# RUBY LASER INDUCED EMISSION FROM NO$_2$

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Two different types of emission from excited NO$_2$ were observed using pulsed ruby laser light at 6943 Å. The first type of fluorescence was seen in the near-IR and results from the single photon excitation of NO$_2$ from the ground ($^2A_1$) state. By observing the emission as a function of time an unexpected behavior was observed in the near IR and could be explained by a consecutive deactivation mechanism, wherein a secondary species is preferentially detected. A second type of emission recently observed in the blue spectral region is weaker and is due to a multiphoton process. The intensity of the blue emission is a function of the cube of the laser intensity at low pressures and approaches the square at high pressures. We attribute this variation to simultaneous deactivation of the NO$_2^*$ intermediate by collision (square) and by anti-Stokes Raman scattering off of the NO$_2^*$ (cube).

## 1. Introduction

The consecutive two-step photodissociation of NO$_2$ as well as the presence of a multiphoton induced emission in the blue has been previously reported using a ruby laser [1,2].

Many studies on the fluorescence and quenching of NO$_2$ have been performed [3–9], but in spite of this extensive research the behavior of an electronically excited NO$_2$ is still not completely understood. In particular, few studies have been performed using excitation in the red where the NO$_2$ absorption is weak.

We present here the results of fluorescence lifetime and quenching studies using the ruby laser excitation at 6943 Å along with the results of further experiments on the multiphoton induced fluorescence.

## 2. Experimental

The NO$_2$ was excited using a Korad K-1 pulsed ruby laser emitting at $\lambda = 6943$ Å. The pulse energy was 2.2 J, pulse duration was 15 ns, and the linewidth was specified as being 0.06 Å. The pulse was generated using a Korad electro-optical Pockels cell $Q$-switch. The fluorescence cell was a 21.2 cm diameter Pyrex bulb with flat Pyrex windows attached on sleeves. The filter combinations were composed of Corning glass and Kodak Wratten filters. An RCA 8575 PMT was used to detect the blue emission while an RCA C31000F PMT was used to detect the near IR emission. The detection system was sensitive over 3800 to 4400 Å and 7500 to 9000 Å for the blue and IR experiments respectively. The time resolved emissions were displayed on a Tektronix 7904 oscilloscope and photographed. The laser intensity was attenuated using flat Pyrex mounted in aluminum channelling as described previously [2].

## 3. Results

### 3.1 Near infrared emission

The results are presented here principally in the form of graphs. The self-quenching constant and radiative lifetime of NO$_2$ are determined from the Stern–Volmer plot of pure NO$_2$, as shown in fig. 1. The quenching constants of NO$_2^*$ for a series of other gases were similarly measured and these results are shown in table 1.

Although exponential decay was observed at low pressures ($p < 30$ mtorr), as the pressure of NO$_2$ was increased a growth of emission with time was observed,
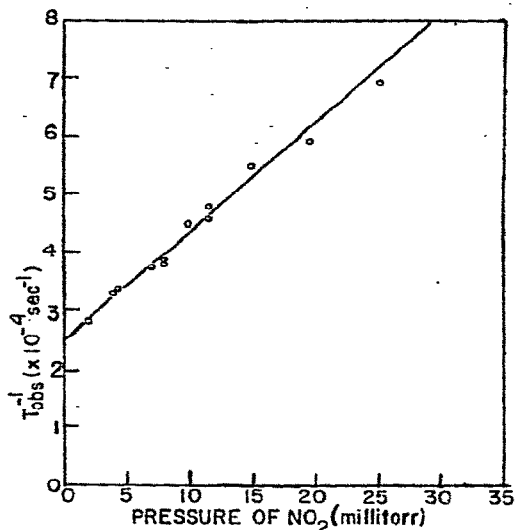
Fig. 1. The Stern–Volmer, $1/\tau_{obs}$ versus $P_{NO_2}$, plot for pure $NO_2$.

followed by a decay which appeared exponential. At high pressures ($p \geqslant 220$ mtorr) one could observe a second maximum of lower intensity. The shapes of the curves are reminiscent of a consecutive decay process

$$A \xrightarrow{\lambda_1} B \xrightarrow{\lambda_2} C \rightarrow \text{etc.} \tag{1}$$

