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### Title

ABSOLUTE PHOTODISSOCIATION QUANTUM YIELDS FOR THE NO<sub>3</sub> FREE RADICAL

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## Materials & Molecular Research Division

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ABSOLUTE PHOTODISSOCIATION QUANTUM YIELDS  
FOR THE NO<sub>3</sub> FREE RADICAL

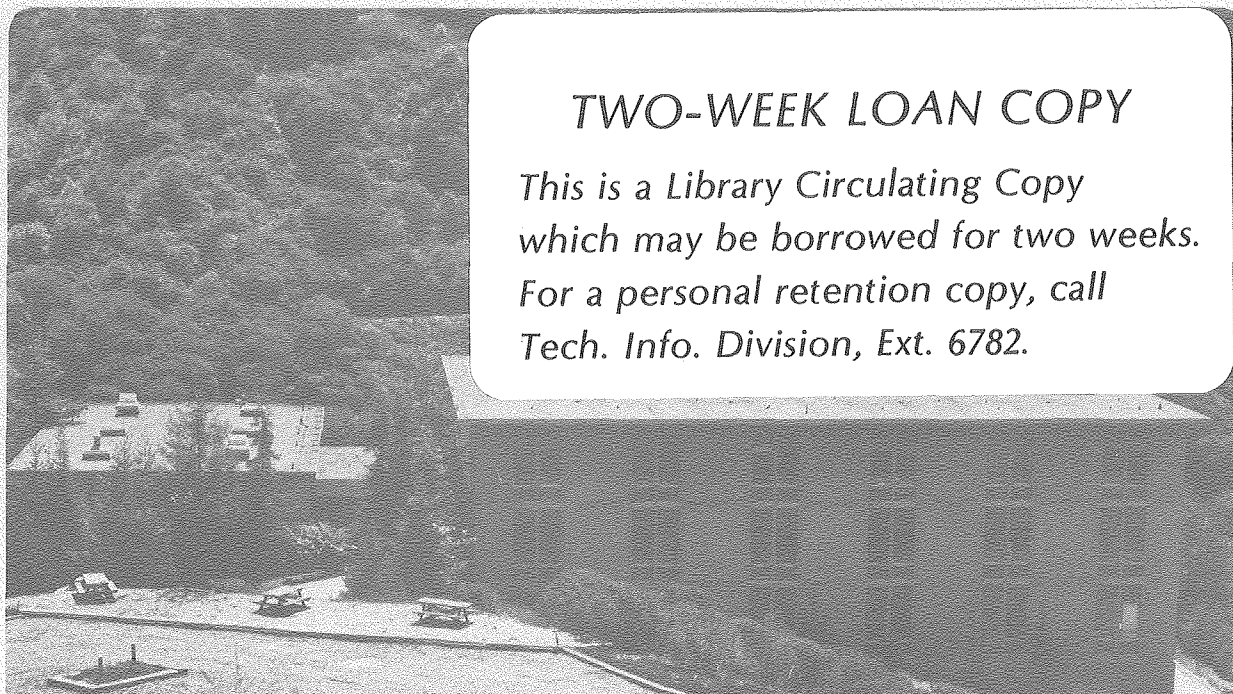
Frank Magnotta and Harold S. Johnston

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Absolute Photodissociation Quantum Yields for the  $\text{NO}_3$  Free Radical

