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OF ClONO<sub>2</sub>

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Quantum Yield for  $\text{NO}_3$  Production from Photolysis of  $\text{ClONO}_2$

By

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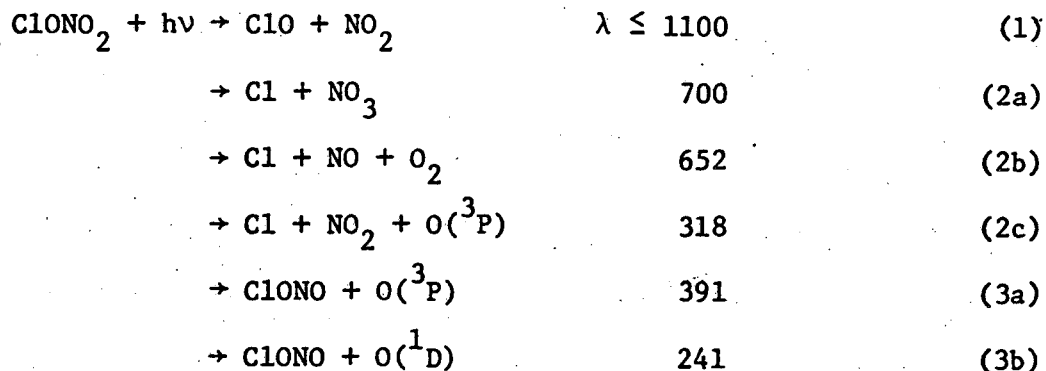
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**Abstract**

Chlorine nitrate,  $\text{ClONO}_2$ , was photolyzed at 249 nm by a 10 ns pulse from an excimer laser, and the primary product  $\text{NO}_3$  was followed by tunable dye-laser absorption at 662 nm. With Ar or Ar plus  $\text{CH}_4$  as carrier gases between 20 and 100 Torr, the primary quantum yield for  $\text{NO}_3$  was 0.55 (- 0.1 to + 0.3).

## Introduction

There are several possible products of  $\text{ClONO}_2$  photolysis, which are listed here with the threshold wavelengths (nm)



Three previous studies of this process have obtained apparently conflicting results.

Smith, Chou, and Rowland [1] photolyzed  $\text{ClONO}_2$  at 302.5 nm. No direct measurements were made for  $\text{ClO}$ ,  $\text{Cl}$ ,  $\text{ClONO}$ ,  $\text{NO}_3$ , or  $\text{O}$ ; but they measured the final chemical products and overall quantum yields. They found  $\text{O}_2$ ,  $\text{Cl}_2$ , and  $\text{N}_2\text{O}_5$  to be the predominant final products, and the overall quantum yield for  $\text{ClONO}_2$  destruction was 4. The lack of  $\text{HCl}$  as a product when  $\text{C}_2\text{H}_6$  was added was interpreted as evidence against path (2). A multi-step mechanism involving homogeneous and heterogeneous reactions and with (3a) as the primary process was used to explain the results.

Chang, Barker, Davenport, and Golden [2] photolyzed  $\text{ClONO}_2$  at low pressure in a silica Knudsen cell with molecular beam sampling into a mass spectrometer. Photolysis was by a filtered beam from a high-intensity, high-pressure xenon lamp. The wavelength band was 260 to 380 nm, and about half of the photolysis occurred below 300 nm. In the

apparatus atomic chlorine, atomic oxygen,  $\text{NO}_3$ , and  $\text{ClO}$  could be observed if present. The authors reported the following primary quantum yields:  $\phi(\text{O}) \leq 0.1$ ,  $\phi(\text{Cl}) = 1.0 \pm 0.2$ ,  $\phi(\text{NO}_3) = 0.5 \pm 0.3$ ,  $\phi(\text{ClO}) \leq 0.04$ . On the basis of these results, they concluded that (2a) was the predominant reaction pathway.

