational state, report lifetime values ranging from one half to one microsecond. In all cases, OH was excited to a multitude of rotational levels in the $A^2\Sigma^+$ state by means of burning gases, microwave discharges, or pulse photolysis. OH fluorescence lifetimes were then normally measured for the entire rotational manifold involved, although in two later cases [6, 7] a high resolution monochromator was employed to detect fluorescence from individually excited rotational states. Even here, however, it was possible that lifetime measurements could have been influenced by cascading from higher rotational levels, since the entire manifold had been populated.

We would like to report results from a recent laser

study which involved the selective populating of specific K levels in the $\nu' = 1$ manifold of the $A^2\Sigma^+$ electronic state. The natural lifetime of each K level was then determined by monitoring the fluorescence corresponding to the (1, 1) transition. Of considerable significance in this study was the fact that cascading problems were completely avoided as were any possible interactions between OH radicals (either excited or ground state) due to the very low concentration of OH employed, 10^8 - 10^9 cm $^{-3}$.

2. Experimental

A room temperature distribution of ground state OH was produced under steady-state conditions by means of ozone photolysis with a 2.5 kW xenon arc lamp. The relevant reactions in this system were:



Since the OH was formed under cw conditions it typically would undergo many thousands of collisions before being sampled by the OH laser probe. The resi-

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dence time of the OH formed in the aperture of the cw light source was primarily dictated by its time of diffusion out of this zone, typically 3 ms. Under these conditions the steady-state concentration of OH was in the range of 10^9 to 10^8 per cm^3 . However, concentrations of OH as low as 10^7 per cm^3 were detected in several cases where lifetime measurements were not being made. Once formed the OH was then excited to a distinct K' level in the $A^2\Sigma^+$, $v' = 1$ state using a frequency doubled tunable dye laser. This dye laser was transversely pumped with a 250 mJ intracavity doubled (5300 Å) neodymium glass laser. The dye laser output was narrowed to 3 Å with a 316 line/nm echelle grating used as a rear etalon, and was further narrowed to 0.3 Å by placing a narrow-gap Fabry-Pérot etalon within the dye laser cavity. Rhodamine 6G was used to achieve outputs of 15–20 mJ in the region 560–570 nm. This output was then frequency doubled to give ≈ 1 mJ pulses of 20 ns duration. The laser was tuned by directing the UV output into a 3/4 m spectrograph which was set for third order and gave a dispersion of 62 Å/inch at 2800 Å. The spectrograph was calibrated, using a Perkin-Elmer iron hollow-cathode lamp. Wavelength assignments were taken from Diecke and Crosswhite [9].

The fluorescence scatter chamber was designed to give a scattered light reduction factor of $\approx 10^{-10}$. The UV laser radiation entered the chamber through a 6" tubulation containing several collimating rings. A similar tubulation, uncollimated, was used at the exit window. The photolysis beam was rendered approximately parallel by placing a 2.4" focal length quartz lens at the focal length distance from the lamp cathode. Additional collimation was had by passing the beam through a set of 0.7" collimating rings. The beam entered the vessel at right angles to the laser probe and was trapped at the opposite side by a Wood's light horn. A similar horn was positioned directly above the detection system. Fluorescence decays were detected with an RCA 8850 photomultiplier tube fitted with a 150 Å 1/2 bw bandpass filter centered at 3125 Å for the 1–1 transition of OH. The photomultiplier tube output was coupled to a Tektronix 7623 storage oscilloscope which was fitted with a type C-27 polaroid camera. The time constant of the electronic sampling network was variable from 50 to 5 ns. All lifetime measurements were carried out using 20 ns time constants.

Because ozone is known to decompose relatively

rapidly on metal surfaces [10] an all glass reaction cell and gas handling manifold were used in this study. This laboratory has previously determined the rate of thermal decomposition of ozone in a glass cell to be 0.06 % per minute at room temperature [11]. The method of ozone preparation and the purification procedure have been described previously [11]. The hydrogen used in this study was Air Products Research Grade (99.999 %). The helium and argon were Matheson UHP Gold Label (99.999 %). In all cases, the reaction cell was evacuated to at least 1×10^{-5} torr before reactants were admitted to the cell. The gas handling system itself was typically pumped down to 10^{-7} torr. Reactant concentrations were measured on an MKS Baratron capacitance manometer where all pressure measurements could be made to 2 % or better.

3. Results and discussion

In all some 28 transitions were initially tuned across. These were found to be in good agreement with the calculated absorption intensities [9], using a Boltzmann distribution calculated for $T = 298$ K (i.e., $K'' = 1$, 22.5 %; $K'' = 2$, 27.0 %; $K'' = 3$, 22.8 %; $K'' = 4$, 15.0 %; $K'' = 5$, 7.8 %). Of those transitions which could be tuned to, four were selected for sampling which covered the K' levels of 0, 1, 2, and 4.

