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PHOTODISSOCIATION OF NO_2 BY PULSED LASER LIGHT AT 6943Å

by

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ABSTRACT

Nitrogen dioxide was photodissociated using a pulsed ruby laser at 6943Å. 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 SO + O:

$$SO + O \rightarrow SO_2^* + h\nu$$

$$SO_2^* \rightarrow SO_2 + h\nu$$

The time delay between the two emissions was found to be of the
(1) order of 30 nanoseconds.[1] (Smith observed emission correspond-
ing to a lifetime of SO_2 excited of 12 nanoseconds in pulse elec-
(2) tron beam studies.[2])

The purpose of the present work has been to investigate the possibility of a reverse mechanism of this type occurring in the dissociation of NO_2. Photodissociation becomes energetically
(3) possible at wavelengths below about 3945Å.[3] Some dissociation still occurs around 4070Å due to the availability of the vibrational and rotational energy of the molecule. At 4358Å, however,
(4) no dissociation is found.[4]

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

(1) $NO_2 + h\nu \rightarrow NO_2^*$

$NO_2^* + h\nu \rightarrow NO + O$

(2) $NO_2 + 2h\nu \rightarrow NO + O$

(3) $NO_2 + h\nu \rightarrow NO_2^*$

$NO_2^* + NO_2^* \rightarrow NO_2 + NO + O$

A fourth possible mechanism would be:

$$(4) \quad NO_2^* + NO_2 \rightarrow 2NO + O_2$$

The reaction of ground state molecules is 26 kilocalories endothermic or for the excited molecule it would need the equivalent energy absorbed from photons at wavelengths of about 10,000Å 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 NO_2 with O-atoms is included:

$$(5) \quad NO_2 + O \rightarrow NO + O_2$$

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 photo-initiation of the polymerization of styrene
(5) and of P-isopropylstyrene.[5] G. Porter has reported the initiation of the explosive reaction of H_2 and Cl_2 by a two photon ab-
(6) sorption at 6943Å leading to dissociation of the Cl_2.[6] Speiser has used a Q-switched ruby laser to achieve a two photon absorp-
(7) tion in iodoform, followed by the liberation of iodine.[7]

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
(8) of phthalocyanine.[8]

EXPERIMENTAL

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

The gases used were obtained from the Matheson Company, East Rutherford, New Jersey. 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 mixtures of NO_2 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_2, 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 9.5cm. 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 two minute 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_2 was frozen out of the sample and the amount of O_2 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_2 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., <.01%).

The dimerization which occurs in NO_2 ($2NO_2 \rightleftarrows N_2O_4$) had to be considered in these experiments. The true pressures of NO_2 were calculated for a series of gas pressures at 20°C using the equilib-
(9) rium constants of Harris and Churney.[9] The results are shown in Fig. (1). All pressures of NO_2 cited in this paper refer to true pressures of NO_2 in the equilibrium mixtures.

The absorption coefficient of NO_2 was measured at 6943Å using a Beckman DK-2 spectrophotometer. The experimental value of α = .15 $cm^{-1}atm^{-1}$ was in good agreement with the value found by Dixon
(10) in this region of the spectrum.[10] Dixon also reports that Beer's Law is valid in the pressure region of these experiments.

Results

Using various pressures of NO_2 in the cell, oxygen was produced by firing the laser five times for each data point. Fig. (2) depicts the O_2 production curve in a mixture of 47% argon and 53% (NO_2 + N_2O_4), which is representative of our observations below

15mm of NO_2. Both O_2 as a percentage of total gas pressure and the number of O_2 molecules formed are plotted against the pressure of NO_2.

In order to have sufficient amounts of O_2 produced for purposes of gas analysis it was desirable to irradiate each sample 5 times. Calculations showed that the fractional loss of O_2 via the back reaction: $2NO + O_2 \rightarrow 2NO_2$, 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 ~4300Å 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_2 into NO and an O-atom is put at 71.8 kcal/mole, 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:

$$NO_2 + h\nu_1 \rightarrow NO_2^*$$

$$NO_2^* + h\nu_2 \rightarrow NO + O.$$

(followed by $NO_2 + O \rightarrow NO + O_2$)

From the known absorption coefficient at 6943Å, 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 NO_2.