By

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## Abstract

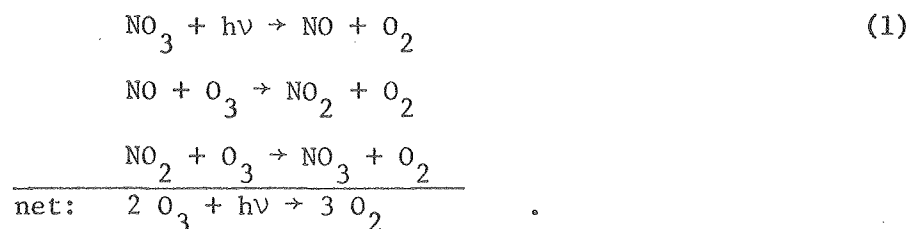
This investigation evaluated the channel-specific absolute photodissociation quantum yields for the nitrate free radical,  $\text{NO}_3$ , as a function of wavelength in the visible absorption region. The technique of tunable laser flash photolysis was coupled with real-time analysis of products by atomic and molecular resonance fluorescence. Absolute calibration of the method was achieved by ultraviolet photolysis of  $\text{NO}_2$  and by visible photolysis of  $\text{ClNO}$ . At the surface of the earth with an overhead sun the photolysis coefficients for the two product channels are calculated to be

$$j(\text{NO} + \text{O}_2) = 0.022 \pm 0.002 \text{ s}^{-1}$$

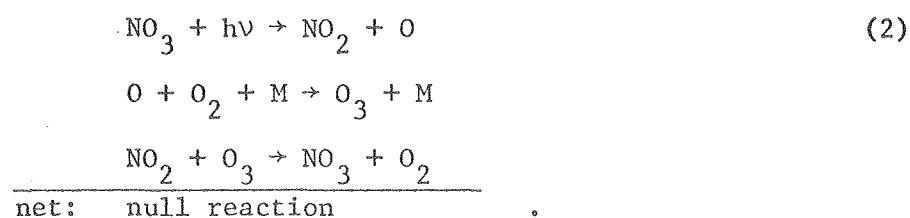
$$j(\text{NO}_2 + \text{O}) = 0.15 \pm 0.018 \text{ s}^{-1}$$

## Introduction

The photochemistry of the nitrate free radical ( $\text{NO}_3$ ) is potentially important in the balance of ozone in the troposphere and lower stratosphere. Nitrogen dioxide and ground state oxygen atom,  $\text{O}(^3\text{P})$  are energetically possible products for light of wavelengths less than 580 nm while NO and  $\text{O}_2$  could be produced at any wavelength below 8.0  $\mu\text{m}$ . If the photolysis products are NO and  $\text{O}_2$ ; the net effect is catalytic destruction of ozone:



However, the alternative products lead to no net chemical reaction:



Graham and Johnston (1978) determined the relative  $\text{NO}_3$  absorption cross sections at one atmosphere total pressure from 400 to 704 nm in a long-path cell containing  $\text{N}_2\text{O}_5$  and  $\text{O}_3$  in a carrier gas of  $\text{N}_2$ . They determined the absolute value at one wavelength, 652 nm, by a molecular modulation technique. From the effect of light on the rate of the  $\text{N}_2\text{O}_5$  catalyzed decomposition of ozone, they established that both  $\text{NO} + \text{O}_2$  and  $\text{NO}_2 + \text{O}$  occur as products of  $\text{NO}_3$  photolysis. Using broad-band

fluorescent photolytic lamps of different colors, they were able to fit the data to photochemically active bands with synthetic shapes. The average quantum yield for the channel  $\text{NO} + \text{O}_2$  was found to be  $0.22 \pm 0.05$  between 520 and 640 nm, and for  $\text{NO}_2 + \text{O}$  the average quantum yield was  $0.78 \pm 0.16$  between 470 and 600 nm. Below 580 nm, the combined quantum yields appeared to be close to unity.

The present study photolyzed  $\text{NO}_3$  with a tunable pulsed dye laser, where the pulse width was about 0.4  $\mu\text{s}$ . The products,  $\text{NO}$  or  $\text{O}$ , were followed as a function of time for up to 2 ms by the method of resonance fluorescence. Extrapolation of the product fluorescence decay profile to zero time was the primary experimental quantity. Low levels of  $\text{NO}_3$  were maintained in an ozone-free system by the controlled unimolecular decomposition of  $\text{N}_2\text{O}_5$  in  $\text{N}_2$  at a total pressure of 10 torr and at 296 K (Connell and Johnston, 1979).