Adler-Golden and Wiesenfeld [3] photolyzed  $\text{ClONO}_2$  with a broad-band flash lamp with a pulse width of 20  $\mu\text{s}$ . The wavelength of the radiation extended from 200 nm to the infrared with a distribution comparable to a black-body at 6500 K. Atomic oxygen and atomic chlorine were followed by resonance absorption in the vacuum-ultraviolet region. They clearly detected atomic oxygen, but did not report a value for the quantum yield. They were also able to measure the pseudo first-order kinetics of the  $\text{O} + \text{ClONO}_2$  reaction, beginning 200  $\mu\text{s}$  after the initiation of the flash. Atomic Cl was looked for but not seen, and on the basis of the sensitivity of the apparatus they estimated that  $\phi(\text{Cl}) \leq 0.04$ . These authors favored (3a) as the primary path of  $\text{ClONO}_2$  photolysis.

This study was designed to measure the primary  $\text{NO}_3$  quantum yield using excimer-laser flash photolysis of  $\text{ClONO}_2$  at 249 nm and a dye-laser absorption probe of the  $\text{NO}_3$ (0-0) band at 661.9 nm.

### Experimental

The flash photolysis/laser absorption (FP/LA) technique was used to observe the  $\text{NO}_3$  product from  $\text{ClONO}_2$  photolysis. The apparatus is shown in Figure 1. The FP/LA cell consisted of a 191.5 cm long, 3.3 cm i.d. jacketed quartz cell equipped with stainless steel end caps and  $\text{CaF}_2$  windows. The outputs from an Ar ion pumped CW dye laser (Spectra Physics

581A) with 0.05 nm bandwidth and an unstable-resonator excimer laser (Lumonics TE-860-2M) operating on KrF at 249 nm were propagated coaxially down the cell. A pair of calibrated masks served to define the excimer laser photolysis and dye laser probe beams so as to make the photolysis volume larger than the probe volume. This insured that the probe beam sampled only the photolysis volume, and minimized the effects of diffusion out of the probe volume. When set up with the "unstable resonator" option, the laser produced a compact, slowly diverging beam with rectangular cross sections, but it had a hole in the center of the rectangle. The intense portion of the beam excluding this hole was used. The dye laser was operated using R640 and tuned to the  $\text{NO}_3$  A-X(0,0) transition at 661.9 nm using a 1 meter monochromator, operated in second order with a 1200  $\ell/\text{mm}$  grating blazed at 500 nm, and coupled to a vidicon tube and optical multichannel analyzer (OMA). The wavelength scale of the OMA was calibrated by overlaying the output from a Neon pilot lamp on to the dye laser signal. Photolysis laser energies were measured using a pyroelectric joulemeter (Gentec) calibrated by  $\text{ClNO}$  actinometry. Data were recorded using a fast photodiode detector/amplifier combination interfaced to a transient waveform recorder (Biomation 805) and signal averager. The photolysis laser was operated at 1 Hz and a typical experiment was the sum of 256 or 512 laser shots.

Flow rates were such that the residence times of chlorine nitrate in the photolysis cell was about 6 seconds. Chlorine nitrate was entrained in a stream of Ar passed through a saturator held at 157 K, and then diluted with either Ar or  $\text{CH}_4$  to the desired pressure and concentration using needle valves placed in the carrier gas flow

lines. After passing through the photolysis cell, the  $\text{ClONO}_2$  concentration was measured by UV absorption at 215 nm in an absorption cell of one-meter pathlength. This system consisted of a chopped deuterium lamp whose output passed down the 1 meter cell and entered a 0.3 meter monochromator (0.3 nm resolution) equipped with a PMT and associated phase sensitive detection electronics. The UV monitoring cell was connected to the photolysis cell by a 3/4 inch O.D. Pyrex tube, which is large enough to eliminate pressure drops between the cells. This was confirmed by simultaneous measurement of flowing  $\text{NO}_2/\text{N}_2$  mixtures in each cell. After exiting the monitoring cell the mixture was removed by a throttled and trapped roughing pump. The combination of short gas residence time, small photolysis volume, and low photodissociation efficiency, resulted in less than 3%  $\text{ClONO}_2$  destruction in the cell. Absorption cross sections used at the monitoring and photolysis wavelengths ( $\sigma_{215} = 3.60 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ ,  $\sigma_{249} = 6.39 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ ) were those of Molina and Molina [4].

