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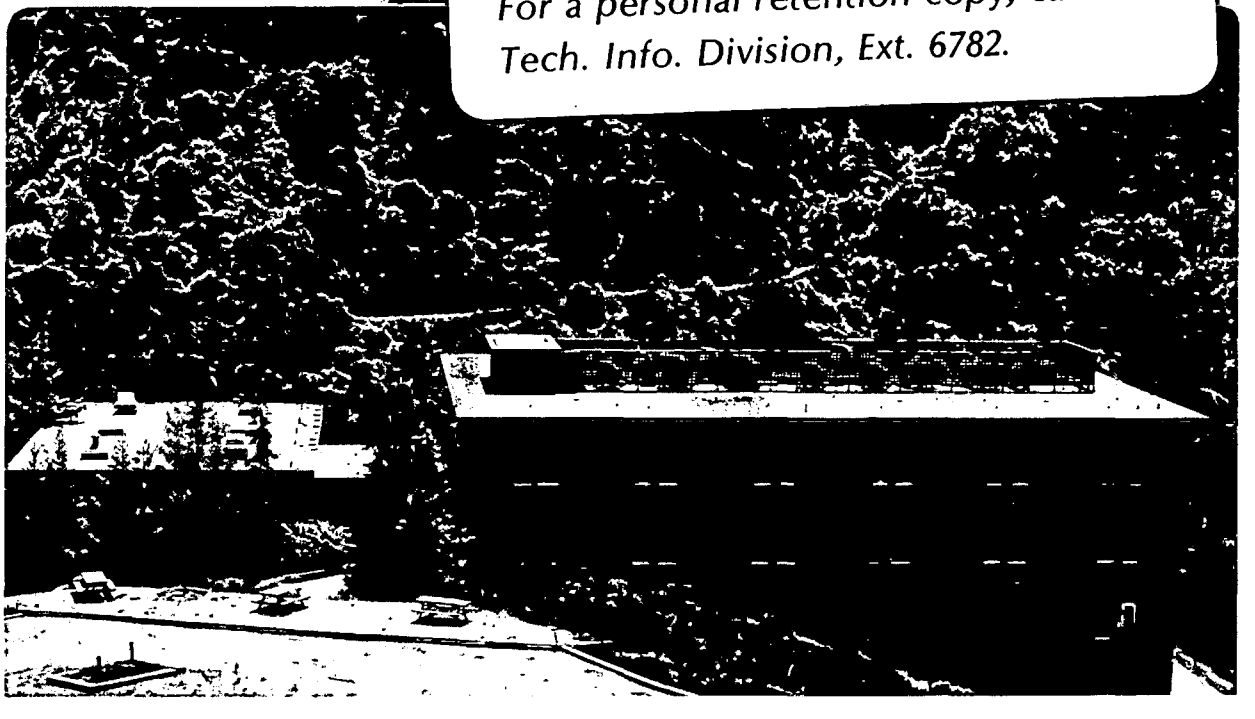

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Quantum Yield for NO_3 Production from Photolysis of $ClONO_2$

By

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Abstract

Chlorine nitrate, $ClONO_2$, was photolyzed at 249 nm by a 10 ns pulse from an excimer laser, and the primary product NO_3 was followed by tunable dye-laser absorption at 662 nm. With Ar or Ar plus CH_4 as carrier gases between 20 and 100 Torr, the primary quantum yield for NO_3 was 0.55 (- 0.1 to + 0.3).

Introduction

There are several possible products of $ClONO_2$ photolysis, which are listed here with the threshold wavelengths (nm)

$ClONO_2 + h\nu \rightarrow ClO + NO_2$	$\lambda \leq 1100$	(1)
$\rightarrow Cl + NO_3$	700	(2a)
$\rightarrow Cl + NO + O_2$	652	(2b)
$\rightarrow Cl + NO_2 + O(^3P)$	318	(2c)
$\rightarrow ClONO + O(^3P)$	391	(3a)
$\rightarrow ClONO + O(^1D)$	241	(3b)

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

Smith, Chou, and Rowland [1] photolyzed $ClONO_2$ at 302.5 nm. No direct measurements were made for ClO, Cl, ClONO, NO_3, or O; but they measured the final chemical products and overall quantum yields. They found O_2, Cl_2, and N_2O_5 to be the predominant final products, and the overall quantum yield for $ClONO_2$ destruction was 4. The lack of HCl as a product when C_2H_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 $ClONO_2$ 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, NO_3, and ClO could be observed if present. The authors reported the following primary quantum yields: $\phi(O) \leq 0.1$, $\phi(Cl) = 1.0 \pm 0.2$, $\phi(NO_3) = 0.5 \pm 0.3$, $\phi(ClO) \leq 0.04$. On the basis of these results, they concluded that (2a) was the predominant reaction pathway.