### Experimental

The details of the experimental method are described elsewhere (Magnotta, 1979; Magnotta and Johnston, to be submitted to J. Chem. Phys., 1980), and only a brief summary tied closely to the terms in the definition of quantum yield  $\phi$  will be given here:

$$\phi = \frac{\text{number of molecules of products formed}}{\text{number of photons absorbed}} \quad (3)$$

Variation with wavelength is indicated by a subscript  $i$ , the product channel  $\text{O} + \text{NO}_2$  is indicated by a superscript  $o$ , and the reactant  $\text{NO}_3$  is identified by subscript 3. With these conventions, the quantum yield for production of atomic oxygen is

$$\phi_{3i}^o = \frac{\text{number of atoms of O produced per cm}^3}{\text{number of photons absorbed by NO}_3 \text{ per cm}^3} \quad (4)$$

$$= \frac{C_{3i}^o F^o}{\sigma_{3i} [\text{NO}_3] E_{3i}} \quad (5)$$

where  $C_{3i}^o$  is the number of photons counted from resonance fluorescence of atomic oxygen,  $\sigma_{3i}$  is the absorption cross section of  $\text{NO}_3$  at wavelength  $i$  in units of  $\text{cm}^2$ ,  $[\text{NO}_3]$  is the concentration of  $\text{NO}_3$  in units of molecules  $\text{cm}^{-3}$ ,  $E_{3i}$  is "fluence" of the laser pulse in units of photons  $\text{cm}^{-2}$ , and  $F^o$  is the calibration factor that converts the observed counts  $C_{3i}^o$  into the concentration of atomic oxygen produced as primary product by the laser pulse. For pulses of high fluence, the denominator of (5) must be replaced by  $[\text{NO}_3] [1 - \exp(-E_{3i}\sigma_{3i})]$ , and this difference was utilized (see below) to obtain absolute values of the cross section at selected wavelengths.

The nitrate free radical  $\text{NO}_3$  was present at low concentrations in equilibrium with nitrogen dioxide and di-nitrogen pentoxide



$$K = [\text{NO}_2][\text{NO}_3]/[\text{N}_2\text{O}_5] \quad (7)$$

In a continuously flowing stream of nitrogen carrier gas, the concentration of  $\text{N}_2\text{O}_5$  ( $4$  to  $20 \times 10^{14}$  molecules  $\text{cm}^{-3}$ ) was measured by infrared absorption in a Beckman IR-7 spectrophotometer; and the concentration of  $\text{NO}_2$  was measured by fluorescence of visible light as excited by a Liconix 401 helium-cadmium laser (compare, Fincher et al., 1977).

Measurements were made with 50 seconds of integration time, which

determines  $10^{11}$  molecules  $\text{cm}^{-3}$  to 10 percent precision with a 95 percent confidence level. The measured concentrations of  $\text{NO}_2$  and the derived concentrations of  $\text{NO}_3$  were in the range of  $10^{12}$  to  $10^{13}$  molecules  $\text{cm}^{-3}$ . These measurements, combined with  $\text{N}_2\text{O}_5$  equilibrium constant and infrared cross section measurements by Graham and Johnston (1978), resulted in determination of the absolute  $\text{NO}_3$  concentration.

A flash-lamp pumped laser capable of producing 1 to 2 joules of visible radiation in a 0.4  $\mu\text{s}$  long pulse was the source of  $\text{NO}_3$  photolysis (Phase-R, Model 2100-B). The repetition rate was one shot every four seconds, and typically 500 to 1000 shots were accumulated in a multi-channel storage computer. The fluence  $E_{3i}$  in (5) was derived from a measurement of total photons per flash using a spectrally flat pyro-electric joulemeter (Gen-Tec-ED200) and periodic measurement of the beam area by use of a piece of photographic paper placed in the beam in front of the photolysis cell. The cavity was adjusted to give a band width of about 0.5 to 1 nm, which matches the resolution of the  $\text{NO}_3$  spectrum as observed by Graham and Johnston (1978). Wavelength of the photolysis beam was measured by sending a small portion through a one-meter grating monochromator to a Princeton Applied Research optical multichannel analyzer.