Chlorine nitrate was prepared via the reaction of  $\text{Cl}_2\text{O}$  with  $\text{N}_2\text{O}_5$  by the method of Schmeisser [5]



Chlorine monoxide was condensed into a trap containing excess, freshly prepared  $\text{N}_2\text{O}_5$ . The trap was equipped with a  $\text{P}_2\text{O}_5$  drying tube, placed in a trichloroethylene slush at 200 K, and allowed to warm to 273 K during which the reaction occurred. The  $\text{ClONO}_2$  was distilled



from the trap held at 175 K into a trap at 157 K, leaving behind any residual  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ , or  $\text{HNO}_3$ . The  $\text{ClONO}_2$  was then pumped at 157 K to remove any  $\text{Cl}_2$ ,  $\text{Cl}_2\text{O}$ , or  $\text{OClO}$  impurities. The final product was a faintly yellow liquid. A measurement of UV absorption cross sections agreed well with Molina and Molina [4]. No impurities were found above the detection limits of 0.4%,  $\text{Cl}_2\text{O}$ ; 0.8%,  $\text{NO}_2$ ; 0.07%,  $\text{OClO}$ ; 4.2%,  $\text{Cl}_2$ ; 0.2%,  $\text{N}_2\text{O}_5$ . Argon (> 99.99%) and  $\text{CH}_4$  (> 99.99%) were supplied by Lawrence Berkeley Laboratories and used without further purification.

## Results

The time domain behavior of  $\text{NO}_3$  in a typical  $\text{ClONO}_2$  photolysis experiment is shown in Figure 2. This experiment was conducted using  $6.2 \times 10^{14}$  molecules  $\text{cm}^{-3}$  of  $\text{ClONO}_2$ , a laser fluence of  $1.7 \times 10^{17}$  photons  $\text{cm}^{-2}$  per shot, 1 shot per second, time resolution of 2  $\mu\text{s}$ /channel, and a carrier gas mixture of 17 Torr  $\text{CH}_4$  and 3 Torr Ar. Argon was always present in these experiments since it (and never  $\text{CH}_4$ ) was used to flow through the  $\text{ClONO}_2$  saturator. Figure 2 shows a prompt rise in the  $\text{NO}_3$  concentration coincident with the laser pulse followed by a slow rise peaking after about 200  $\mu\text{s}$ . The slowly-produced  $\text{NO}_3$  was about 15% of the initial increase in this example. This secondary  $\text{NO}_3$  occurred both in pure argon and in the presence of methane, although its magnitude was less when  $\text{CH}_4$  was present.

The amount of  $\text{NO}_3$  initially formed,  $C$ , was calculated from  $\ln I_0/I = \sigma CL$ , where  $\sigma$  was  $1.90 \times 10^{-17}$   $\text{cm}^2$  molecule $^{-1}$  [6] and  $L$  was 192 cm. The primary quantum yield  $\phi_{\text{NO}_3}^0$  is the ratio of this concentration

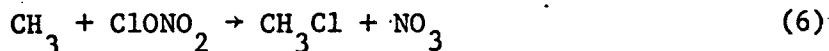
to the amount of  $\text{ClONO}_2$  photolyzed as calculated from  $\text{ClONO}_2$  concentration, laser pulse fluence, and the cross section of  $\text{ClONO}_2$  [4] for 249 nm radiation. The experimental conditions and experimental results are given in Table 1. The quantum yields are plotted against laser fluence in Figure 3. The initial quantum yields appear to be  $0.55 \pm 0.1$  independent of fluence,  $\text{ClONO}_2$  concentration, presence or absence of methane, and total pressure.

