

# Photodissociation of Nitrogen Dioxide by Pulsed Laser Light at 6943 Å

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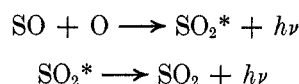
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Publication costs assisted by the National Aeronautics and Space Administration

Nitrogen dioxide was photodissociated using a pulsed ruby laser at 6943 Å. The energy of a single photon at this wavelength was equivalent to only 57% of the dissociation energy. The mechanism proposed to account for the results was the consecutive absorption of two photons, the first resulting in a short-lived excited state. The second photon is then absorbed by the excited species resulting in dissociation.

## Introduction

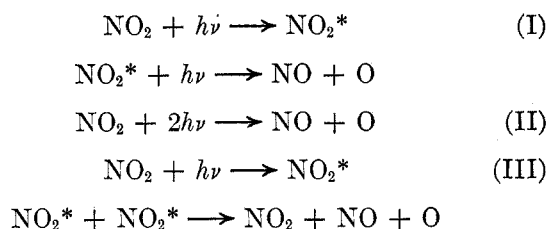
In work done previously in this laboratory it was demonstrated that two-photon emission was present in the reaction



The time delay between the two emissions was found to be of the order of 30 nsec.<sup>1</sup> (Smith observed emission corresponding to a lifetime of  $\text{SO}_2^*$  of 12 nsec in pulse electron beam studies.<sup>2</sup>)

The purpose of the present work has been to investigate the possibility of a reverse mechanism of this type occurring in the dissociation of  $\text{NO}_2$ . Photodissociation becomes energetically possible at wavelengths below about 3945 Å.<sup>3</sup> Some dissociation still occurs around 4070 Å due to the availability of the vibrational and rotational energy of the molecule. At 4358 Å, however, no dissociation is found.<sup>4</sup>

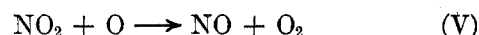
At higher wavelengths, up to approximately 7900 Å, the combined energy of two photons would once again make the dissociation reaction possible. The following three mechanisms are considered for discussion



A fourth possible mechanism would be



The reaction of ground state molecules is 26 kcal endothermic or for the excited molecule it would need the equivalent energy absorbed from photons at wavelengths of about 10,000 Å or less. However, such a reaction has not been observed as noted above. The net result of any of these mechanisms is the production of oxygen when the fast reaction of  $\text{NO}_2$  with O atoms is included



The simultaneous absorption of two photons has been observed by several investigators. Pao and Rentzepis were the first to report a multiphoton process terminating in a specific chemical reaction: the photoinitiation of the polymerization of styrene and of *p*-isopropylstyrene.<sup>5</sup> Porter has reported the initiation of the explosive reaction of  $\text{H}_2$  and  $\text{Cl}_2$  by a two photon absorption at 6943 Å leading to dissociation of the  $\text{Cl}_2$ .<sup>6</sup> Speiser has used a Q-switched ruby laser to achieve a two photon absorption in iodoform, followed by the liberation of iodine.<sup>7</sup>

The absorption in some cases may have been, at least in part, consecutive rather than simultaneous, with a short-lived excited intermediate absorbing the second photon. Porter has observed this consecutive two-photon absorption in the photodissociation of phthalocyanine.<sup>8</sup>

## Experimental Section

A Korad K-1QP laser system was used in these experiments. The 9/16-in. ruby rod was operated with a passive Q-switch containing cryptocyanine dye to obtain single pulses of 1–2 J energy and 10 nsec duration at 6943 Å. The energy of the laser output was verified using a Korad KJ-2 calorimeter.

The gases used were obtained from the Matheson Co., East Rutherford, N. J. The argon was supplied at 99.995% purity and was used without further purification. The nitrogen dioxide was further purified until it was better than 99.99% purity. Several mix-

(1) J. A. Emerson, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, N. Y., 1969.

(2) W. H. Smith, *J. Chem. Phys.*, **51**, 3410 (1969).

(3) J. G. Calvert and J. M. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 217, 219.