The relative cross sections for  $\text{NO}_3$

$$\sigma_{3i} = (\ln I_0 / I) / [\text{NO}_3]L \quad (8)$$

where  $L$  is the optical path length, were based on those of Graham and Johnston. Absolute cross sections were obtained in this study at 585.0 and 589.3 nm by simultaneously fitting  $\phi_3^0$  and  $\sigma_3$  to a series of experiments at one wavelength and for a wide range of laser energies. These cross sections were larger than those of Graham and Johnston by



by a factor of 1.5, and the cross sections used in this study are the previous ones increased by this factor.

The photolysis fragments of  $\text{NO}_3$  were determined by real-time photon counts,  $\text{C}_3^{\text{O}}$  or  $\text{C}_3^{\text{NO}}$ , from resonance fluorescence of atomic oxygen or of nitric oxide. The resonance fluorescence (Clyne and Cruse, 1972) of atomic oxygen,  $2^3\text{P}_j$ , was excited by a microwave discharge (2450 MHz) lamp fitted with  $\text{MgF}_2$  window, and atomic oxygen lines at 130.2, 130.5, and 130.6 nm were sent through the cell at right angles to the laser beam. Resonantly scattered radiation was collected along the third orthogonal axis, and it was focused onto a cesium-iodide vacuum-ultraviolet photomultiplier tube. Similarly, nitric oxide was measured by detecting fluorescence excited by gamma band emission ( $\text{A}^2\Sigma - \text{X}^2\Pi$ ) near 226 nm from a microwave discharge through pure air, using an interference filter centered at 215 nm. Signals were processed by a high speed amplifier-discriminator coupled to a multichannel scaler, multiple shots were superimposed for data averaging, and calculations with the data were done by an on-line PDP 8L minicomputer. The experiments were carried out in a small fluorescence cell with multiple baffles and horns to reduce scattered light. The detection limits (signal/noise = 1) of this method were calculated to be  $5 \times 10^{10}$  molecules  $\text{NO cm}^{-3}$  and  $1.4 \times 10^7$  atoms  $\text{O cm}^{-3}$ .

An evaluation of the calibration factor F was obtained by carrying out this experiment on  $\text{NO}_2$  (observation of O and NO) and on ClNO (observation of NO) in the same apparatus as that used for  $\text{NO}_3$  photolysis studies. The quantum yields and cross-sections for  $\text{NO}_2$  have been determined (Harker et al., 1977) between 375 and 420 nm and results for ClNO

in the visible range of the spectrum have been summarized by Calvert and Pitts (1967). A comparison of NO produced from NO<sub>2</sub> in the near ultraviolet and from ClNO in the visible region showed the joulemeter to be uniform with wavelength, but its absolute calibration was in error by about a factor of two. For the case of observation of atomic oxygen, the quantum yield expression for photolysis of NO<sub>2</sub> (in the N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> reaction mixture itself) in the near ultraviolet wavelength region is

$$\phi_{2j}^O = \frac{C_{2j}^O F^O}{\sigma_{2j} [\text{NO}_2] E_{2j}} \quad (9)$$

where subscript 2 identifies NO<sub>2</sub> and subscript j distinguished this wavelength region from that used for NO<sub>3</sub>.