### Discussion

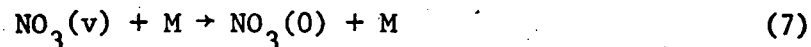
These experiments had a short (10 ns) pulse width and narrow band (248 - 249 nm) photolysis wavelength. The product  $\text{NO}_3$  appeared with about 0.55 quantum yield within 2  $\mu\text{s}$  following the photolysis pulse. This  $\text{NO}_3$  could not be the product of a secondary chemical reaction of some species with  $\text{ClONO}_2$  unless the rate constant was greater than  $5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This study did reveal some secondary production of  $\text{NO}_3$  (Figure 2) with quantum yields between 0.1 and 0.2. Possible mechanisms for the secondary production of  $\text{NO}_3$  include the following: (i) The reaction of atomic chlorine with chlorine nitrate



(ii) The reaction of atomic chlorine with methane to produce methyl radicals which further react



and (iii) the formation of some  $\text{NO}_3$  in excited vibrational states, which becomes measurable with the 0-0 transition only after deactivation to the ground vibrational state

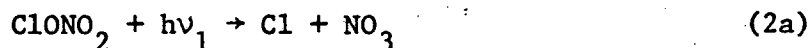


The observed quantum yield is consistently 0.55. If (7) is the cause of the secondary  $\text{NO}_3$ , then the observed quantum yield for  $\text{NO}_3$  is about 0.75. Because of this uncertainty in interpreting the secondary  $\text{NO}_3$ , the value and error limits on  $\phi(\text{NO}_3)$  are considered to be 0.55 (- 0.1 to + 0.3). This study supports (2a) as the most important channel, but it does not exclude partial contributions from other channels.

It is difficult to compare these results with those of Smith et al. [1]. Their method was indirect, and their interpretations, based on final products, depend on a multi-step mechanism including homogeneous and heterogeneous reactions. They explicitly reject channel (2a), whereas this study indicates it to represent 55% or more of the primary products. It is possible to propose alternate paths for some of the products observed by Smith et al. For example, their product  $\text{N}_2\text{O}_5$  might have come from  $\text{NO}_2 + \text{NO}_3$  where the  $\text{NO}_2$  was produced from  $\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$ . Their  $\text{O}_2$  might have come from various reactions by these secondary oxygen atoms, and their  $\text{Cl}_2$  might have been formed by  $\text{Cl} + \text{ClONO}_2$ . Although these considerations do not explain all of their results, it may be that a large component of (2a) is consistent with their data.

The present results tend to disagree with the article by Adler-Golden and Wiesenfeld [3], who conclude that the quantum yield from channels (2) is less than 0.04. They observed no chlorine atoms in the photolysis of  $\text{ClONO}_2$ . They stated that their observations of oxygen atoms started after 200  $\mu\text{s}$ , but in this time small amounts of

$\text{Cl}_2\text{O}$  impurity in the  $\text{ClONO}_2$  might have scavenged chlorine atoms. The rate constant for the reaction,  $\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + \text{ClO}$ , is  $9.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [7], which is 445 fold larger than that for  $\text{Cl} + \text{ClONO}_2$  [8]. Also, these authors concluded that atomic oxygen was the predominant primary product of  $\text{ClONO}_2$  photolysis, whereas this study finds  $\text{NO}_3$  to be a predominant primary product. A possible source of this disagreement may arise from their relatively slow (20  $\mu\text{s}$ ), broad band (200 - 1000 nm) flash lamp, which might be expected to produce secondary oxygen atoms from photolysis of  $\text{NO}_3$ . Their results showed a linear relation between atomic oxygen production and flash-lamp energy, and they state that secondary O production would show a quadratic dependence on energy. However, this conclusion depends on the magnitude of the photolytic constants for  $\text{ClONO}_2$  and  $\text{NO}_3$ . Consider the mechanism



The rate of production of atomic oxygen is

$$\frac{d[\text{O}]}{dt} = j_1 [\text{ClONO}_2] \left(1 - e^{-j_2 \tau}\right) \quad (9)$$

If the term  $j_2 \tau$  is small compared to one (where  $\tau$  is the pulse duration), the integral of atomic-oxygen production over the pulse is quadratic in pulse energy

$$\int_{\text{pulse}} d[\text{O}] = j_1 j_2 [\text{ClONO}_2] \tau^2 / 2 \quad (10)$$

since both  $j_1$  and  $j_2$  are proportional to pulse energy.