The simultaneous process is expected to produce only small amounts of product such as mentioned by Porter in the initiation of the H_2 - Cl_2 reaction[6], 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 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 NO_2 by the consecutive absorption process is the production of the NO_2^* state by the laser light. Calculations made from Beer's Law using an average photon flux of 5×10^{18} photons/pulse (calculated from pulse energy measurements) showed that the number of excited molecules created during each pulse:

$$NO_2^* = 1 \times 10^{16} \text{ (particles/mm) } P(NO_2)$$

or for the five pulses:

$$NO_2^* = 5 \times 10^{16} \text{ (particles/mm) } P(NO_2)$$

where $P(NO_2)$ is the pressure of NO_2 in millimeters.
This relationship is plotted along with the O_2 production curve in Fig. (2). Collisional deactivation at very low pressures becomes

negligible, and a comparison with a tangent drawn to the experimental O_2 production curve at the lowest pressures suggests that about one in five of the 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:

$$+\frac{d(NO_2^*)}{dt} = \gamma_1 (NO_2) \tag{1}$$

$$-\frac{d(NO_2^*)}{dt} = \gamma_2 (NO_2^*) = +\frac{d(O_2)}{dt} \tag{2}$$

$$-\frac{d(NO_2^*)}{dt} = (\lambda_1 + \lambda_2 + \ldots)(NO_2^*) \tag{3}$$

where equation (1) governs the production of the singly excited species; equation (2) governs the loss of the NO_2^* via the absorption of the second photon; hence, also the production of O_2. Equation (3) governs the loss of the NO_2^* due to collisional deactivation with λ_1, λ_2, etc. relating to the quenching effects of
(11) the various components of the gas mixture.[11] 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 O_2 production during the laser pulse time ($T = 10^{-8}$ sec.) yields the expression:

$$(O_2) = \frac{\gamma_2\gamma_1(NO_2)T}{(\gamma_2 + \lambda_1 + \lambda_2 + \ldots)} \times \left[1 + \frac{1}{(\gamma_2 + \lambda_1 + \lambda_2 + \ldots)T}\left(e^{-(\gamma_2 + \lambda_1 + \lambda_2)T} - 1\right)\right] \tag{4}$$

If collisional quenching of the reaction is set equal to zero, the fraction of the NO_2^* which eventually absorbs a second photon and dissociates, is given by:

$$\frac{NO_2^* \rightarrow O_2}{NO_2^*} = \frac{O_2}{\gamma_1 (NO_2) T} = \left[1 + \frac{1}{\gamma_2 T} \left(e^{-\gamma_2 T} - 1 \right) \right] \qquad (5)$$

The value of this expression was calculated for several values of the second absorption coefficient. The results are shown in Figure (3). From this curve our experimental observation of the dissociation of one in five singly excited molecules corresponds to an α_2 = 3.5 atm^{-1} cm^{-1}.

In order to test the validity of the theory presented, O_2 production curves were calculated for a mixture containing 50% (NO_2 + N_2O_4) and 50% Argon (a mixture similar to the experimental mixture of 53% (NO_2 + N_2O_4) and 47% Argon which is reported). The coefficient for the second absorption, α_2, was taken as 3.5 atm^{-1} cm^{-1} and quenching efficiencies were reasonably approximated as .5 for NO_2, .1 for Ar and 1.0 for the N_2O_4 molecule. If the dimerization is ignored, oxygen production levels off at higher pressures. When the quenching of the N_2O_4 molecule is taken into account, oxygen production reaches a maximum and begins to diminish. These calculated curves are shown in Figure 4.

Preliminary experiments have verified this diminishing oxygen yield at higher pressures and have suggested a possible quenching efficiency for the N_2O_4 molecule that exceeds gas kinetic

expectations. We are continuing our investigations in the higher pressure region where the deactivation processes dominate and are studying the effects of various other gases, such as CO_2, on the overall reaction.

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11. γ_1, γ_2, λ_1, λ_2 etc. all have dimensions of reciprocal time. γ_1 was calculated from Beer's Law as (a function of the coefficient for the first absorption process light, intensity and cell geometry), $\gamma_1 = 2.0 \times 10^6$ sec^{-1}. $\gamma_2 = 4.6 \times 10^7$ sec^{-1} was derived from experimental observations of O_2 production at lowest pressures of NO_2 (see subsequent discussion). From Beer's Law γ_2 corresponds to $\alpha_2 = 3.5$ atm^{-1}cm^{-1}. The general form of λ_1, λ_2, etc. is $\lambda = Qk(M)$, where Q is the quenching efficiency of a gas component, $k \cong 2 \times 10^{-10}$ part^{-1} sec^{-1}, and (M) is the number of quenching particles in the reaction volume.