By combining (5) and (9), one obtains an expression for the quantum yield for production of O + NO<sub>2</sub> from NO<sub>3</sub> photolysis

$$\phi_{3i}^O = \phi_{2j}^O \frac{C_{3i}^O \sigma_{2j} [\text{NO}_2] E_{2j}}{C_{2j}^O \sigma_{3i} [\text{NO}_3] E_{3i}} \quad (10)$$

and there is a corresponding expression for the quantum yield for O<sub>2</sub> + NO products in terms of NO<sub>2</sub> or ClNO as calibrating reaction. All terms on the right hand side were measured as a part of this experiment, with  $\phi_{2j}^O$  set to 1.0 at 351.8 nm.

### Results

Determinations of absolute quantum yields of atomic oxygen and of nitric oxide were carried out from 470 to 680 nm at approximately 4.5 nm intervals. Day-to-day reproducibility was typically better than five percent, and multiple determinations at each wavelength were averaged. A smooth curve was drawn through points of  $\phi$  vs wavelength, and values

at each nm were interpolated. In expressions for the photolysis constant  $j$  under atmospheric conditions, the function of interest is the product of quantum yield and cross section,  $\phi\sigma$ . The lower panel in Figure 1 gives the cross section  $\sigma$  as a function of wavelength, and the upper two panels give the products  $\phi_{3i}^O\sigma_{3i}$  and  $\phi_{3i}^{NO}\sigma_{3i}$  for the two channels of  $\text{NO}_3$  photolysis. The values for wavelength, quantum yield  $\phi$ , and absolute yield  $\phi\sigma$  are given for the  $\text{O} + \text{NO}_2$  channel in Table 1A and for  $\text{NO} + \text{O}_2$  channel in Table 1B.

### Discussion

In atmospheric models the important terms in the photolysis rate coefficient are the absolute yield  $\phi\sigma$  and the local intensity of solar radiation  $I$ :

$$j = \int_{\lambda_1}^{\lambda_2} \phi_{\lambda} \sigma_{\lambda} I_{\lambda} d\lambda \quad (11)$$

where  $\lambda$  is the wavelength of solar radiation. Values of solar intensity ( $I_{\lambda}$ ) are tabulated for 5 nm intervals, at the earth's surface, with an overhead sun, including absorption by molecular oxygen and ozone, and corrected for raleigh and particulate scattering (Gelinas et al., 1973). With these solar flux data, the present absolute yields  $\phi\sigma$  (Table 1) give the following photolysis coefficients

$$\begin{aligned} j(\text{NO} + \text{O}_2) &= 0.022 \pm 0.002 \text{ s}^{-1} \\ j(\text{NO}_2 + \text{O}) &= 0.15 \pm 0.018 \text{ s}^{-1} \end{aligned} \quad (12)$$

These values differ significantly from those found by Graham and Johnston (1978), which were

$$\begin{aligned}j(\text{NO} + \text{O}_2) &= 0.040 \text{ s}^{-1} \\j(\text{NO}_2 + \text{O}) &= 0.099 \text{ s}^{-1}\end{aligned}\quad (13)$$

In part this difference may be due to differences in total pressure, 10 torr in this study and one atmosphere in the previous one. Probably the major difference concerns the difference in wavelength resolution between the two investigations. Graham and Johnston had broad-band fluorescent bulbs of three different colors (red, yellow, green), and this study used a tunable dye laser with wavelength spread of 0.5 to 1 nm. The two studies actually agree fairly well as to magnitude of the quantum yields, but Graham and Johnston ascribed these average quantum yields over too wide a wavelength range for the channel  $\text{O}_2 + \text{NO}$  and over too narrow a range for the other channel.

The quantum yields for both channels fall to zero with increasing wavelength above 620 nm. There is very little photolysis under the strong peaks at 623 nm and virtually no photolysis under the extremely strong peak at 663 nm. An unsuccessful effort was made to detect resonant fluorescence from these peaks, and an unsuccessful effort was made to excite one of these strong peaks and observe fluorescence at somewhat longer wavelengths. No fluorescence could be detected, and it is postulated that the electronic excitation energy transfers upon collision into the excited vibrational levels of the ground electronic state.