On the other hand if  $j_2\tau$  is larger than one, the oxygen signal is linear in pulse energy

$$\int_{\text{pulse}} d[\text{O}] = j_1 [\text{ClONO}_2] \tau \quad (11)$$

The article by Adler-Golden and Wiesenfeld [3] does not give quantitative values for photolytic rate constants, but approximate relative values can be inferred from the data given. The flash lamp has a radiation distribution similar to a black body at 6500 K, and "flash lamp operation led to substantial  $\text{ClONO}_2$  decomposition." By using cross sections for  $\text{ClONO}_2$  [4] between 200 and 360 nm, cross sections [9] and quantum yields [10] for  $\text{NO}_3$  photolysis between 400 and 650 nm, and a relative radiation distribution based on the Planck function for 6500 K, we estimate that  $\text{NO}_3$  photolysis to produce  $\text{NO}_2 + \text{O}$  is more than six times as fast as  $\text{ClONO}_2$  photolysis in their experiments. If  $\text{ClONO}_2$  underwent "substantial decomposition," then  $\text{NO}_3$  would be almost completely photolyzed, and the linear relation (11) would be applicable even for this secondary production of atomic oxygen.

Chang et al. [2] found little or no production of atomic oxygen or  $\text{ClO}$  as primary products, and they found  $\phi(\text{Cl})$  to be  $1.0 \pm 0.2$  and  $\phi(\text{NO}_3)$  to be  $0.5 \pm 0.3$ . The present study finds  $\phi(\text{NO}_3)$  to be 0.55 (- 0.1 to + 0.3). These quite different methods give about the same quantum yield for  $\text{NO}_3$ . These two studies agree that channel (2a) is the most important single process, and the two studies are in complete agreement if channels (2b) and/or (2c) contribute to the quantum yield of atomic chlorine.

**Acknowledgment**

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Table 1. The  $\text{NO}_3$  quantum yields from laser flash photolysis at 249 nm and from laser absorption at 662 nm.

$\frac{[\text{ClNO}_3]}{10^{14}}$	Pressure		$\frac{E}{10^{16}}$	Light abs $10^{13}$	$\phi_{\text{NO}_3}^o$
	Torr				
a	Ar	$\text{CH}_4$	b	c	
4.88	20	-	4.93	1.92	0.58
8.03	20	-	15.9	8.14	0.55
6.96	20	-	2.97	1.32	0.55
6.90	20	-	10.3	4.54	0.63
6.64	100	-	2.92	1.24	0.57
6.29	100	-	17.6	7.06	0.59
6.15	100	-	15.1	5.92	0.64
6.01	3	17	4.49	1.71	0.55
7.21	3	17	2.24	1.03	0.57
7.06	3	17	1.23	.555	0.52
6.01	3	17	5.32	2.04	0.57
6.19	3	17	17.2	6.80	0.51
6.84	3	17	8.34	3.64	0.55
6.99	40	60	18.4	8.24	0.50
7.06	40	60	8.25	3.72	0.58
7.23	40	60	4.30	1.99	0.49
6.80	40	60	2.42	1.05	0.59
3.08	5	95	12.8	2.51	0.56
3.02	5	95	4.10	0.763	0.44
3.05	5	95	13.4	2.56	0.48
3.09	5	95	6.73	1.33	0.55

<sup>a</sup>Molecules  $\text{cm}^{-3}$ , <sup>b</sup>Photons  $\text{cm}^{-2}$  shot<sup>-1</sup>, <sup>c</sup>Photons  $\text{cm}^{-3}$  shot<sup>-1</sup>.



## Figure Captions

Figure 1. Schematic diagram of experimental method.

Figure 2. Example of experimental data during one run, showing  $\text{NO}_3$  concentration as a function of time as measured by laser absorption at 662 nm. Photolysis of  $\text{ClONO}_2$  was by excimer laser pulses at 249 nm, 10 ns pulse width. Each point is 2  $\mu\text{s}$  wide and represents the average of 512 laser pulses at 1 Hz.