Adler-Golden and Wiesenfeld [3] photolyzed $ClONO_2$ with a broad-band flash lamp with a pulse width of 20 μs. 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 $O + ClONO_2$ reaction, begining 200 μs 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 $\phi(Cl) \leq 0.04$. These authors favored (3a) as the primary path of $ClONO_2$ photolysis.

This study was designed to measure the primary NO_3 quantum yield using excimer-laser flash photolysis of $ClONO_2$ at 249 nm and a dye-laser absorption probe of the NO_3(0-0) band at 661.9 nm.

Experimental

The flash photolysis/laser absorption (FP/LA) technique was used to observe the NO_3 product from $ClONO_2$ 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 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 co-axially 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 NO_3 A-X(0,0) transition at 661.9 nm using a 1 meter monochromator, operated in second order with a 1200 ℓ/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 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 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 $ClONO_2$ 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 NO_2/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 photo-dissociation efficiency, resulted in less than 3% $ClONO_2$ destruction in the cell. Absorption cross sections used at the monitoring and photolysis wavelengths (σ_{215} = 3.60 x 10^{-18} cm^2 $molecule^{-1}$, σ_{249} = 6.39 x 10^{-19} cm^2 $molecule^{-1}$) were those of Molina and Molina [4].

Chlorine nitrate was prepared via the reaction of Cl_2O with N_2O_5 by the method of Schmeisser [5]

$$Cl_2O + N_2O_5 \rightarrow 2\ ClONO_2 \quad . \tag{4}$$

Chlorine monoxide was condensed into a trap containing excess, freshly prepared N_2O_5. The trap was equipped with a P_2O_5 drying tube, placed in a trichloroethylene slush at 200 K, and allowed to warm to 273 K during which the reaction occurred. The $ClONO_2$ was distilled

from the trap held at 175 K into a trap at 157 K, leaving behind any residual NO_2, N_2O_5, or HNO_3. The $ClONO_2$ was then pumped at 157 K to remove any Cl_2, Cl_2O, or 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%, Cl_2O; 0.8%, NO_2; 0.07%, OClO; 4.2%, Cl_2; 0.2%, N_2O_5. Argon (> 99.99%) and CH_4 (> 99.99%) were supplied by Lawrence Berkeley Laboratories and used without further purification.

Results

The time domain behavior of NO_3 in a typical $ClONO_2$ photolysis experiment is shown in Figure 2. This experiment was conducted using 6.2×10^{14} molecules cm^{-3} of $ClONO_2$, a laser fluence of 1.7×10^{17} photons cm^{-2} per shot, 1 shot per second, time resolution of 2 μs/channel, and a carrier gas mixture of 17 Torr CH_4 and 3 Torr Ar. Argon was always present in these experiments since it (and never CH_4) was used to flow through the $ClONO_2$ saturator. Figure 2 shows a prompt rise in the NO_3 concentration coincident with the laser pulse followed by a slow rise peaking after about 200 μs. The slowly-produced NO_3 was about 15% of the initial increase in this example. This secondary NO_3 occurred both in pure argon and in the presence of methane, although its magnitude was less when CH_4 was present.

The amount of NO_3 initially formed, C, was calculated from $\ell n I_o/I = \sigma CL$, where σ was 1.90×10^{-17} cm^2 $molecule^{-1}$ [6] and L was 192 cm. The primary quantum yield $\phi^o_{NO_3}$ is the ratio of this concentration

to the amount of $ClONO_2$ photolyzed as calculated from $ClONO_2$ concentration, laser pulse fluence, and the cross section of $ClONO_2$ [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 ± 0.1 independent of fluence, $ClONO_2$ 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 NO_3 appeared with about 0.55 quantum yield within 2 μs following the photolysis pulse. This NO_3 could not be the product of a secondary chemical reaction of some species with $ClONO_2$ unless the rate constant was greater than 5×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. This study did reveal some secondary production of NO_3 (Figure 2) with quantum yields between 0.1 and 0.2. Possible mechanisms for the secondary production of NO_3 include the following: (i) The reaction of atomic chlorine with chlorine nitrate