There is another unanswered question here. The quantum yield for the sum of both channels is about one at 590 to 600 nm, but it falls slowly to a uniform value of about 0.8 at lower wavelengths, that is,

higher energies. If one reexamines what this method actually measures in terms of Eq. (10), it can be seen that the primary observable is the product of cross section and quantum yield,  $\sigma\phi$ . This method obtained a different cross section from that of Graham and Johnston at 585 and 589 nm, and this correction factor was applied at all wavelengths. It is now postulated that the correction for cross section between these two studies is wavelength dependent, and at shorter wavelengths the quantum yields are about 20 percent higher and the cross sections are about 20 percent lower than the values in Table 1. However, the photolysis coefficients,  $j$ , depend primarily on the product  $\sigma\phi$ , and this product was directly observed and may be presumed to be better known than the two component functions. It is recommended that modelers use the values of  $\phi\sigma$  in Table 1. Errors could be made if these values of  $\phi$  are combined with other values of  $\sigma$ .

#### Acknowledgment

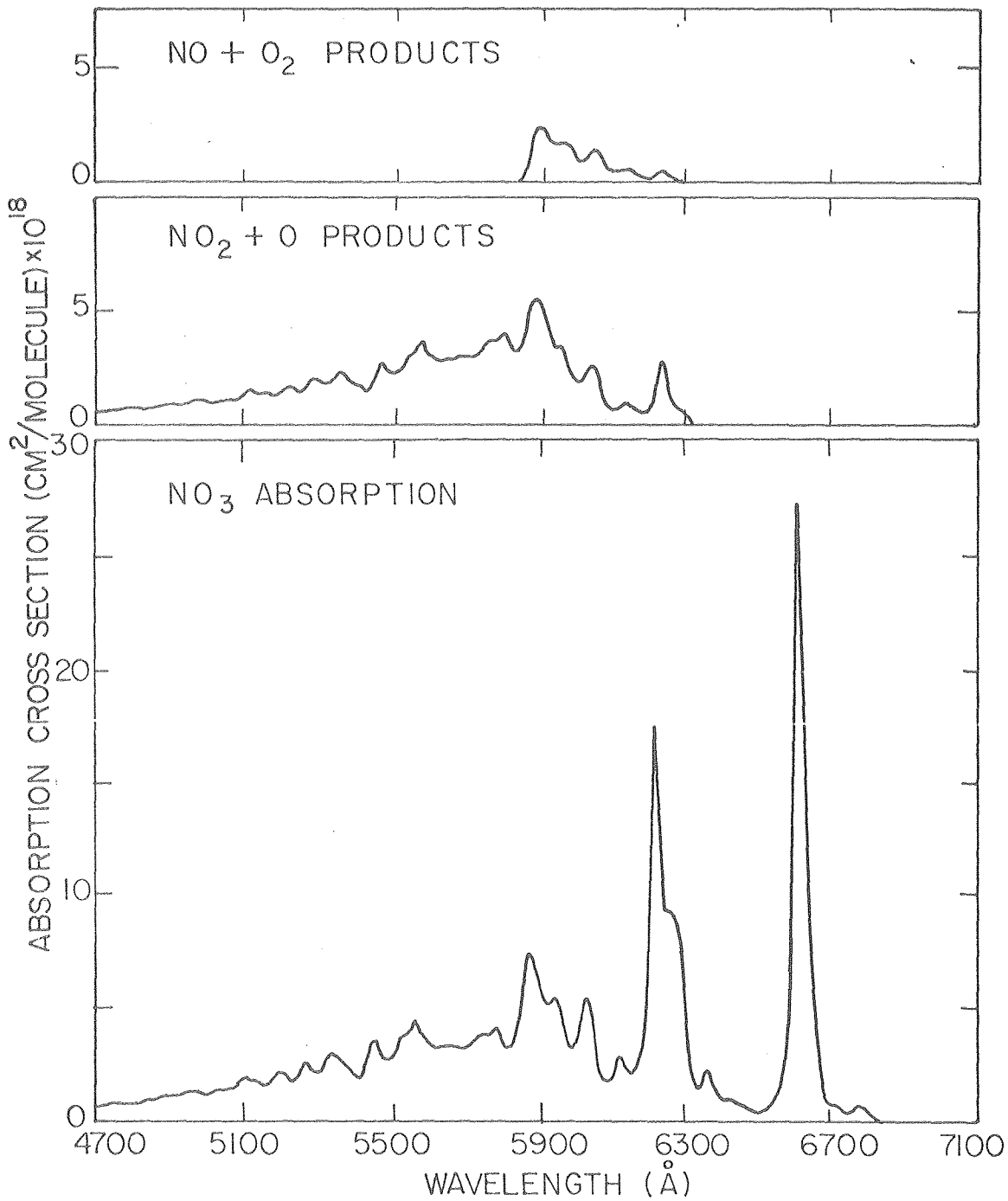
This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48.