Figure 3. Primary  $\text{NO}_3$  quantum yield from  $\text{ClONO}_2$  at 249 nm as a function of laser fluence and composition of carrier gases:  $\circ$ , 20 Torr Ar;  $\bullet$ , 20 Torr Ar +  $\text{CH}_4$ ;  $\triangle$ , 100 Torr Ar; +, 100 Torr Ar +  $\text{CH}_4$ .

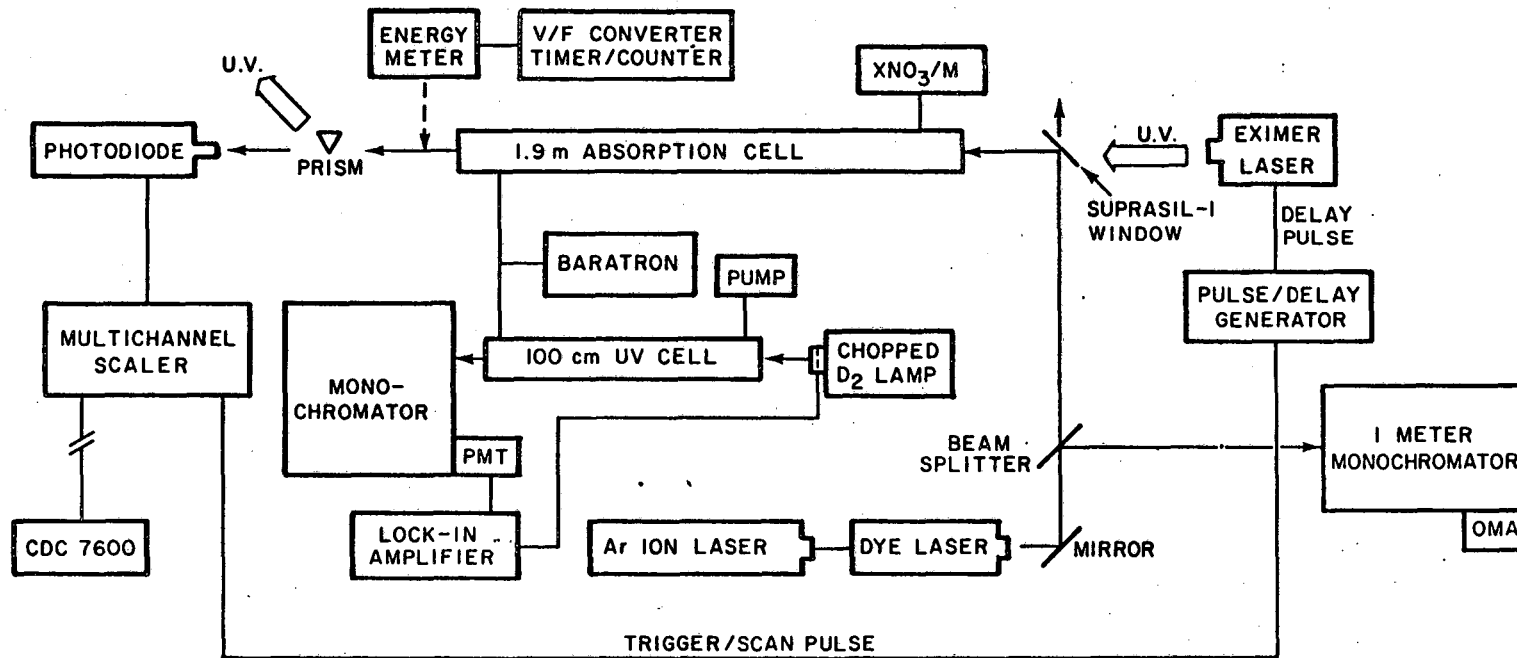