(4) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961, p 47.

(5) Y. H. Pao and P. M. Rentzepis, *Appl. Phys. Lett.*, **6**, 93 (1965).

(6) G. Porter, *Nature (London)*, **215**, 502 (1967).

(7) S. Speiser and S. Kimel, *J. Chem. Phys.*, **51**, 5614 (1969).

(8) G. Porter and J. I. Steinfeld, *ibid.*, **45**, 3456 (1966).

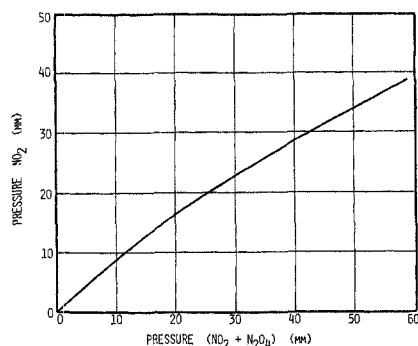


Figure 1. Partial pressure of NO<sub>2</sub> vs. pressure of (NO<sub>2</sub> + N<sub>2</sub>O<sub>4</sub>) equilibrium mixture at 20°.

tures of NO<sub>2</sub> and argon were prepared and gas analyses were performed on a CEC 21-130 mass spectrometer.

The fluorescent lights in the laboratory were found to cause some dissociation of the NO<sub>2</sub>; therefore, the storage vessels containing the gas mixtures were covered with black cloth and the laboratory was in virtually total darkness at all times.

A cylindrical quartz cell of 9.5-cm path length was filled to the desired pressure with the mixture to be irradiated and placed in the path of the laser beam. The laser was fired five times at 2-min intervals. Each flash was monitored to ensure that the laser had produced only a single pulse, using a RCA-1P21 photomultiplier. The output signal of the phototube was recorded on film by a Tektronix 545-A oscilloscope fitted with a camera. The NO<sub>2</sub> was frozen out of the sample and the amount of O<sub>2</sub> present was measured against the argon standard on the mass spectrometer. Each set of experiments was run in one time span so that effects of variables related to laser operation, room temperature, etc. would be minimized.

Samples of NO<sub>2</sub> were repeatedly exposed to only the light from the xenon flash lamp of the laser under normal experimental conditions to ensure that no oxygen was being produced in this way. The results consistently showed no detectable formation of oxygen (*i.e.*, <0.01%).

The dimerization which occurs in NO<sub>2</sub> (2NO<sub>2</sub> ⇌ N<sub>2</sub>O<sub>4</sub>) had to be considered in these experiments. The true pressures of NO<sub>2</sub> were calculated for a series of gas pressures at 20° using the equilibrium constants of Harris and Churney.<sup>9</sup> The results are shown in Figure 1. All pressures of NO<sub>2</sub> cited in this paper refer to true pressures of NO<sub>2</sub> in the equilibrium mixtures.

The absorption coefficient of NO<sub>2</sub> was measured in the region of 6943 Å using a Beckman DK-2 spectrophotometer. The experimental value of  $\alpha = 0.15 \text{ cm}^{-1} \text{ atm}^{-1}$  was in good agreement with the value found by Dixon in this region of the spectrum.<sup>10</sup> Dixon also reports that Beer's law is valid in the pressure region of these experiments. Due to the fine structure of the NO<sub>2</sub> bands, the actual absorption coefficient for the very narrow laser line may be somewhat different.

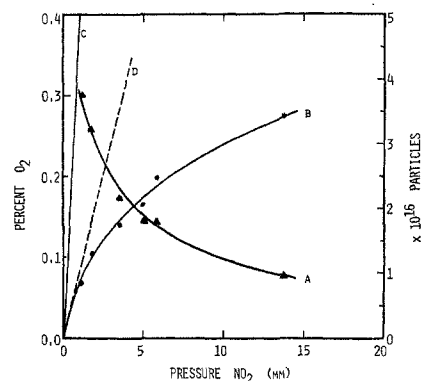


Figure 2. O<sub>2</sub> formed by five pulses in a mixture of 53% NO<sub>2</sub> and 47% argon: (A) as percent of total gas pressure and (B) as number of particles vs. pressure of NO<sub>2</sub>; (C) number of NO<sub>2</sub>\* formed by five pulses vs. pressure of NO<sub>2</sub>; (D) tangent drawn to production curve at lowest pressures of NO<sub>2</sub>.