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Table 1. Non-zero values of quantum yield  $\phi$  and absolute yield  $\phi\sigma$  (where  $\sigma$  is cross section for  $\text{NO}_3$  in units of  $10^{-19} \text{ cm}^2$ ) as a function of wavelength  $\lambda$  for the range 470 to 685 nm. A. Products are  $\text{NO}_2 + \text{O}$ . B. Products are  $\text{NO} + \text{O}_2$ . 12

A. Products are $\text{NO}_2 + \text{O}$ .															
A.	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$
	470	0.770	5.5	505	0.753	12.7	540	0.780	20.6	575	0.930	36.7	610	0.410	8.1
	471	0.770	5.6	506	0.752	13.1	541	0.782	19.2	575	0.940	40.1	611	0.400	8.4
	472	0.769	6.1	507	0.752	12.5	542	0.784	19.2	576	0.950	42.3	612	0.380	9.4
	473	0.769	6.2	508	0.751	11.6	543	0.786	16.4	577	0.960	42.5	613	0.370	11.7
	474	0.768	6.3	509	0.751	12.3	544	0.788	16.0	578	0.965	41.4	614	0.360	11.8
	475	0.768	6.6	510	0.750	14.2	545	0.790	18.7	580	0.970	42.3	615	0.340	9.9
	476	0.767	7.2	511	0.750	16.5	546	0.792	23.6	581	0.975	45.6	616	0.320	8.1
	477	0.767	7.6	512	0.751	17.7	547	0.794	29.7	582	0.980	44.4	617	0.280	6.8
	478	0.766	7.4	513	0.751	16.6	548	0.796	32.0	583	0.985	38.5	618	0.270	7.2
	479	0.766	7.2	514	0.752	15.5	549	0.798	29.0	584	0.990	35.7	619	0.250	7.4
	480	0.765	7.1	515	0.753	15.4	550	0.800	26.2	585	1.000	35.9	620	0.230	8.3
	481	0.765	7.3	516	0.753	15.4	551	0.804	25.1	586	0.990	39.7	621	0.200	11.6
	482	0.764	7.0	517	0.754	14.3	552	0.808	25.5	587	0.940	47.8	622	0.190	21.1
	483	0.764	6.8	518	0.754	13.3	553	0.812	26.3	588	0.880	57.6	623	0.180	31.6
	484	0.763	6.9	519	0.755	14.1	554	0.816	29.2	589	0.750	60.4	624	0.150	25.5
	485	0.763	7.3	520	0.755	15.9	555	0.820	33.3	590	0.750	62.1	625	0.120	15.2
	486	0.762	8.2	521	0.756	17.4	556	0.824	35.5	591	0.730	55.3	626	0.090	9.2
	487	0.762	8.9	522	0.756	19.0	557	0.828	36.3	592	0.710	50.1	627	0.080	8.1
	488	0.761	8.9	523	0.757	18.3	558	0.832	38.5	593	0.690	43.5	628	0.070	7.0
	489	0.761	9.5	524	0.757	16.6	559	0.836	41.9	594	0.660	37.8	629	0.060	5.9
	490	0.760	10.3	525	0.758	15.3	560	0.840	39.6	595	0.650	37.1	630	0.050	4.7
