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PHOTOCHEMISTRY OF  $\text{NO}_x$  AND  $\text{HNO}_x$  COMPOUNDS

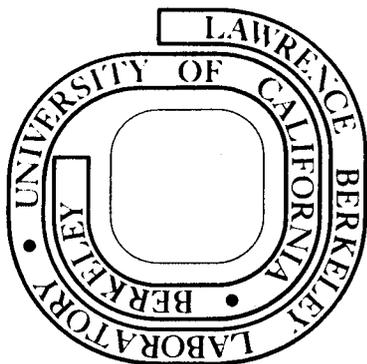
Harold S. Johnston and Richard Graham

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Photochemistry of  $\text{NO}_x$  and  $\text{HNO}_x$  Compounds

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Cross sections for absorption of radiation between 190 and 700 nm are given for  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ , and  $\text{HNO}_3$ . The quantum yields and the primary products of photolysis of each of these substances are discussed. This article includes spectral data obtained in this laboratory for  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ , and  $\text{HNO}_3$  and it includes spectral data from the literature for  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}_4$ . The quantum yields are based both on results from this laboratory and from the literature.

### Introduction

The photolysis of the oxides of nitrogen and of the oxyacids of nitrogen involves the absorption cross section  $\sigma$  and the primary quantum yield  $\phi$ , each a function of wave length. The cross section  $\sigma$  is defined at the average wave length  $\lambda$  by

$$\ln I_0(\lambda)/I(\lambda) = \sigma(\lambda) [A]L$$

where  $[A]$  is the concentration of substance A in molecules  $\text{cm}^{-3}$ ,  $L$  is the optical path length in cm,  $I_0$  is the incident beam over the narrow wavelength band in units of photons  $\text{cm}^{-2} \text{sec}^{-1}$ , and  $I$  is the transmitted intensity. The cross section  $\sigma$  is in units of  $\text{cm}^2$ , depends on wavelength  $\lambda$ , and for broadbands of radiation depends on the band width of radiation  $\Delta\lambda$ . The quantum yield for photolysis of A is the ratio of molecules of A destroyed per photon of radiation absorbed

$$\phi = \frac{\text{molecules of A destroyed}}{\text{photons of radiation absorbed}}$$

The quantum yield for  $\overset{\text{forming}}{\text{A}}$  a given product P is the ratio of the number of molecules of P formed per photon of radiation absorbed by A.

This article briefly reviews the literature for absorption cross sections of  $\text{N}_2\text{O}$  (190-315 nm),  $\text{HNO}_3$  (190-325 nm),  $\text{N}_2\text{O}_4$  (240-390 nm),  $\text{N}_2\text{O}_5$  (285-380 nm); and it presents data from this laboratory for  $\text{NO}_2$  (190-420 nm),  $\text{N}_2\text{O}_5$  (205-285 nm),  $\text{HNO}_2$  (300-397 nm), and  $\text{NO}_3$  (450-680 nm). This article briefly reviews

the literature for the quantum yields for photolysis of  $N_2O$ ,  $NO_2$ ,  $N_2O_4$ , and  $N_2O_5$ ; and it presents data from this laboratory for the quantum yields of  $HNO_3$  and  $HNO_2$ . The possible photolysis products of  $NO_3$  are discussed. This article does not discuss nitric oxide (NO), which is a separate, full-sized research problem all in itself and which is being analyzed by others.

The purpose of this article is to collect in one place the values of cross section  $\sigma$  and quantum yield  $\phi$ . The cross sections are given in Tables 1 to 3 and in Figures 1 to 5. The quantum yields are indicated on some of the figures and are discussed separately for each case.

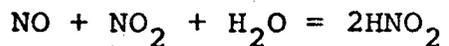
#### Experimental

The apparatus has been described previously (1). It consists of a silica cell 15 cm in diameter and 2 meters long. It is equipped with nickel-coated stainless-steel end caps and with three mirrors to give multiple pass operation (White cell). Spectra were taken with optical paths between 8.6 and 34 meters. Deuterium arc sources were used for radiation between 190 and 420 nm, and tungsten filament sources were used above 420 nm. Wave lengths were calibrated from a low-pressure mercury arc. A McPherson one-third meter vacuum spectrometer was used.

