

## Monitoring of Radicals by a Tunable Dye Laser

K. H. BECKER, D. HAAKS, and T. TATARCZYK

Institut für Physikalische Chemie der Universität Bonn

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It has been shown<sup>1-5</sup> that tunable dye lasers can be used for resonance fluorescence excitation of molecules and chemically unstable radicals. But this method was limited to species which could be excited by radiation of wavelength above 3400 Å, the lower limit of dye lasers. Very recently, BAARDSEN and TERHUNE<sup>6</sup> have successfully used the second harmonic of a dye laser for fluorescence excitation of OH into the  $A^2\Sigma^+$ ,  $v=1$  level at 2822 Å with subsequent observation of the (0,0) band between 3050 and 3100 Å.

We have also doubled the frequency of a pulsed dye laser to excite OH radicals. The OH radicals were produced under controlled conditions in order to examine the relationship between fluorescence intensity and radical concentration; from our measurements the detection limit for these radicals can thus be estimated.

The experimental arrangement is shown in Figure 1. The dye laser was pumped by a 100 Joule flash lamp with a duration of 1.7  $\mu$ s and a risetime of 0.2  $\mu$ s. A dielectric coated mirror with 100% reflectance over the wavelength region of 4300 to 6800 Å and a plane grating (1200 groves/mm, blaze at 5000 Å) formed the laser cavity. The radiation was de-coupled in the zeroth order of the grating. The laser was operated with a  $2 \times 10^{-4}$  M solution of Rhodamin-B in ethanol, emitting a tunable radiation from 6000 to 6400 Å within

a pulse duration of 0.5  $\mu$ s and a band width of 1 Å. The second harmonic of the laser beam was generated by a KDP crystal (1.5 cm  $\times$  1.5 cm  $\times$  2.5 cm). In order to increase the efficiency of frequency doubling the laser beam was focussed on the crystal by a  $f=10$  cm lens. The output was tunable between 3000 and 3200 Å, with an energy of 0.1 mJoule or about  $10^{14}$  quanta within the 0.2  $\mu$ s pulse duration and a spectral band width of less than 0.5 Å.

The OH radicals were produced in a flow-tube by the fast reaction  $H + NO_2 \rightarrow OH + NO$ <sup>7,8</sup>. The total pressure in the tube was approximately 1 Torr, consisting mainly of argon as an inert diluent. The hydrogen atoms were generated by flowing a hydrogen/argon mixture through a microwave discharge. The pumping speed through the 6 cm diameter flow-tube was 11 l/s. Even if secondary reactions involving hydroxyl radicals were to occur, under our experimental conditions, in an excess of H atoms, the steady state concentration of OH is mainly determined by the equivalent  $NO_2$  concentration, which was calculated from the known inlet rate of  $NO_2$  and the pumping speed. This  $NO_2$  concentration was taken as a measure of the OH concentration.

In Fig. 2 the fluorescence intensity in arbitrary units is plotted against the OH concentration. The OH ( $A^2\Sigma^+$ ,  $v=0 \rightarrow X^2\Sigma, v=0$ ) resonance fluorescence was measured by a  $f/2.5$  spectrometer in combination with an EMI 6256-S photomultiplier; the spectral resolution was about 30 Å. The decaying OH fluorescence excited by the second harmonic of the laser pulse was monitored by an oscilloscope.

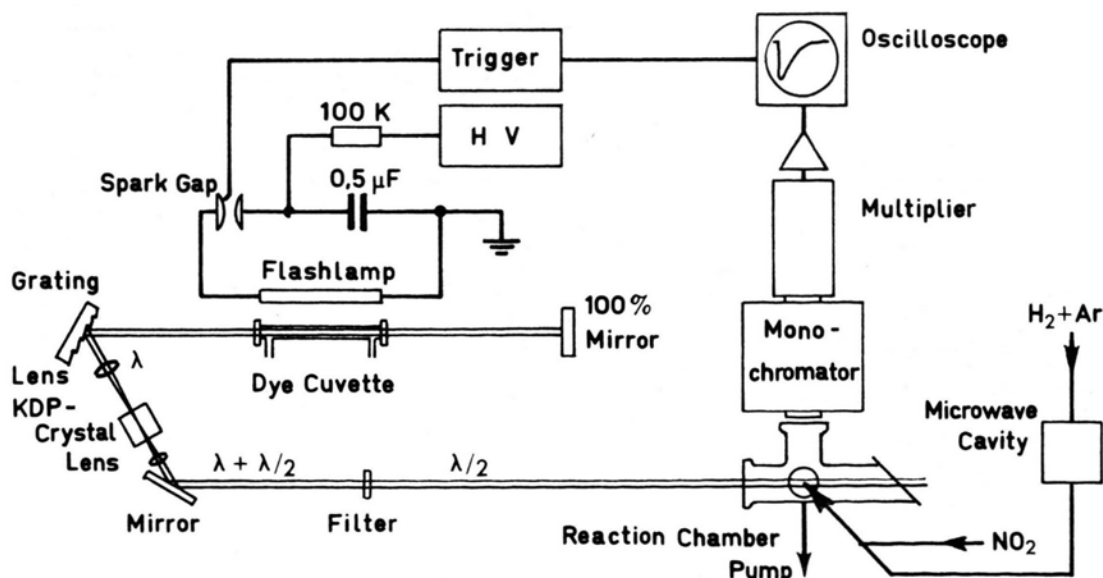


Fig. 1. Diagram of the fluorescence chamber and the tunable dye laser.