$$Cl + ClONO_2 \rightarrow Cl_2 + NO_3 \qquad (5)$$

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

$$CH_3 + ClONO_2 \rightarrow CH_3Cl + NO_3 \qquad (6)$$

and (iii) the formation of some NO_3 in excited vibrational states, which becomes measurable with the 0-0 transition only after deactivation to the ground vibrational state

$$NO_3(v) + M \rightarrow NO_3(0) + M \qquad (7)$$

The observed quantum yield is consistently 0.55. If (7) is the cause of the secondary NO_3, then the observed quantum yield for NO_3 is about 0.75. Because of this uncertainty in interpreting the secondary NO_3, the value and error limits on $\phi(NO_3)$ 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, dependend 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 N_2O_5 might have come from $NO_2 + NO_3$ where the NO_2 was produced from $NO_3 + h\nu \rightarrow NO_2 + O$. Their O_2 might have come from various reactions by these secondary oxygen atoms, and their Cl_2 might have been formed by $Cl + ClONO_2$. 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 $ClONO_2$. They stated that their observations of oxygen atoms started after 200 μs, but in this time small amounts of

Cl_2O impurity in the $ClONO_2$ might have scavenged chlorine atoms. The rate constant for the reaction, $Cl + Cl_2O \rightarrow Cl_2 + ClO$, is 9.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [7], which is 445 fold larger than that for $Cl + ClONO_2$ [8]. Also, these authors concluded that atomic oxygen was the predominant primary product of $ClONO_2$ photolysis, whereas this study finds NO_3 to be a predominant primary product. A possible source of this disagreement may arise from their relatively slow (20 μs), broad band (200 - 1000 nm) flash lamp, which might be expected to produce secondary oxygen atoms from photolysis of 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 $ClONO_2$ and NO_3. Consider the mechanism

$$ClONO_2 + h\nu_1 \rightarrow Cl + NO_3 \qquad (2a)$$

$$NO_3 + h\nu_2 \rightarrow NO_2 + O \qquad (8)$$

The rate of production of atomic oxygen is

$$\frac{d[O]}{dt} = j_1[ClONO_2]\left(1 - e^{-j_2\tau}\right) \qquad (9)$$

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

$$\int_{pulse} d[O] = j_1 j_2 [ClONO_2]\tau^2/2 \qquad (10)$$

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

$$\int_{\text{pulse}} d[O] = j_1[ClONO_2]\tau \qquad (11)$$

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 $ClONO_2$ decomposition." By using cross sections for $ClONO_2$ [4] between 200 and 360 nm, cross sections [9] and quantum yields [10] for NO_3 photolysis between 400 and 650 nm, and a relative radiation distribution based on the Planck function for 6500 K, we estimate that NO_3 photolysis to produce NO_2 + O is more than six times as fast as $ClONO_2$ photolysis in their experiments. If $ClONO_2$ underwent "substantial decomposition," then 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 ClO as primary products, and they found $\phi(Cl)$ to be 1.0 ± 0.2 and $\phi(NO_3)$ to be 0.5 ± 0.3. The present study finds $\phi(NO_3)$ to be 0.55 (- 0.1 to + 0.3). These quite different methods give about the same quantum yield for 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 NO_3 quantum yields from laser flash phtolysis at 249 nm and from laser absorption at 662 nm.

$\frac{[ClNO_3]}{10^{14}}$	Pressure / Torr		$\frac{E}{10^{16}}$	$\frac{\text{Light abs}}{10^{13}}$	$\phi^o_{NO_3}$
a	Ar	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

[a] Molecules cm^{-3}. [b] Photons cm^{-2} $shot^{-1}$. [c] Photons cm^{-3} $shot^{-1}$.

Figure Captions

Figure 1. Schematic diagram of experimental method.

Figure 2. Example of experimental data during one run, showing NO_3 concentration as a function of time as measured by laser absorption at 662 nm. Photolysis of $ClONO_2$ was by excimer laser pulses at 249 nm, 10 ns pulse width. Each point is 2 μs wide and represents the average of 512 laser pulses at 1 Hz.

