

## Short Communication

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### Quenching rates for NO<sub>2</sub> ( $\tilde{A}^2B_2$ ) from fluorescence decay measurements

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The interpretation of quenching measurements on the visible fluorescence of NO<sub>2</sub> is complicated by the presence of two excited electronic states having different lifetimes [1], by non-exponential fluorescence decay [2, 3], by gross perturbation of the emitting states by high vibrational levels of the ground state [4], by extreme variability of radiative lifetime from one band to another [5], and by the operation of radiationless processes that can cause a manifold of Born–Oppenheimer states to become populated when only a single level is excited [6]. Some quenching measurements based on Stern–Volmer plots of fluorescence intensity were made before the complex nature of the NO<sub>2</sub> visible spectrum was fully appreciated [7–9]. Such measurements necessarily relate to vibronic relaxation as well as electronic quenching and involve an averaged lifetime and an ill-defined electronic state. Quenching data obtained so far from lifetime measurements [3, 10] have used decay rates averaged over the whole fluorescence decay curve and so also include a contribution from the initial rapid vibrational relaxation, as mentioned in ref. 10. The present note gives some results of quenching measurements based on decay rates determined from the latter part of the fluorescence decay curve under conditions (moderately high NO<sub>2</sub> pressure) where further vibrational relaxation should be unimportant and where the relatively short-lived  $^2B_1$  levels should either have radiated or have relaxed into the  $^2B_2$  manifold [6]. Even when extremely narrow-band excitation is used the distribution of levels produced by relaxation is quite complex; in the present work wide-band (0.2–0.3 nm) excitation was used and no attempt was made to characterize the vibrational and rotational levels involved.

#### 1. Experimental

NO<sub>2</sub> was prepared by reacting Matheson C.P. NO with excess 99.9% O<sub>2</sub>, the product being dried with P<sub>2</sub>O<sub>5</sub> and redistilled under vacuum. Matheson ultrahigh purity O<sub>2</sub> and commercial welding grade argon were passed through a liquid nitrogen trap containing P<sub>2</sub>O<sub>5</sub> before use. Gas pressures were measured with a Texas Instruments quartz spiral gauge. The fluorescence cell was a blackened 10 l bulb with Woods horns opposite the quartz excitation and observation windows.

The pulsed nitrogen laser (nominal peak output 100 kW) and Hansch-type dye laser which excited the NO<sub>2</sub> fluorescence were built in the laboratory. The fluorescence was observed through a short-wavelength cut-off Corning filter with an EMI 9558QA photomultiplier tube. The output of the photomultiplier was taken to a PAR model 160 boxcar integrator which plotted the decay curves directly on an X-Y recorder. All decay curves were obtained using a 1.6 μs boxcar aperture, with 50 μs time base, 0.1 s or 0.3 s time constant, 8 Hz pulse repetition frequency and 5 min scan time. Decay curves for pure NO<sub>2</sub> were measured during the period 20 - 35 μs after the nominal 10 ns exciting flash from the dye laser. As the amount of quenching increased, these times were reduced in proportion. All curves were fitted satisfactorily by a single exponential. In practice, NO<sub>2</sub> was introduced into the 10 l bulb at a pressure of about 30 mTorr, giving an "unquenched" lifetime of about 15 μs. Quencher, either argon or oxygen, was then added and the lifetime was remeasured, after which the mixture was pumped out and a fresh sample of NO<sub>2</sub> introduced.

## 2. Results and discussion

Results for quenching by argon and oxygen are given in Table 1. The quenching rate constants obtained are seen to be somewhat lower, in general, than those found in experiments where vibrational and non-radiative relaxation are likely to have been important. It is also noticeable that, within the experimental error, there is no marked dependence of quenching rate on the wavelength of observation. The results for argon, with excitation at 417.6 nm, are consistently below those obtained with excitation at longer wavelengths and probably reflect the increased involvement of the <sup>2</sup>B<sub>1</sub> state when excitation occurs below 500 nm. However, no such effect is present with O<sub>2</sub> and excitation at 422.1 nm.

TABLE 1  
Quenching data for argon and oxygen

λ excitation (nm)	λ observation (filter) (nm)	Rate constant <sup>a</sup>	Literature values
<i>Argon</i>			
417.6	> 460 (CS 3-71)	1.5 ± 0.3 × 10 <sup>-11</sup>	<sup>b</sup> 2.1 × 10 <sup>-11</sup> [9]
417.6	> 560 (CS 3-66)	1.2 ± 0.5 × 10 <sup>-11</sup>	<sup>c</sup> 3.2 × 10 <sup>-11</sup> [10]
417.6	> 630 (CS 2-58)	1.1 ± 0.4 × 10 <sup>-11</sup>	
542.9	> 560 (CS 3-66)	2.4 ± 0.5 × 10 <sup>-11</sup>	
542.9	> 630 (CS 2-58)	2.5 ± 0.5 × 10 <sup>-11</sup>	
607.7	> 630 (CS 2-58)	2.9 ± 0.5 × 10 <sup>-11</sup>	
<i>Oxygen</i>			
422.1	> 460 (CS 3-71)	2.2 ± 0.2 × 10 <sup>-11</sup>	<sup>d</sup> 2.5 × 10 <sup>-11</sup> [8]
422.1	> 560 (CS 3-66)	2.2 ± 0.3 × 10 <sup>-11</sup>	3.4 × 10 <sup>-11</sup> [9]
543.0	> 560 (CS 3-66)	2.0 ± 0.2 × 10 <sup>-11</sup>	3.6 × 10 <sup>-11</sup> [10]
609.3	> 630 (CS 2-58)	2.0 ± 0.4 × 10 <sup>-11</sup>	

<sup>a</sup>Units: cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>Excitation at 435.8 nm. <sup>c</sup>Excitation at 694.3 nm.

<sup>d</sup>Normalized to self-quenching value of ref. 9. Excitation at 404.7, 435.8 and 480.8 nm.

The self-quenching rate was measured by extrapolation to zero pressure of NO<sub>2</sub> with excitation at 607.7 nm (filter CS 2-58) and 417.0 nm (filter CS 3-67,  $\lambda > 550$  nm). At 607.7 nm the rate constant obtained was  $7.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and at 417.0 nm the value was  $6.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with estimated errors of about  $1.2 \times 10^{-11}$ . The short excitation wavelength data gave a typical curved Stern-Volmer plot at low pressures [8]. Hence the rate constant was obtained from the slope of the reciprocal lifetime graph at NO<sub>2</sub> pressures greater than 15 mTorr. In contrast, the 607.7 nm data gave a linear reciprocal lifetime plot. The rate constant values are in good agreement with the values of  $7.1 \times 10^{-11}$  and  $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  given in refs. 9 and 10, respectively. Thus it would appear that vibrational relaxation was not very important in the earlier measurements of self-quenching rates.

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