Figure 2 shows that under our experimental conditions there was no deviation from a linear relationship between fluorescence intensity and radical concentration by saturation effects up to 20 mTorr, indicating that the absorbing medium is still optically thin<sup>9</sup>. With a hydroxyl concentration of  $10^{12}$  radicals/cm<sup>3</sup> we observed about 400 photo-electrons per laser pulse at the

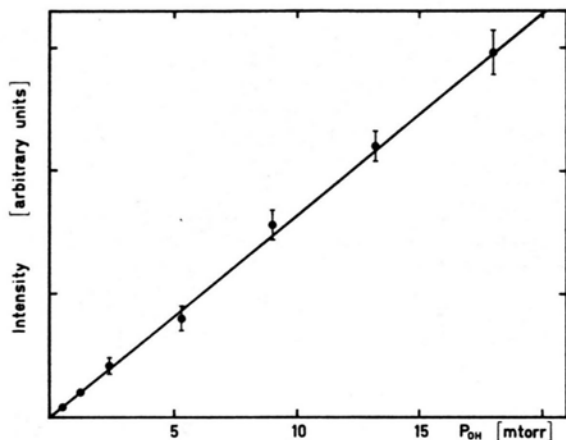


Fig. 2. Fluorescence intensity in arbitrary units as function of the OH radical concentration.

multiplier cathode. In order to calculate the fluorescence efficiency possible quenching processes have to be considered. Recent measurements<sup>10</sup> in our laboratory on the deactivation rates of OH( $A^2\Sigma^+$ ,  $v=0$ ) radicals produced by the water photolysis at 1236 Å gave the following rate constants in units [ $\text{cm}^3 \times \text{molecule}^{-1} \times \text{s}^{-1}$ ]:

H<sub>2</sub>O:  $4.5 \times 10^{-10}$ ; H<sub>2</sub>:  $6.5 \times 10^{-11}$ ; N<sub>2</sub>:  $1 \times 10^{-11}$ ;  
He:  $1 \times 10^{-12}$ ; Ar:  $5 \times 10^{-12}$ .

Several of these rate constants were also measured by other authors<sup>11-14</sup>. For molecular oxygen HOOYERMAYERS and ALKEMADE<sup>12</sup> reported a rate constant of  $6.6 \times 10^{-11}$ . For low rotational levels of OH( $A^2\Sigma^+$ ,  $v=0$ ) the natural lifetime was recently determined as  $\tau = 0.8 \mu\text{s}$ <sup>10</sup> in excellent agreement with  $0.78 \mu\text{s}$  previously reported by GERMAN and ZARE<sup>15</sup>.

With the above numbers the fluorescence efficiency,  $(1/\tau) [1/\tau + \sum k_{M_i}(M_i)]^{-1}$  with  $k_{M_i}$  as rate constant of the quenching species  $M_i$ , is higher than 97% taking into account 1 Torr Ar and 0.1 Torr H<sub>2</sub> but neglecting quenchers below 0.1 Torr such as H atoms, NO<sub>2</sub> and NO. The fluorescence decay curve showed a somewhat smaller efficiency, probably due to the quenching by H atoms which may not be negligible.

The sensitivity in our case is comparable to that reported by BAARDSEN and TERHUNE<sup>6</sup>, taking the different fluorescence efficiencies and intensities of the laser beams into account. If photon counting techniques are used, with our dye laser a hydroxyl concentration of at least  $10^7$  radicals/cm<sup>3</sup> should be detectable at reduced total pressure with about 100% fluorescence efficiency. In the visible spectrum the detectable radical concentration is probably even one to two orders of magnitude lower because of the higher beam power. A detection limit of  $10^6$  radicals/cm<sup>3</sup> under atmospheric conditions, as suggested to be feasible for OH by BAARDSEN and TERHUNE<sup>6</sup>, would demand an even higher laser output within a band width not exceeding the width of the OH lines which is determined by Lorentz broadening under these conditions. In the atmosphere a maximum OH fluorescence efficiency of  $2 \times 10^{-3}$  can be expected. Raman as well as Rayleigh scattering could also lower the fluorescence sensitivity under atmospheric conditions.

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