Figure 3. Primary NO_3 quantum yield from $ClONO_2$ at 249 nm as a function of laser fluence and composition of carrier gases: ○, 20 Torr Ar; ●, 20 Torr Ar + CH_4; △, 100 Torr Ar; +, 100 Torr Ar + CH_4.

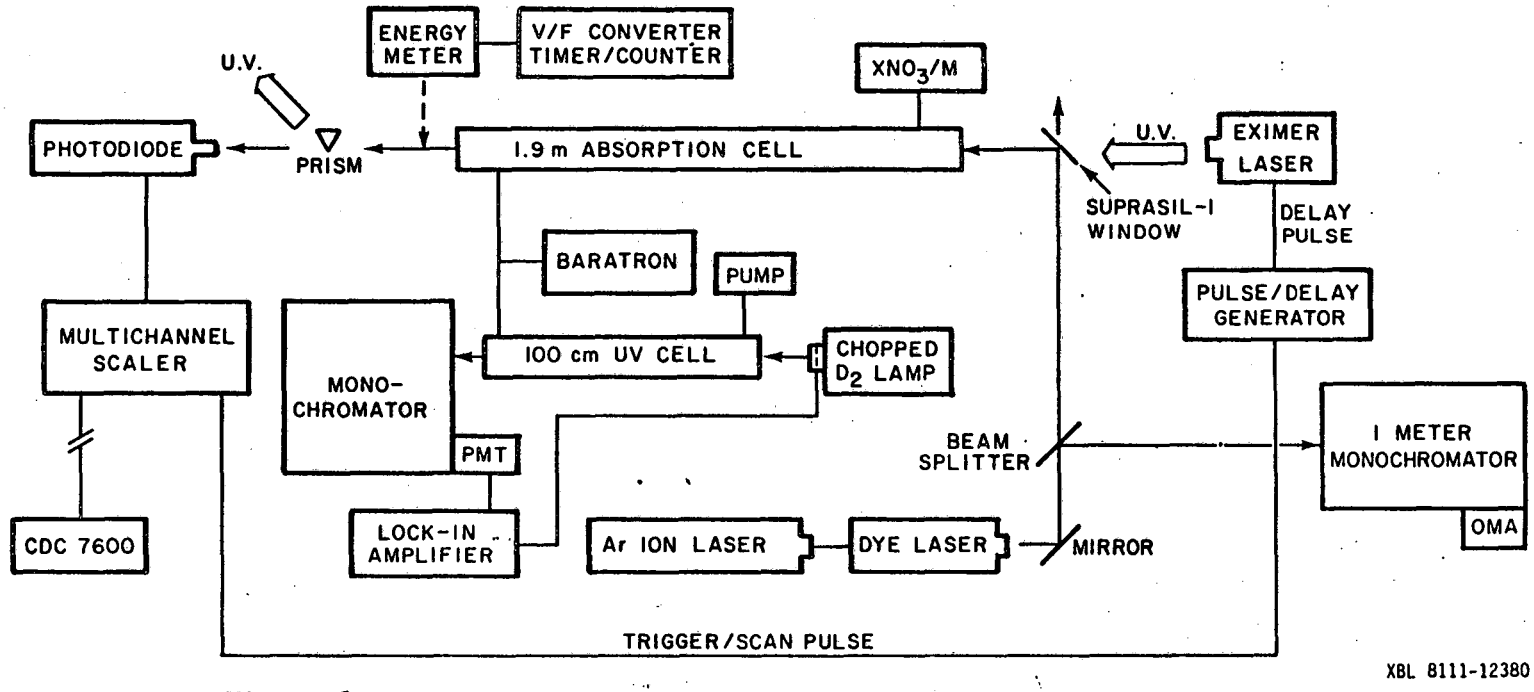
ENERGY METER
V/F CONVERTER TIMER/COUNTER
U.V.
XNO_3/M
PHOTODIODE
PRISM
1.9 m ABSORPTION CELL
U.V.
EXIMER LASER
SUPRASIL-I WINDOW
DELAY PULSE
BARATRON
PUMP
PULSE/DELAY GENERATOR
MULTICHANNEL SCALER
MONO-CHROMATOR
100 cm UV CELL
CHOPPED D_2 LAMP
BEAM SPLITTER
I METER MONOCHROMATOR
PMT
OMA
CDC 7600
LOCK-IN AMPLIFIER
Ar ION LASER
DYE LASER
MIRROR
TRIGGER/SCAN PULSE
XBL 8111-12380