One can readily calculate the time for B to reach a maximum as being

Table 1
Quenching rate constants of $NO_2^*$ for a series of added gases

| Gas | Mol. wt. | Quenching constant (cm³/part s) |
|---|---|---|
| He | 4 | $2.5 \times 10^{-11}$ |
| Ar | 40 | $3.2 \times 10^{-11}$ |
| $N_2$ | 28 | $3.9 \times 10^{-11}$ |
| CO | 28 | $4.8 \times 10^{-11}$ |
| NO | 30 | $6.7 \times 10^{-11}$ |
| $O_2$ | 32 | $3.6 \times 10^{-11}$ |
| $CO_2$ | 44 | $7.7 \times 10^{-11}$ |
| $N_2O$ | 44 | $8.6 \times 10^{-11}$ |
| $NO_2$ [a] | 46 | $5.7 \times 10^{-11}$ [b] |

[a] The collision free radiative lifetime was determined to be $41 \pm 4$ μs.

[b] Due to rapid simultaneous vibrational deactivation this number is difficult to interpret in terms of solely electronic quenching.
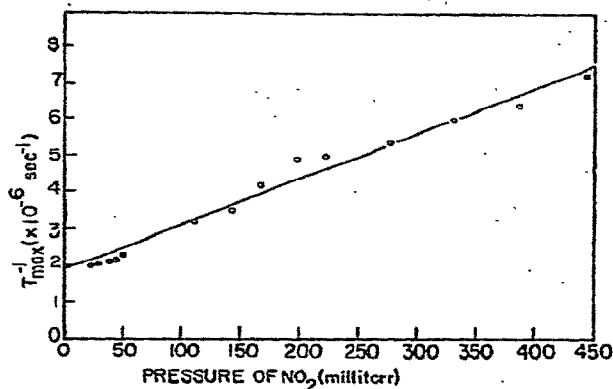


Fig. 2. Inverse time to maximum as a function of $P_{NO_2}$.

$$\tau_{max} = (\lambda_1 - \lambda_2)^{-1} \ln(\lambda_1/\lambda_2). \tag{2}$$

Assuming the pseudo-first order rate constants $\lambda$ to be proportional to pressure, $\lambda = k(M)$, one can write the following;

$$\frac{1}{\tau_{max}} = \left[ \frac{(k_1 - k_2)}{\ln(k_1/k_2)} \right] (M). \tag{3}$$

The reciprocal of the measured time to maximum was plotted versus the $NO_2$ pressure and a linear relationship was found, as is shown in fig. 2.
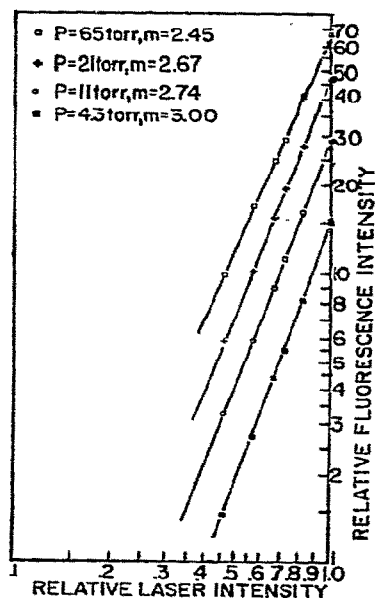


Fig. 3. The log of relative emission intensity versus log of relative laser intensity plots for a series of pressures.

### 3.2. Blue emission

The blue emission was observed at much higher pressures of $NO_2$ than the IR emission (1 torr and over compared to less than 0.5 torr, respectively). If the intensity of the fluorescence can be written as being,

$$I_F = kI_L^n, \tag{4}$$

then the slope of a log $I_F$ versus log $I_L$ plot will give the order, $n$. The data on the blue emission is plotted as the log of the relative fluorescent intensity versus the log of the laser intensity, and is shown for several different fixed pressures of $NO_2$ in fig. 3. As can be seen from these plots the order varies from 2.45 at a total pressure of 65 torr to 3.00 at a total pressure of 4.3 torr. If the data for the different pressures are fitted to an equation of the form,

$$I_F = C_1 I_L^2 + C_2 I_L^3, \tag{5}$$

which is the sum of a two and a three photon induced process, then one can obtain the ratios $C_2/C_1$ as a function of pressure as given in table 2. This ratio is seen to be inversely proportional to pressure, and a least squares analysis gives the result

$$C_2/C_1 = 25.2/P \text{ (torr)}. \tag{6}$$

The first part of (5) $C_1 I_L^2$ (two photon process) therefore depends on pressure one order higher than the second part $C_2 I_L^3$ (three photon process).