Figure 1

XBL 8111-12380

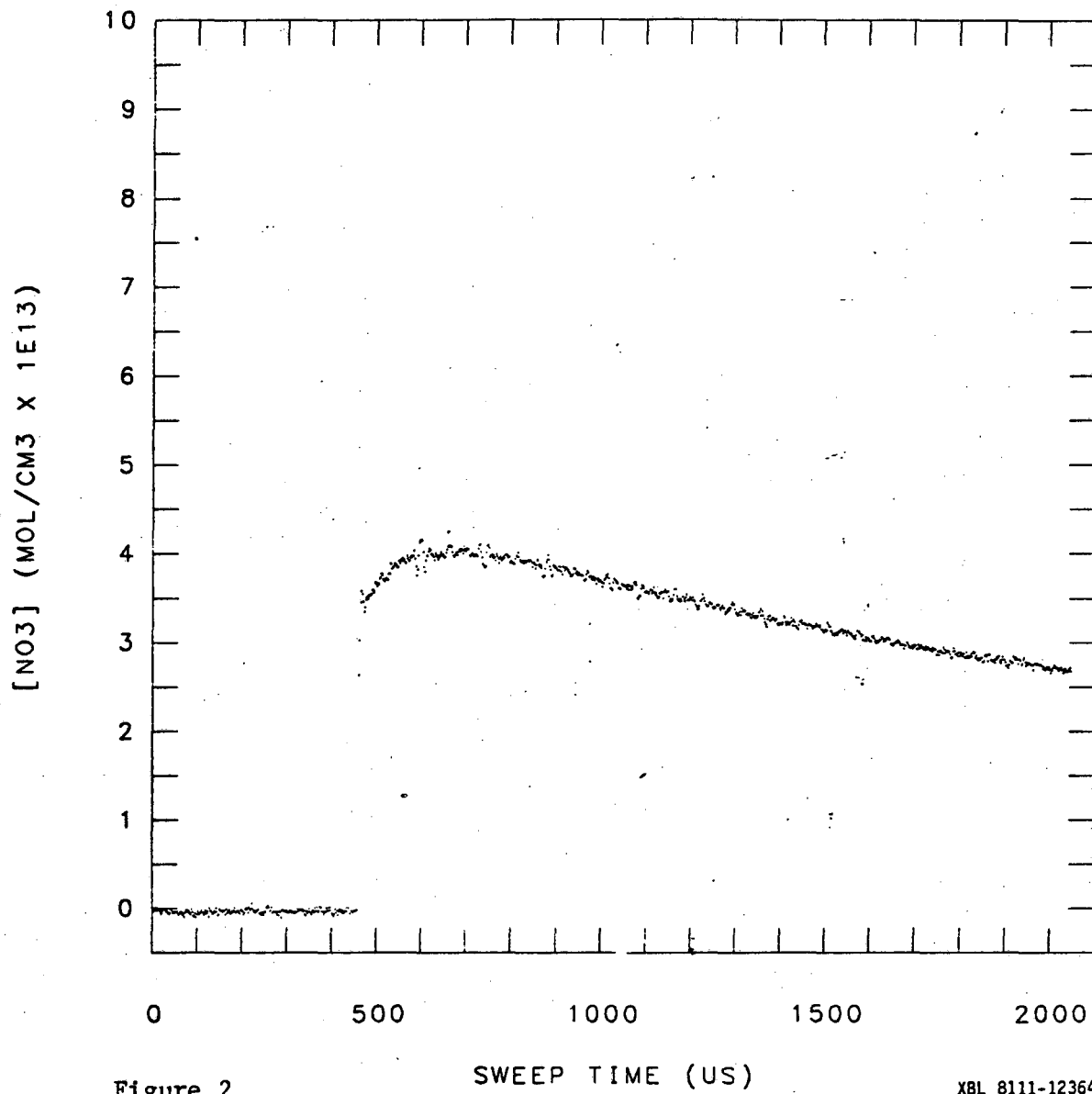


Figure 2

SWEEP TIME (US)

XBL 8111-12364

# PRIMARY NO<sub>3</sub> QUANTUM YIELD FROM ClONO<sub>2</sub> AT 249 nm

- 20 Torr Ar
- 20 Torr Ar + CH<sub>4</sub>
- △ 100 Torr Ar
- + 100 Torr Ar + CH<sub>4</sub>