Figure 1

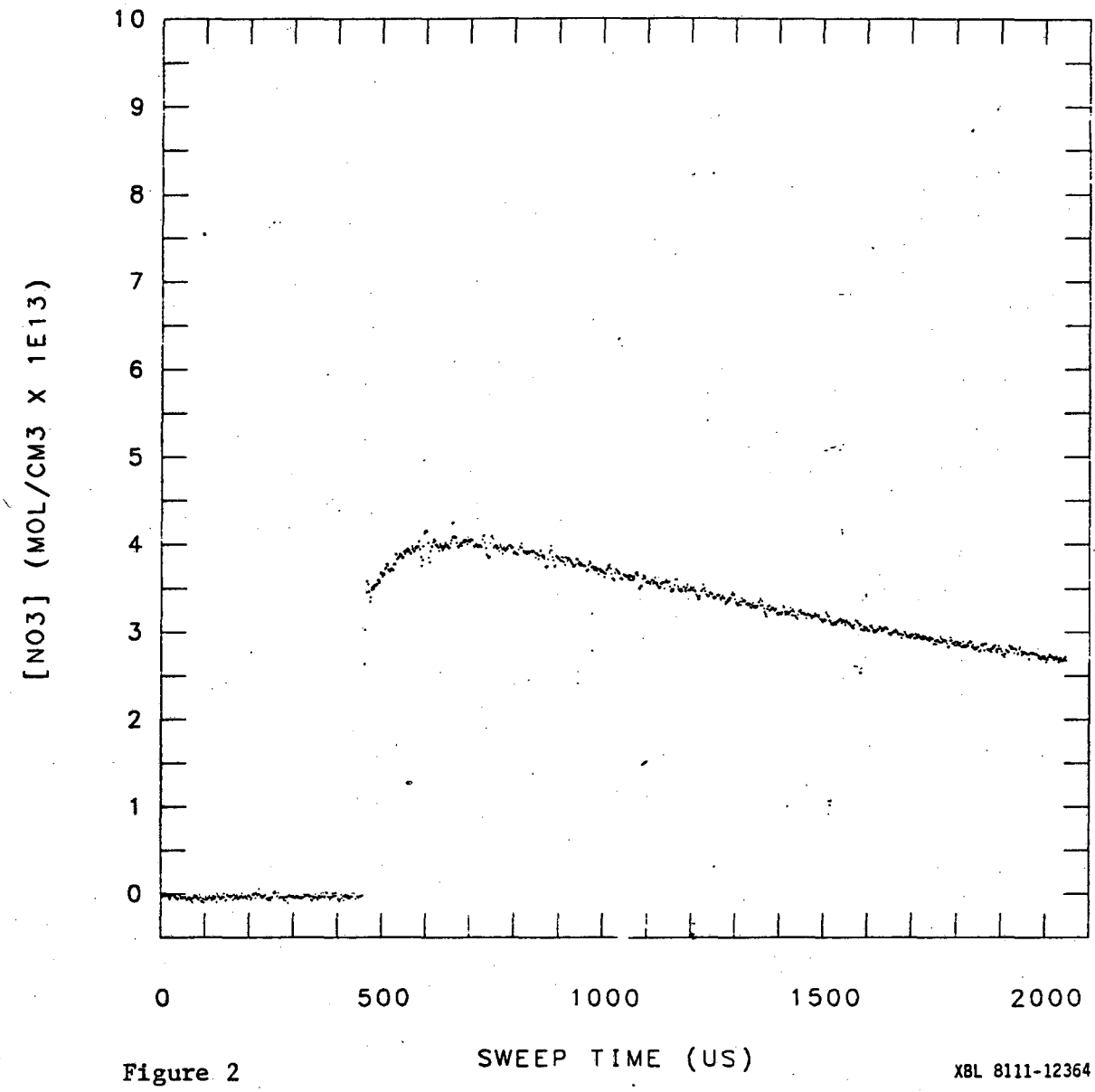
10
9
8
7
6
5
4
3
2
1
0
[NO3] (MOL/CM3 X 1E13)
0
500
1000
1500
2000
SWEEP TIME (US)
XBL 8111-12364