Figure Captions

Figure 1 - Partial pressure of NO_2 vs. pressure of (NO_2 + N_2O_4) equilibrium mixture at 20°C.

Figure 2 - O_2 formed by five pulses in a mixture of 53% NO_2 and 47% Argon: (a) as percent of total gas pressure and (b) as number of particles vs. pressure of NO_2; (c) number of NO_2^* formed by five pulses vs. pressure of NO_2; and (d) tangent drawn to production curve at lowest pressures of NO_2.

Figure 3 - Fraction of NO_2^* which absorbs a second photon with zero quenching vs. the second absorption coefficient, α_2.

Figure 4 - Calculated values for a mixture of 50% (NO_2 + N_2O_4) and 50% Argon: (a) total number of NO_2^* formed per pulse vs. pressure of NO_2; O_2 production curves for (b) zero quenching, (c) quenching but no dimerization, (d) quenching and dimerization of NO_2 as shown in Fig. 1.

Figure - 1

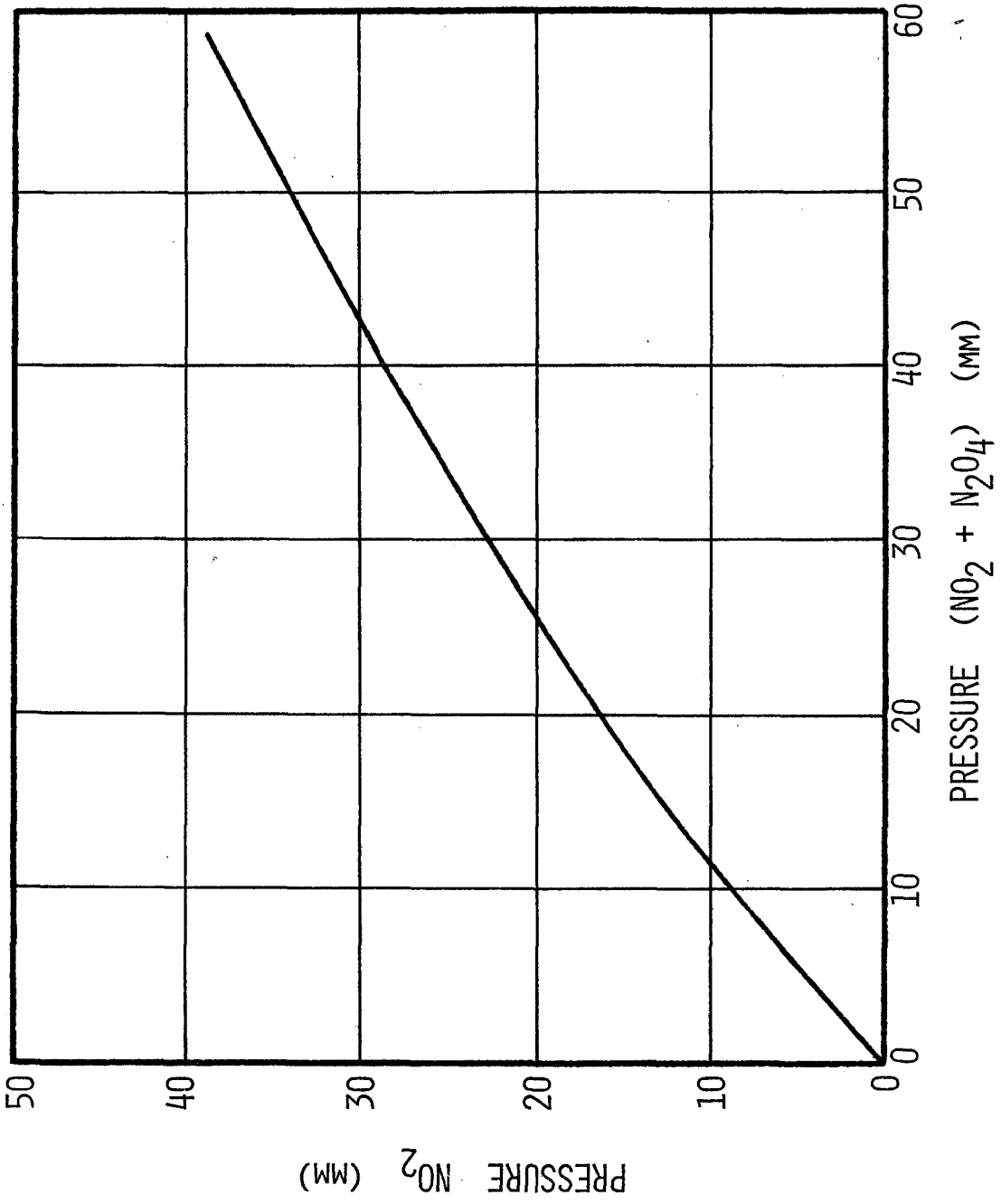

PRESSURE NO_2 (MM)
0
10
20
30
40
50
0
10
20
30
40
50
60
PRESSURE (NO_2 + N_2O_4) (MM)