Table 2
Relative ($3h\nu/2h\nu$) process ratio as a function of pressure of $NO_2$

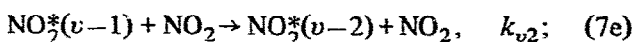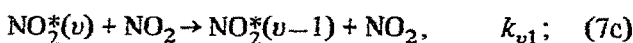| Ratio $C_2/C_1$ | $P$(torr) |
|---|---|
| 6.19 | 4.3 |
| 3.12 | 10.8 |
| 1.07 | 20.6 |
| 0.51 | 65.1 |
| $C_2/C_1 = 25.2/P$(torr) | |

## 4. Discussion

### 4.1. Near infrared emission

The fluorescence behavior of $NO_2$ has been extensi-

vely studied. The lifetime measurements yield values ranging from fairly short ones, 0.5 to 3.7 $\mu$s [3], which correspond to expected lifetimes calculated form the integrated absorption coefficient, to anomalously long lifetimes of up to 120 $\mu$s [4]. These long lifetimes have been explained in terms of extensive mixing of the electronically excited states ($^2B_2$, $^2B_1$) with the $^2A_1$ ground state [5]. A simple step-ladder model of consecutive vibrational deactivation in $NO_2^*$ has been used in previous attempts at explaining the nature of emission from $NO_2^*$ [6,7].

The radiative lifetime of 41 $\mu$s for $NO_2^*$ obtained here is in good agreement with the 46 $\mu$s lifetime obtained in another study of $NO_2$ excited by a ruby laser as performed by Calvert and co-workers [8]. Their quenching constant of $8 \times 10^{-11}$ cm$^3$/part s compares reasonably well with that of $5.7 \times 10^{-11}$ cm$^3$/part s reported here. Care must be taken in the interpretation of these self-quenching constants due to the simultaneous electronic and vibrational relaxation occurring in $NO_2^*$. The quenching constants for the other gases are in reasonable agreement with those obtained by Myers et al., using excitation at 4358 Å [9].

Extension of the consecutive deactivation model of vibrational relaxation [6,7] to data presented here suggests that the following mechanism be used to interpret the results:

$$NO_2 + h\nu_L \rightarrow NO_2^*(v), \qquad \gamma_1 = I_L \sigma_1; \tag{7a}$$

$$NO_2^*(v) \rightarrow NO_2 + h\nu_F, \qquad k_F; \tag{7b}$$

$$NO_2^*(v) + NO_2 \rightarrow NO_2^*(v-1) + NO_2, \qquad k_{v1}; \tag{7c}$$

$$NO_2^*(v-1) \rightarrow NO_2 + h\nu_F, \qquad k_F; \tag{7d}$$

$$NO_2^*(v-1) + NO_2 \rightarrow NO_2^*(v-2) + NO_2, \qquad k_{v2}; \tag{7e}$$

$$NO_2^* + M \rightarrow NO_2 + M, \qquad k_Q. \tag{7f}$$

The mechanism shown above predicts the time to the first emission maximum (see equations) to be given by the relation,

$$\frac{1}{\tau_{max}} = \left[ \frac{(k_{v1} - k_{v2})}{\ln(k_{v1}/k_{v2})} \right] (NO_2), \tag{8}$$

where $k_{v1} > k_{v2}$ must be true in order to observe the emission maximum, and where $k_Q$, the electronic relaxation is slow compared to vibrational relaxation. The slope of the $1/\tau_{max}$ versus $P_{NO_2}$ plot (fig. 2) gives
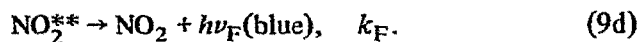
a value of $4 \times 10^{-10}$ cm$^3$/parts. Direct measurement of the rise-time to maximum gives estimates of $(4-7) \times 10^{-10}$ cm$^3$/parts for $k_{v1}$ and $(3-5) \times 10^{-10}$ cm$^3$/parts for $k_{v2}$, but the presence of emission from other states makes accurate analysis difficult.