	491	0.760	10.2	526	0.758	15.2	561	0.845	35.2	596	0.630	38.3	631	0.040	2.9
	492	0.759	9.9	527	0.759	16.7	562	0.850	33.3	597	0.610	36.4	632	0.030	1.4
	493	0.759	9.9	528	0.759	19.8	563	0.855	32.3	598	0.590	30.5	633	0.020	0.6
	494	0.758	9.7	529	0.760	23.3	564	0.860	31.1	599	0.570	24.0	634	0.020	0.4
	495	0.758	10.1	530	0.760	23.2	565	0.865	31.2	600	0.560	20.0	635	0.010	0.1
	496	0.757	11.5	531	0.762	21.2	566	0.870	32.8	601	0.540	19.3	636	0.005	0.1
	497	0.757	12.4	532	0.764	20.2	567	0.875	32.6	602	0.520	21.5	637	0.003	0.1
	498	0.756	11.9	533	0.766	19.3	568	0.880	33.0	603	0.510	25.2	638	0.001	0.0
	499	0.756	11.4	534	0.768	19.8	569	0.885	34.0	604	0.500	29.2	639	0.000	0.0
	500	0.755	10.8	535	0.770	22.7	570	0.900	33.2	605	0.490	29.9			
	501	0.755	10.4	536	0.772	26.1	571	0.905	33.2	606	0.470	23.2			
	502	0.754	10.0	537	0.774	26.9	572	0.910	32.9	607	0.460	15.6			
	503	0.754	10.5	538	0.776	23.9	573	0.915	33.0	608	0.440	10.2			
	504	0.753	11.5	539	0.778	21.3	574	0.920	34.3	609	0.430	8.3			
B. Products are $\text{NO} + \text{O}_2$ .															
B.	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$	$\lambda$	$\phi$	$\phi\sigma$
	585	0.000	0.0	595	0.310	17.7	605	0.250	15.3	615	0.130	3.8	625	0.025	2.5
	586	0.050	2.0	596	0.305	18.5	606	0.245	12.1	616	0.100	2.5	626	0.020	1.5
	587	0.120	6.1	597	0.300	17.9	607	0.240	8.1	617	0.085	2.1	627	0.015	1.0
	588	0.250	16.4	598	0.290	15.0	608	0.230	5.3	618	0.070	1.9	628	0.010	0.5
	589	0.300	24.2	599	0.280	11.8	609	0.220	4.3	619	0.060	1.8	629	0.005	0.0
	590	0.310	25.7	600	0.270	9.7	610	0.210	4.1	620	0.050	1.8	630	0.000	0.0
	591	0.315	23.9	601	0.265	9.5	611	0.200	4.2	621	0.045	2.6			
	592	0.319	22.5	602	0.260	10.8	612	0.185	4.6	622	0.040	4.4			
	593	0.315	19.9	603	0.260	12.9	613	0.170	5.4	623	0.035	6.1			
	594	0.313	17.9	604	0.255	14.9	614	0.150	4.9	624	0.030	4.2			



XBL799-7117



## Figure Caption

Figure 1. Photochemically active bands from  $\text{NO}_3$  absorption. Top two panels represent  $\phi_{\text{NO}} \sigma_{\text{NO}_3}$  and  $\phi_{\text{O}} \sigma_{\text{NO}_3}$  respectively vs wavelength compared to  $\sigma_{\text{NO}_3}$  shown in bottom panel.