Figure - 2

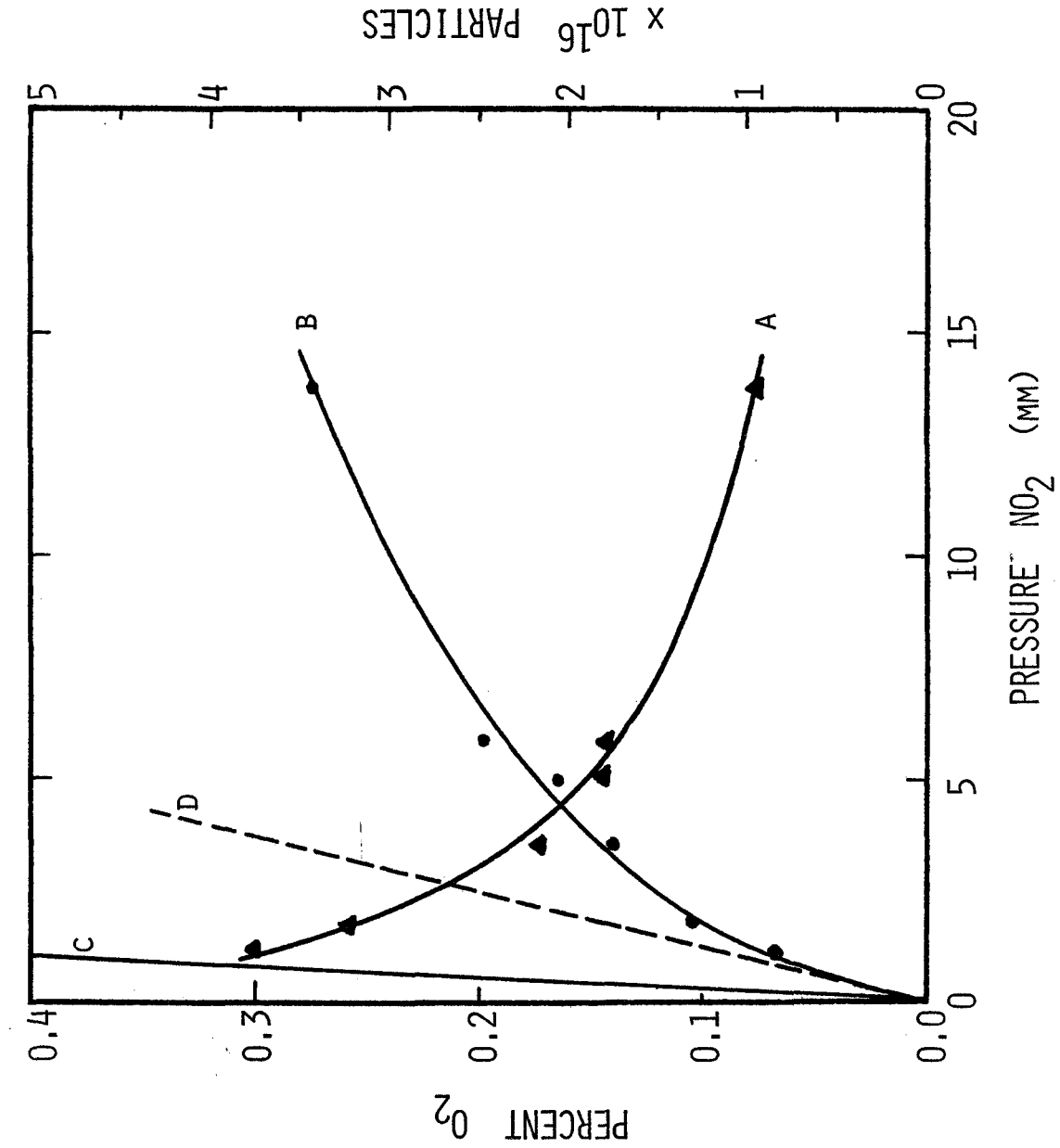

PERCENT O_2
0.0
0.1
0.2
0.3
0.4
0
5
10
15
20
PRESSURE NO_2 (MM)