Materials.--Oxygen was purified by passing through a column containing pellets of 5% palladium on alumina at 350°C, through a silica tube with copper turnings at 600°C, and then through columns of ascarite and phosphoric anhydride (P<sub>2</sub>O<sub>5</sub>). Ozone was prepared by electric discharge through purified oxygen; it was collected on silica gel at Dry Ice temperature and degassed at higher temperatures either into a helium carrier or into a vacuum. Nitric oxide was purified by the method of Dinerman and Ewing (2). Nitrogen dioxide was purified as previously described (1). Dinitrogen pentoxide was prepared from nitrogen dioxide and ozone by the reaction



The NO<sub>3</sub> radical was prepared in a low, steady state concentration by mixing N<sub>2</sub>O<sub>5</sub> with an excess of ozone; in this system ozone undergoes a slow, catalytic decomposition. Nitrous acid vapor was prepared at a low equilibrium concentration in a system with excess NO, small amounts of H<sub>2</sub>O, and very small amounts of NO<sub>2</sub>



#### Discussion of Each Substance

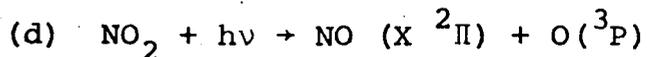
Nitrous oxide.--The absorption cross sections for N<sub>2</sub>O were read from a graph by Bates and Hayes (3). These cross sections are entered in Table 1 and on Figures 1 and 2. The photolysis of nitrous oxide can give the following products as a function of wavelength

- (a)  $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 (X^1\Sigma) + \text{O}(^1\text{D}) \quad \lambda < 337 \text{ nm}$   
 (b)  $\quad \quad \quad \rightarrow \text{N}_2 (X^1\Sigma) + \text{O}(^1\text{S}) \quad \lambda < 210 \text{ nm}$   
 (c)  $\quad \quad \quad \rightarrow \text{NO} (X^2\Pi) + \text{N}(^4\text{S}) \quad \lambda < 250 \text{ nm}$

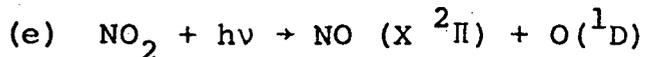
Preston and Barr (4) state that the primary quantum yield for photolysis of nitrous oxide is 1.00 at all wavelengths below 337 nm, and the process forming atomic nitrogen (c) is 0.01 or less.

Nitrogen dioxide.--The photochemistry of  $\text{NO}_2$  has been thoroughly reviewed by Hampson and Garvin (5). Here we present our data for the  $\text{NO}_2$  spectrum and a summary of Hampson and Garvin's conclusions about quantum yields. The absorption spectrum of  $\text{NO}_2$  with 8.6 meter optical path, 1.3 nm resolution (full width at half maximum), averaged over one nm, with  $(1 \text{ to } 10) \times 10^{14}$  molecules  $\text{cm}^{-3}$ , and at 294°K is given by Figure 2, and values at each 5 nm between 190 and 420 nm are listed in Table 1. The concentration of  $\text{N}_2\text{O}_4$  is less than  $10^{10}$  molecules  $\text{cm}^{-3}$  for the points taken below 250 nm, and the contribution of  $\text{N}_2\text{O}_4$  to the spectrum of  $\text{NO}_2$  should be immeasurably small.

Hampson and Garvin (5) concluded that under atmospheric conditions, the primary quantum yield for



is unity from 398 to 244 nm, and the primary quantum yield for

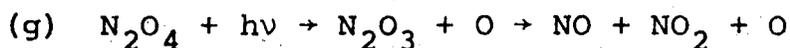
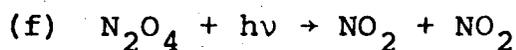


is unity from 244 to 190 nm. There is some temperature and

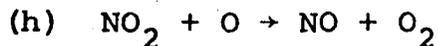
pressure dependent structure to the quantum yield above 398 nm. At 298°K, above 398 nm, Hampson and Garvin recommend as primary quantum yield for formation of O(<sup>3</sup>P) the following values: 400, 0.70; 405, 0.29; 410, 0.12; 415, 0.05; 420, 0.02; 425, 0.01; 435, 0.002; 440, 0.001; above 440, zero. Although the threshold to form O(<sup>1</sup>D) is 244 nm, the detailed pattern of quantum yield as a function of wavelength has not been reported.

Dinitrogen tetroxide.--The absorption spectrum of N<sub>2</sub>O<sub>4</sub> was read from a graph by Hall and Blacet (6), and it is entered in Table 1 from 240 to 390 nm. Although 240 nm is the lowest wavelength given by Hall and Blacet, there is evidence that N<sub>2</sub>O<sub>4</sub> has a strong absorption below 240 nm.

The photolysis of N<sub>2</sub>O<sub>4</sub> can proceed by at least two paths



Since NO<sub>2</sub> is in rapid equilibrium with N<sub>2</sub>O<sub>4</sub>, process (f) would be rapidly reversible, and would give an apparent quantum yield of zero. Reaction (g) would be rapidly followed by



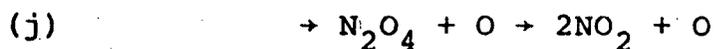
to give a quantum yield of two for formation of nitric oxide. Holmes and Daniels (7) found the overall quantum yield of NO was 0.4±0.1 at 265 nm and 0.2±0.1 at 280 nm. Presumably both processes (f) and (g) occur, and the resulting quantum yield is an average between zero for one process and two for the other.