Calculations using different models, either harmonic oscillator or step-ladder [6,7,10] show $k_{v1}$ and $k_{v2}$ to be in the neighborhood of $(1-5) \times 10^{-10}$ cm$^3$/parts, indicating that the vibrational relaxation is occurring at approximately the gas kinetic collision rate. No production of the emission maxima is observed for addition of gases other than $NO_2$ and therefore it appears that a specific $NO_2^*$–$NO_2$ interaction is responsible for the observed phenomenon. Recent work by Golde and Kaufman on the quenching of vibrational chemiluminescence of $NO_2^{\ddagger}$ from the $NO + O_3$ reaction shows much higher deactivation rates for $NO$ and $NO_2$ than the other gases studied, presumably because of the bond forming potentials that lead to the stable $N_2O_3$ and $N_2O_4$ molecules [11].

All previous studies of $NO_2$ fluorescence, with the exception of that of Calvert and co-workers [8], excited the $NO_2$ at energies above the $(0,0)$ level of the $^2B_1$ state [12], whereas the ruby laser at 6943 Å $(14403$ cm$^{-1})$ lies only above the $(0,0)$ of the $^2B_2$ state at 11956 cm$^{-1}$ [12]. The fluorescence behavior of $NO_2^*$ formed at this longer wavelength may therefore show different behavior from excitation at shorter wavelengths where transitions to both the $^2B_1$ and $^2B_2$ states occur simultaneously, as has been pointed out by Kaufman [11]. The $^2B_2$ state emission is in general more discrete than that of the $^2B_1$ state [13], so the observed phenomena does necessarily conflict with the known behavior of $NO_2^*$ emission.
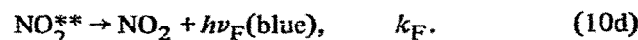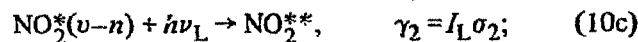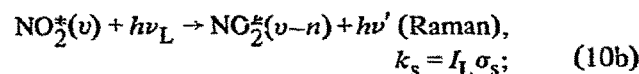
## 4.2 Blue emission

In the previous work where the blue emission was first reported [2] the order of fluorescence intensity with respect to laser intensity was shown to be 2.45, but only a single $NO_2$ pressure of 65 torr had been studied. A possible explanation for a slope of 2.0 had been given using the following mechanism [2]:

$$NO_2 + h\nu_L \rightarrow NO_2^*, \qquad \gamma_1 = I_L \sigma_1; \qquad (9a)$$

$$NO_2^* + M \rightarrow NO_2^{\ddagger} + M, \qquad k_D; \qquad (9b)$$

$$NO_2^{\ddagger} + h\nu_L \rightarrow NO_2^{**}, \qquad \gamma_2 = I_L \sigma_2; \qquad (9c)$$

$$NO_2^{**} \rightarrow NO_2 + h\nu_F(\text{blue}), \qquad k_F. \qquad (9d)$$

Without the deactivating second step the absorption of a second photon lifts the $NO_2^*$ above the dissociation limit where it has a lifetime of $2 \times 10^{-13}$ s, as directly measured by Busch and Wilson via photolysis using a pulsed frequency doubled ruby laser at 3472 Å [14]. The O-atom from the two-photon $NO_2$ photodissociation rapidly reacts with $NO_2$ to form $O_2$. This process was reported previously and showed an $I_L^2$ dependence [1,2].

The mechanism given in eq. (9) would also predict an $I_L^2$ dependence, but additional experiments performed showed an increase in the order from 2.45 to 3.00 as the pressure was decreased (see fig. 3).