## Results

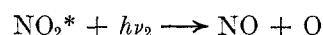
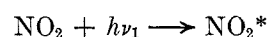
Using various pressures of NO<sub>2</sub> in the cell, oxygen was produced by firing the laser five times for each data point. Figure 2 depicts the O<sub>2</sub> production curve in a mixture of 47% argon and 53% (NO<sub>2</sub> + N<sub>2</sub>O<sub>4</sub>), which is representative of our observations below 15 mm of NO<sub>2</sub>. Both O<sub>2</sub> as a percentage of total gas pressure and the number of O<sub>2</sub> molecules formed are plotted against the pressure of NO<sub>2</sub>.

In order to have sufficient amounts of O<sub>2</sub> produced for purposes of gas analysis it was desirable to irradiate each sample 5 times. Calculations showed that the fractional loss of O<sub>2</sub> via the back reaction: 2NO + O<sub>2</sub> → 2NO<sub>2</sub>, was negligible during the 20 min interval between the first laser pulse and the analysis.

## Discussion

The formation of oxygen as shown in Figure 2 cannot be explained by ordinary photochemical mechanisms. As mentioned earlier, the absorption of light above ~4300 Å does not result in dissociation, but rather the formation of an excited state which eventually fluoresces or is quenched by collision. The dissociation energy of NO<sub>2</sub> into NO and an O atom is put at 71.8 kcal/mol, while an einstein of light quanta at the laser wavelength was calculated to supply only 41 kcal. The results suggest that the energies of two photons are combining to cause dissociation of the molecule. Several mechanisms are possible: the simultaneous absorption of two photons, the consecutive absorption of two photons, and the collisional interaction of two singly excited species.

The results appear to be consistent with the consecutive absorption mechanism represented by



(9) L. Harris and K. L. Churney, *J. Chem. Phys.*, **47**, 1703 (1967).

(10) J. K. Dixon, *ibid.*, **8**, 157 (1940).

(followed by  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ ). From the known absorption coefficient at 6943 Å, and expected radiative and collisional lifetimes, a significant amount of oxygen should be formed, assuming a reasonable coefficient for the second absorption to the continuum, resulting in dissociation of the  $\text{NO}_2$ .

The simultaneous process is expected to produce only small amounts of product such as mentioned by Porter in the initiation of the  $\text{H}_2\text{-Cl}_2$  reaction,<sup>6</sup> much less than those observed. These would also follow a different reaction pattern because the results of Porter should be independent of quenching. The amounts of  $\text{O}_2$  observed are also far in excess of those permitted by the low probability of the collision of two excited species before collisional deactivation occurs.

A primary consideration in discussing the dissociation of  $\text{NO}_2$  by the consecutive absorption process is the production of the  $\text{NO}_2^*$  state by the laser light. Calculations made from Beer's law using an average photon flux of  $5 \times 10^{18}$  photons/pulse (calculated from pulse energy measurements) showed that the number of excited molecules created during each pulse

$$\text{NO}_2^* = 1 \times 10^{16} \text{ (particles/mm)} P(\text{NO}_2)$$

or for the five pulses

$$\text{NO}_2^* = 5 \times 10^{16} \text{ (particles/mm)} P(\text{NO}_2)$$

where  $P(\text{NO}_2)$  is the pressure of  $\text{NO}_2$  in millimeters. This relationship is plotted along with the  $\text{O}_2$  production curve in Figure 2. Collisional deactivation at very low pressures becomes negligible during the pulse time of  $10^{-8}$  sec, and a comparison with a tangent drawn to the experimental  $\text{O}_2$  production curve at the lowest pressures suggests that about one in five of the  $\text{NO}_2^*$  produced eventually absorbs a second photon leading to dissociation.