0
1
2
3
4
5
x 10^{16} PARTICLES
A
B
C
D

Figure - 3

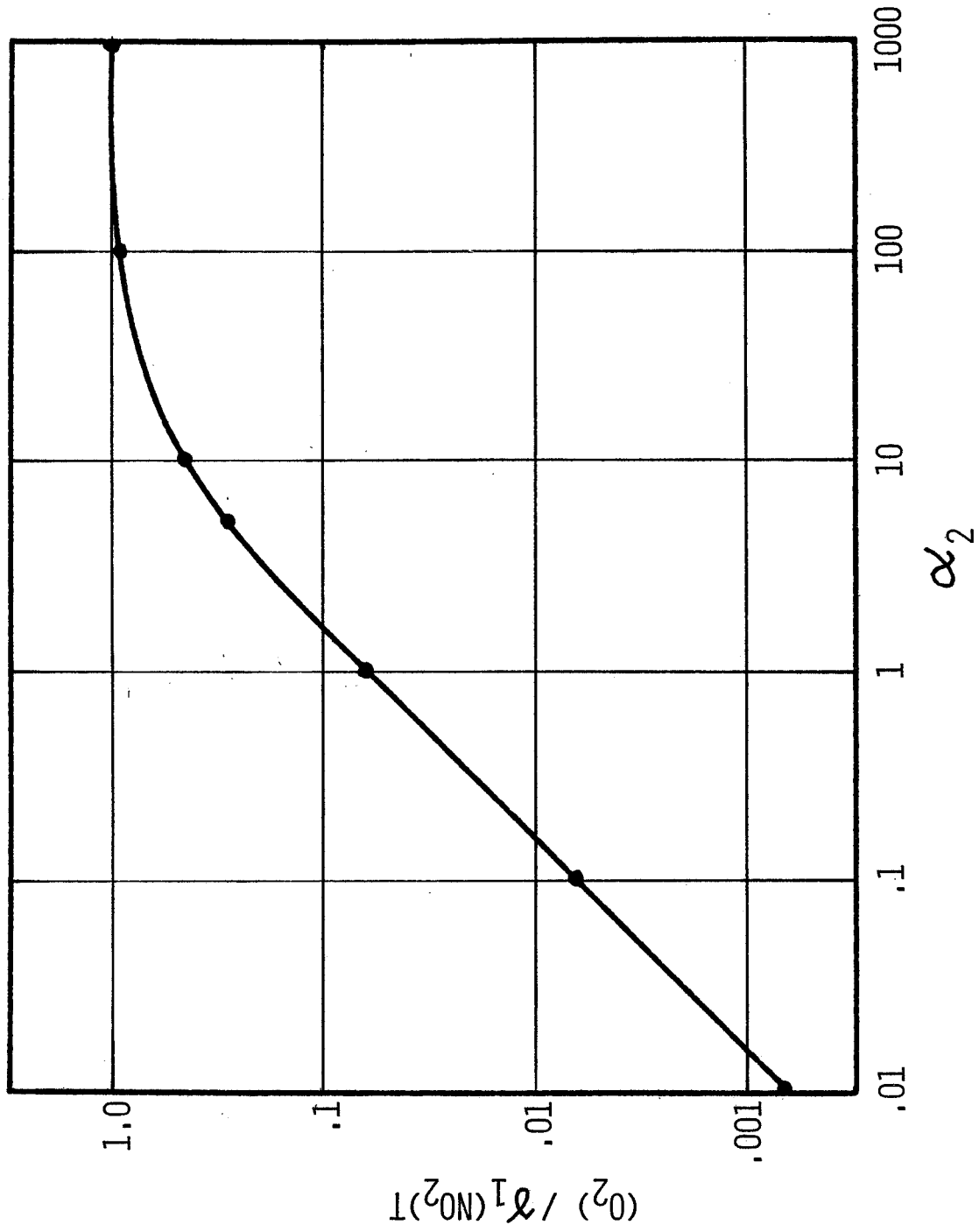
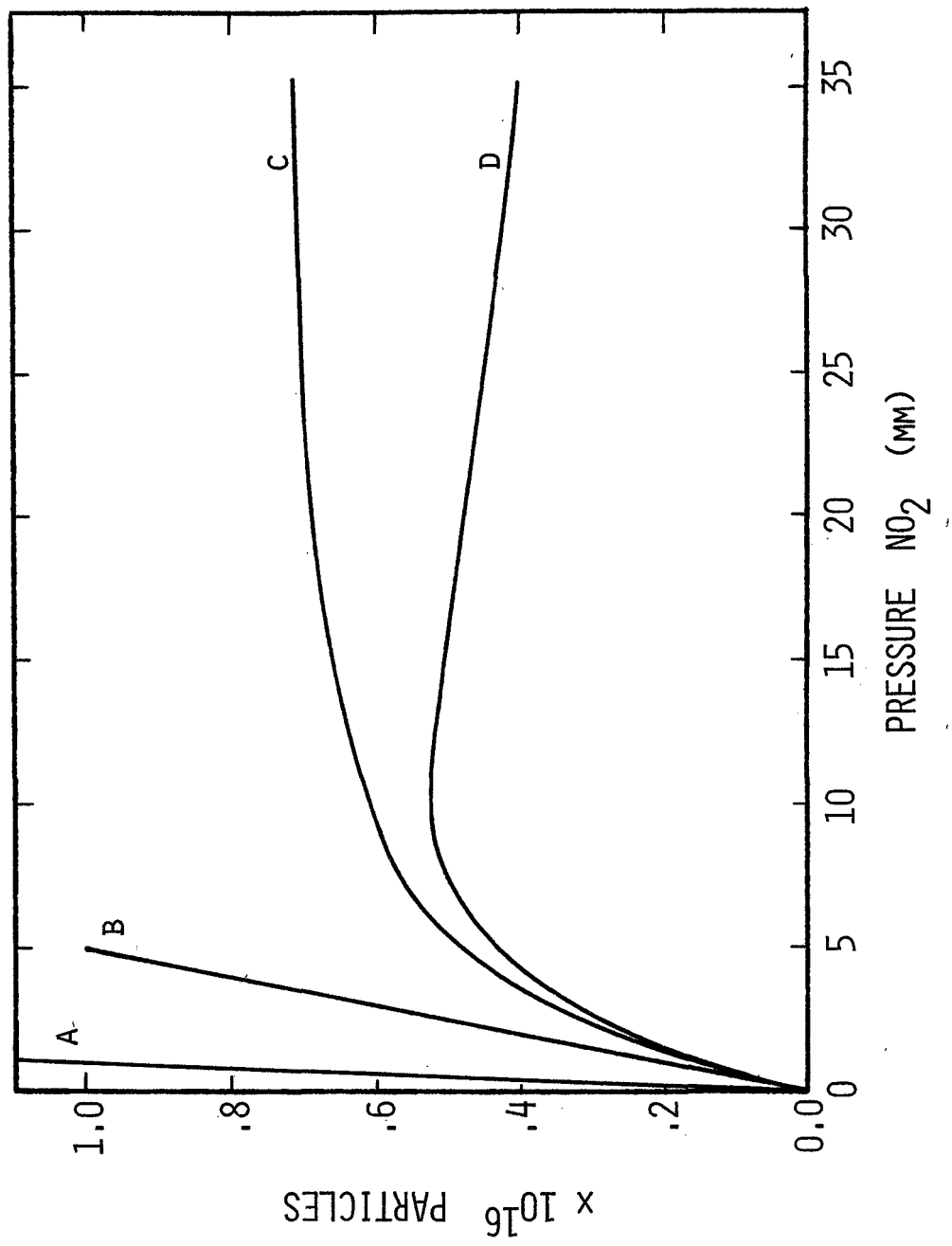


Figure - 4


x 10^16 PARTICLES
1.0
.8
.6
.4
.2
0.0
0
5
10
15
20
25
30
35
PRESSURE NO2 (MM)
A
B
C
D