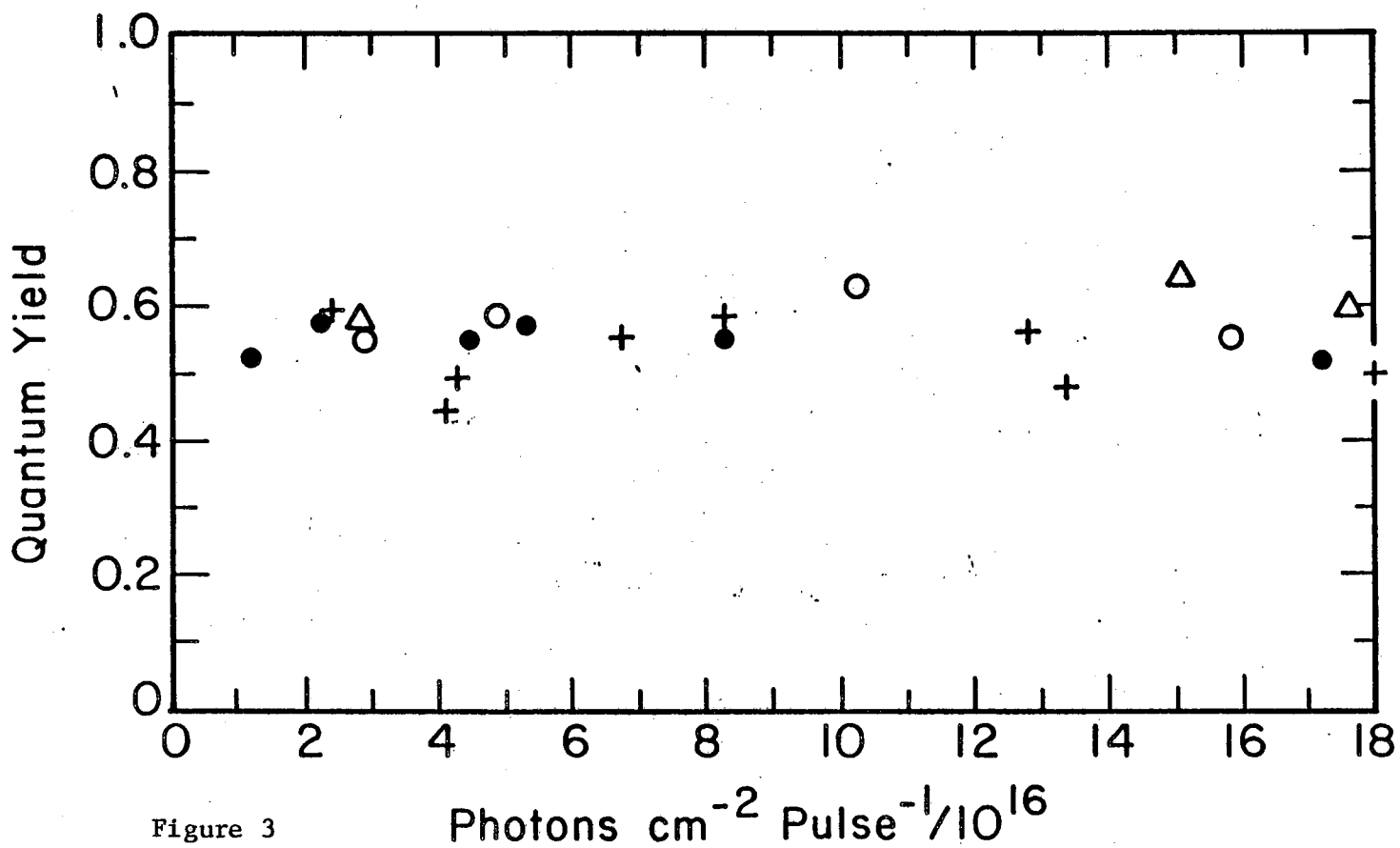


Figure 3

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