Fig. 1 shows a typical semi-logarithmic plot of the fluorescence signal measured from OH as a function of time. Experimental conditions in this case were Ar = 1 torr, $\text{H}_2 = 30$ mtorr and $\text{O}_3 = 10$ mtorr. The laser probe line was $Q_1(4)$, and the lifetime measured for the $K' = 4$ state was 0.670 ± 0.023 μs . The random error uncertainty quoted here is that for 3 standard deviations. Table 1 lists lifetime values for all four K' levels, measured under these same experimental conditions.

Quenching effects on the $v' = 1$ state of $^2\Sigma$ OH have been determined [13], using the Stern-Volmer equation

$$1/\tau_Q = 1/\tau + kQ, \quad (3)$$

where τ_Q is the measured lifetime at some quenching concentration Q , τ is the natural lifetime, and k is the quenching rate constant. Under the conditions indicated in table 1, it was determined that argon would have an ≈ 6 ns effect on the measured lifetimes, and

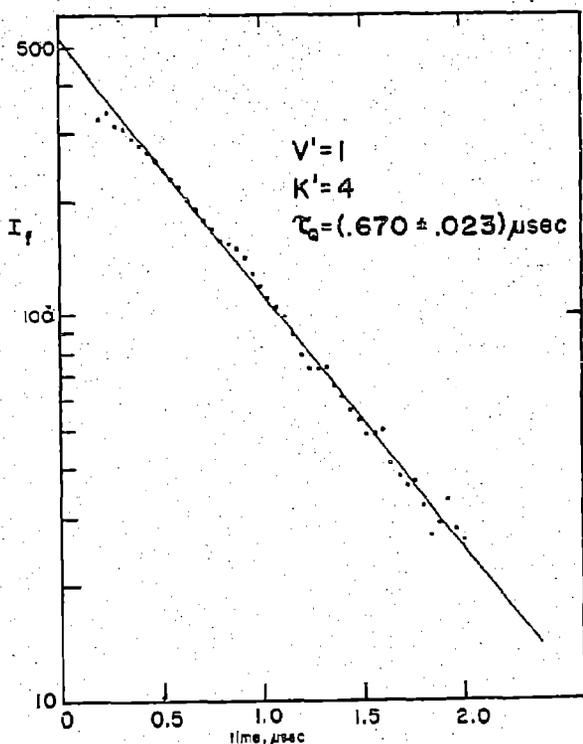


Fig. 1. Semi-logarithmic plot showing the radiative decay of excited OH in the $K' = 4$ level of the $A^2\Sigma^+$ state. Gas mixture - 10 mtorr O_3 , 30 mtorr H_2 and 1.0 torr Ar. $[OH] \approx 10^9$ cm^{-3} .

that hydrogen would have an ≈ 65 ns effect. A systematic quenching correction was made on the measured lifetimes τ_Q according to eq. (3) to obtain corrected lifetime values τ , which are reported in table 1.

These corrected values compare favorably with those obtained previously for $\nu' = 1$, wherein OH was

Table 1

OH fluorescent lifetimes for $\nu' = 1$, $A^2\Sigma^+$. Experimental conditions: $[O_3] = 10$ mtorr; $[H_2] = 30$ mtorr; $[Ar] = 1.0$ torr. Corrections are based on the following quenching numbers: $k_{H_2}[H_2] = 0.122 \mu s^{-1}$; $k_{Ar}[Ar] = 0.011 \mu s^{-1}$

K'	Transition	τ_Q (μs)	τ (μs)	3σ (μs)
0	P ₁₂ 1	0.689	0.759	0.027
1	P ₁₁ 2	0.697	0.768	0.026
2	Q ₁₁ 2	0.690	0.760	0.020
4	Q ₁₁ 4	0.670	0.736	0.023

not selectively excited to individual K' levels: Smith [5] has reported $0.75 \pm 0.11 \mu s$ using a phase-shift technique, and has elsewhere [6] refined this method with a fluorescence-discriminating monochromator to report $\approx 0.65 \pm 0.07 \mu s$ for low-lying K levels. Similarly, Sutherland and Anderson [7] have reported $\approx 0.78 \pm 0.03 \mu s$ using a "delayed coincidence" detection method in conjunction with the discriminating monochromator. Finally, Becker and Haaks [8] have reported a somewhat higher value ($0.92 \pm 0.07 \mu s$) using a non-discriminating pulse-photolysis system.

Note added in proof

Since the final revision of this manuscript was submitted, we have determined the lifetimes of several low-lying levels of the $\nu' = 0$ manifold to be 720 ± 30 ns.

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