We believe that the consecutive absorption process can be described by three rate equations

$$+ \frac{d[\text{NO}_2^*]}{dt} = \gamma_1[\text{NO}_2] \quad (1)$$

$$- \frac{d[\text{NO}_2^*]}{dt} = \gamma_2[\text{NO}_2^*] = + \frac{d[\text{O}_2]}{dt} \quad (2)$$

$$- \frac{d[\text{NO}_2^*]}{dt} = (\lambda_1 + \lambda_2 + \dots)[\text{NO}_2^*] \quad (3)$$

where eq 1 governs the production of the singly excited species; eq 2 governs the loss of the  $\text{NO}_2^*$  via the absorption of the second photon; hence, also the production of  $\text{O}_2$ . Equation 3 governs the loss of the  $\text{NO}_2^*$  due to collisional deactivation with  $\lambda_1$ ,  $\lambda_2$ , etc. relating to the quenching effects of the various components of the gas mixture. Since the duration of the laser pulse is much shorter than the radiative lifetime of  $4 \times 10^{-5}$  sec,<sup>11</sup> loss by fluorescence is considered to be negligible. The coefficients  $\gamma_1, \gamma_2, \lambda_1, \lambda_2$ , all have dimensions of re-

ciprocal time. The rate coefficient for production of the  $\text{NO}_2^*$  was calculated from Beer's law as  $\gamma_1 = 2.0 \times 10^6 \text{ sec}^{-1}$ .<sup>12</sup> The general form of  $\lambda_1, \lambda_2$ , etc. is  $\lambda = Qk(M)$ , where  $Q$  is the quenching efficiency of a gas component,  $k \cong 2 \times 10^{-10} \text{ particles}^{-1} \text{ sec}^{-1}$  and  $(M)$  is the number of particles of that particular gas component in the reaction volume. The only approximation which has been made is the assumption of a constant light intensity for the duration of the pulse. Solving these equations for the net  $\text{O}_2$  production during the laser pulse time ( $T = 10^{-8} \text{ sec}$ ) yields the expression

$$[\text{O}_2] = \frac{\gamma_2 \gamma_1 [\text{NO}_2] T}{(\gamma_2 + \lambda_1 + \lambda_2 + \dots)} \times \left[ 1 + \frac{1}{(\gamma_2 + \lambda_1 + \lambda_2 + \dots) T} \times (e^{-(\gamma_2 + \lambda_1 + \lambda_2 + \dots) T} - 1) \right] \quad (4)$$

If collisional quenching of the reaction is set equal to zero, the fraction of the  $\text{NO}_2^*$  which eventually absorbs a second photon and dissociates, is given by

$$\frac{\text{NO}_2^* \rightarrow \text{O}_2}{\text{NO}_2^*} = \frac{\text{O}_2}{\gamma_1(\text{NO}_2)T} = \left[ 1 + \frac{1}{\gamma_2 T} (e^{-\gamma_2 T} - 1) \right] \quad (5)$$

This expression was calculated for several values of  $\gamma_2$ . Graphical analysis showed that our experimental observation of the dissociation of one in five singly excited molecules corresponds to  $\gamma_2 = 4.6 \times 10^7 \text{ sec}^{-1}$ . Calculating again from Beer's law (using the reaction volume,  $V_R = 15 \text{ cm}^3$ ) yields the coefficient for the second absorption,  $\alpha_2 = 3.5 \text{ atm}^{-1} \text{ cm}^{-1}$ . The value of expression 5 is plotted against different values of the second absorption coefficient in Figure 3.

In order to test the validity of the theory presented,  $\text{O}_2$  production curves were calculated for a mixture containing 50% ( $\text{NO}_2 + \text{N}_2\text{O}_4$ ) and 50% argon (a mixture similar to the experimental mixture of 53% ( $\text{NO}_2 + \text{N}_2\text{O}_4$ ) and 47% argon which is reported). The coefficient for the second absorption,  $\alpha_2$ , was taken as  $3.5 \text{ atm}^{-1} \text{ cm}^{-1}$  and quenching efficiencies were estimated from the results of Myers as 0.5 for  $\text{NO}_2$ , 0.1

(11) D. Neuberger and A. B. F. Duncan, *J. Chem. Phys.*, **22**, 1693 (1954).