If three photons are absorbed simultaneously or consecutively their combined energy would raise the $NO_2$ to the lower levels of the $\tilde{C}$ state or higher levels of the $\tilde{B}$ $(^2B_2)$ state [15], however neither state has been observed in emission, and the estimated probabilities of these processes would be much lower than the approximate measured quantum yield for the blue emission of about $10^{-9}$ [2]. Since Stern–Volmer plots showed that the blue emission had a lifetime compatible with that of $NO_2^*$ below the dissociation limit (the quenching constant was approximately 0.15 times the gas kinetic collision rate) it was concluded that the $I_L^3$ process probably occurs in a manner that yields an $NO_2^{**}$ below the dissociation limit. The following mechanism is proposed to account for the $I_L^3$ dependence:

$$NO_2 + h\nu_L \rightarrow NO_2^*(v), \qquad \gamma_1 = I_L \sigma_1; \qquad (10a)$$

$$NO_2^*(v) + h\nu_L \rightarrow NO_2^*(v-n) + h\nu' \text{ (Raman)}, \qquad k_s = I_L \sigma_s; \qquad (10b)$$

$$NO_2^*(v-n) + h\nu_L \rightarrow NO_2^{**}, \qquad \gamma_2 = I_L \sigma_2; \qquad (10c)$$

$$NO_2^{**} \rightarrow NO_2 + h\nu_F(\text{blue}), \qquad k_F. \qquad (10d)$$

Here the second step is not a collisional deactivation, but rather seems to be an anti-Stokes Raman scattering of the laser light off of the $NO_2^*$ intermediate which thereby removes $n$ effective vibrational quanta in the process.

Using the mechanism (10) above, one can obtain an approximate expression for the quantum efficiency of the blue light as being

$$\phi_f = A \left[ \frac{k_F}{k_F + k_Q(NO_2)} \right] I_L \sigma_s, \qquad (11)$$

where $A$ is a factor depending on pulse duration, laser intensity, and pressure, $\sigma_s$ is the Raman scattering cross section, $k_F$, is the radiative rate constant and $k_Q$ is the electronic quenching constant. The quantum efficiency is defined here as being the number of photons emitted per potential $NO_2^{**}$ formed via a consecutive two photon absorption. A value for $\phi_f$ was estimated previously as being about $\phi_f = 10^{-9}$ for $NO_2$ at a pressure of 30 torr [2]. Using a value of $k_F = 2.7 \times 10^4$ s$^{-1}$ [16] and $k_Q = 4 \times 10^{-12}$ cm$^3/$part s [17] for the $NO_2^*$ in the blue region and estimating the factor $A$ to be about 0.08 for the conditions used, the value of $\sigma_s$ that is required is about $\sigma_s = 2.3 \times 10^{-25}$ cm$^2/$part. A Raman scattering cross section of this magnitude indicates that a resonant type of Raman scattering may be occurring. Such resonant scattering has been observed in the scattering of argon ion laser lines off ground state $NO_2$ [18,19]. This calculated $\phi_F$ depends naturally on the second absorption cross section and the actual value would be expected to be different from that measured by us for the two photon dissociation, but not by many orders of magnitude.

Assuming that the blue emission can be expressed as a sum of the contributions from the two and three photon processes as was assumed above in eq. (5), the data can be fitted to this expression to obtain values for the ratio $C_2/C_1$ as a function of pressure. A plot of log $C_2/C_1$ versus log $P$ gives a slope, $m$, of $m = -1.0$, so the ratio is inversely proportional to pressure, as would be expected if the two photon process requires a collisional step that the three photon process does not. At a relative laser intensity $I_L = 1.0$ (corresponding to 150 MW at 6943 Å, the ratio $C_2/C_1$ can be shown to be unity when $P \approx 25$ torr. The ratio is a measure of the relative importance of the three photon to the two photon process, for the given laser intensity.

## 5. Conclusion

The pulsed ruby laser has been used to excite near-infrared fluorescence in $NO_2$. The values obtained for the radiative lifetime of $NO_2^*$ and for the quenching constants for a series of added gases are similar to values obtained for more energetic excitation. The unusual time resolved behavior at higher pressures is interpreted as being direct observation of the vibrational deactivation process; a value for the vibrational deactivation rate constant of about $4 \times 10^{-10}$ cm$^3/$part s being obtained.

The multiphoton induced fluorescence was studied at a series of different pressures. The order of this "blue" fluorescence was found to be pressure dependent. The data could be separated into a two photon process that required a collisional deactivating step, and a three photon process that required a collisionless deactivation. The latter process is interpreted as an anti-Stokes Raman scattering, which acts as the collisionless deactivating step.

## Acknowledgement

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