Figure 2

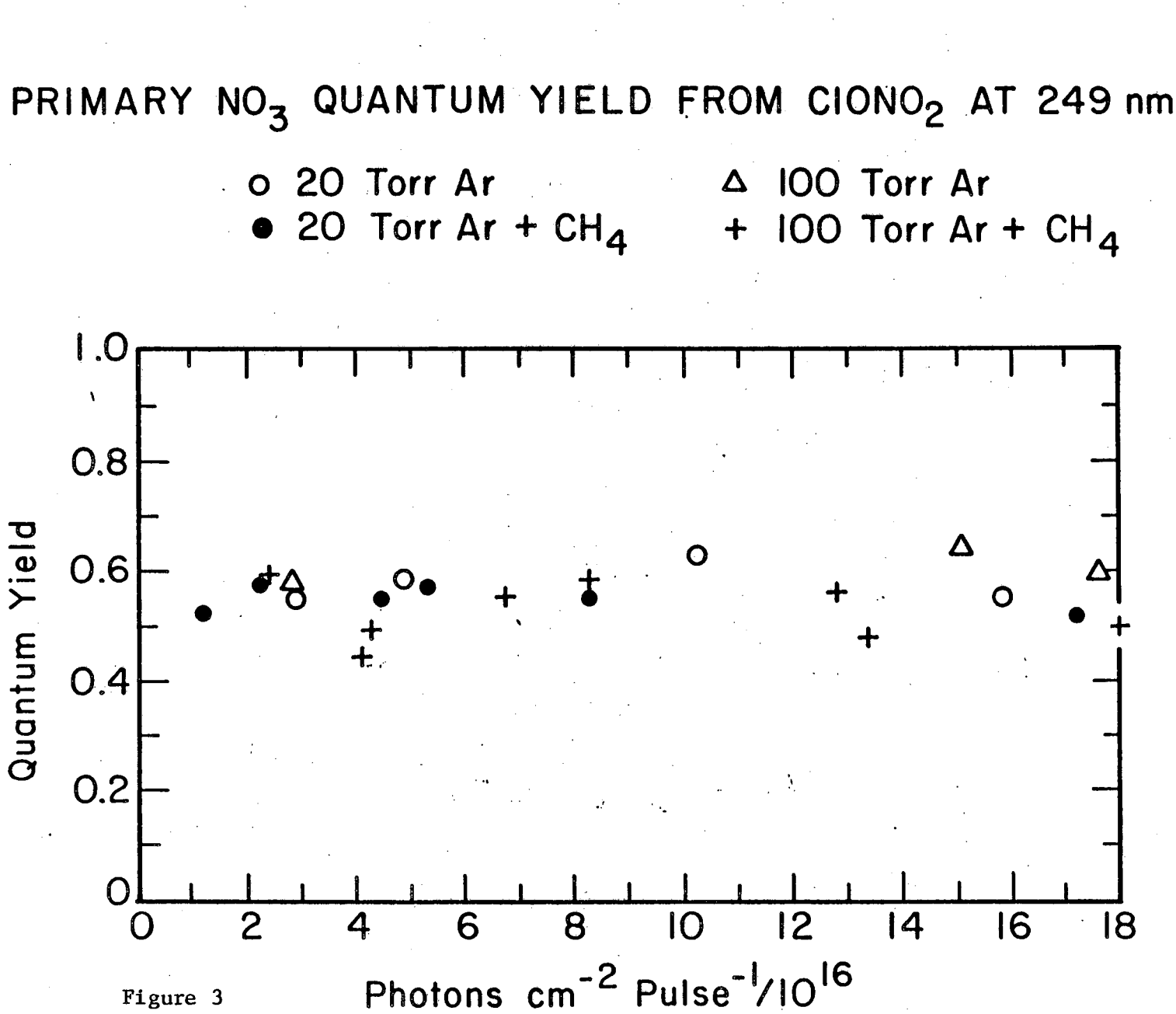
PRIMARY NO_3 QUANTUM YIELD FROM $ClONO_2$ AT 249 nm
o 20 Torr Ar
● 20 Torr Ar + CH_4
Δ 100 Torr Ar
+ 100 Torr Ar + CH_4
Quantum Yield
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
16
18
Photons cm^{-2} $Pulse^{-1}/10^{16}$

Figure 3

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