(12) Applying the approximation that, for small values of  $y$ ,  $e^{-y} = 1 - y$  to Beer's law results in the expression

$$\Delta I = \text{no. of } \text{NO}_2^* = \left[ \frac{I_0 \alpha_1 X}{\left( \frac{\text{No. particles}}{\text{cm}^3 \text{ mm}} \right) \cdot V_R} \right] (\text{NO}_2)$$

where  $I_0$  is the average photon flux,  $\alpha$  is the coefficient for the first absorption,  $X$  is the path length of the cell,  $V_R$  is the volume of gas exposed to the laser light ( $V_R = 15 \text{ cm}^3$ ), and  $(\text{No. particles}/\text{cm}^3 \text{ mm})$  is a conversion factor from pressure to particles. The term in brackets is equal to  $\gamma_1$ .

for Ar, and 1.0 for N<sub>2</sub>O<sub>4</sub>.<sup>13</sup> If the dimerization is ignored, oxygen production levels off at higher pressures. When the quenching of the N<sub>2</sub>O<sub>4</sub> molecule is taken into account, oxygen production reaches a maximum and begins to diminish. These calculated curves are shown in Figure 4.

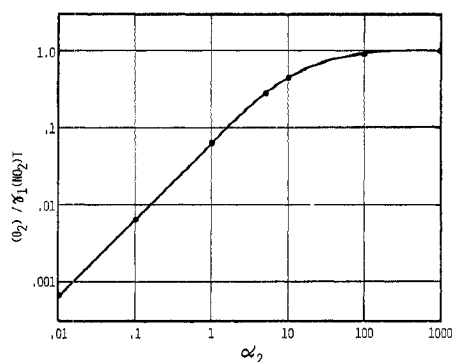


Figure 3. Fraction of NO<sub>2</sub>\* which absorbs a second photon with zero quenching vs. the second absorption coefficient,  $\alpha_2$ .

Preliminary experiments have verified this diminishing oxygen yield at higher pressures and have suggested a possible quenching efficiency for the N<sub>2</sub>O<sub>4</sub> molecule that exceeds gas kinetic expectations. We are continuing our investigations in the higher pressure region where the deactivation processes dominate and are

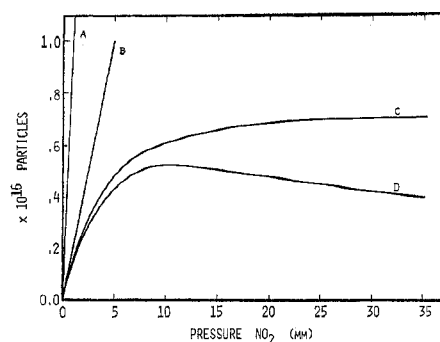


Figure 4. Calculated values for a mixture of 50% (NO<sub>2</sub> + N<sub>2</sub>O<sub>4</sub>) and 50% argon: (A) total number of NO<sub>2</sub>\* formed per pulse vs. pressure of NO<sub>2</sub>; O<sub>2</sub> production curves for (B) zero quenching, (C) quenching but no dimerization, (D) quenching and dimerization of NO<sub>2</sub> as shown in Figure 1.

studying the effects of various other gases, such as CO<sub>2</sub>, on the overall reaction.

*Acknowledgment.* This work was supported by a grant from the National Aeronautics and Space Administration, NGL 33-018-007. Presented in part at the Second International Laser Workshop dealing with "Laser Interaction and Related Plasma Phenomena," held on Aug 30–Sept 3, 1971, at the Rensselaer Polytechnic Institute Graduate Center in Hartford, Conn.

(13) G. H. Myers, D. M. Silver, and F. Kaufman, *J. Chem. Phys.*, **44**, 718 (1966).