Dinitrogen pentoxide.--Dinitrogen pentoxide was prepared from nitrogen dioxide and ozone. Pure nitrogen pentoxide can be frozen out of a system containing excess ozone and sublimed from the white crystals formed. Pure nitrogen pentoxide undergoes a fairly rapid thermal decomposition (Daniels and Johnston) (8) to give  $O_2$  and  $NO_2$ , which overlaps the  $N_2O_5$  spectrum. The  $NO_2$  bands can be suppressed by excess ozone, but then the  $N_2O_5$  spectrum has the  $O_3$  and the  $NO_3$  spectra superimposed. Starting with an excess of  $O_3$ , we carried out repeated scans of the spectrum from 200 to 400 nm. The ozone is catalytically decomposed by the  $N_2O_5$  (Schumacher and Sprenger) (9). For a brief period  $O_3$  is essentially all gone and little or no  $NO_2$  has appeared. This spectrum of  $N_2O_5$  is almost free of interference from  $NO_2$  and  $O_3$ , and the small amount present can be corrected for, in terms of the known spectra.

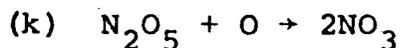
However, a more serious problem was the reaction of  $N_2O_5$  with the walls of the silica vessel to produce some nitric acid. The amount of nitric acid present was deduced as follows: Excess ozone was added to a known initial concentration of  $NO_2$  in the long-path cell. Repeated spectra were taken as the ozone disappeared, and the repeated spectra continued to be taken as the  $N_2O_5$  decomposed to  $NO_2$  and  $O_2$ . The final concentration of  $NO_2$  was obtained by extrapolation of the first-order decay of  $N_2O_5$ . The difference between initial  $NO_2$  and final  $NO_2$  was ascribed to nitric acid,  $HNO_3$ , whose spectrum is known. Thus the observed optical density was corrected for small amounts of  $O_3$  or  $NO_2$  and for relatively large amounts of  $HNO_3$ .

The absorption spectrum of  $4.1 \times 10^{14}$  molecules  $\text{cm}^{-3}$  of  $\text{N}_2\text{O}_5$ , between 205 and 285 nm, 8.6 meter optical path, 1.3 nm resolution, and 295°K, is listed in Table 1 and plotted on Figure 3. In this figure, the effect of  $5.5 \times 10^{14}$  molecules  $\text{cm}^{-3}$  of  $\text{HNO}_3$  has been subtracted. Jones and Wulf (10) have reported  $\text{N}_2\text{O}_5$  cross sections by means of photographic spectroscopy between 285 and 380 nm. At 285 nm Jones and Wulf obtained a cross section of  $5.1 \times 10^{-20} \text{ cm}^2$ , and we obtained  $4.5 \times 10^{-20} \text{ cm}^2$ . The data of Jones and Wulf are included in Table 1 and Figure 3, and they are in satisfactory agreement with our data. The uncertainty in our  $\text{N}_2\text{O}_5$  spectrum, largely based on the uncertainty in correcting for  $\text{HNO}_3$ , is estimated to be  $\pm 20\%$ .

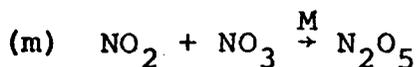
Studies of the photochemistry of  $\text{N}_2\text{O}_5$  are greatly complicated by branching paths and by possible secondary chemical reactions. In pure  $\text{N}_2\text{O}_5$  (almost unobtainable because of the thermal decomposition of  $\text{N}_2\text{O}_5$  to  $\text{NO}_2$ ) the reasonable primary processes are



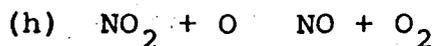
Reaction (j) could be followed by either



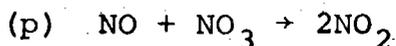
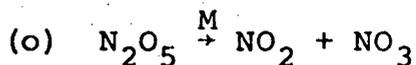
Reaction (i) is reversed by



As NO<sub>2</sub> accumulates it may react with the oxygen atom



N<sub>2</sub>O<sub>5</sub> rapidly reacts with nitric oxide by way of

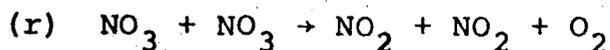
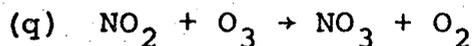
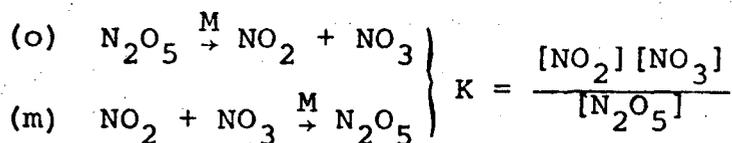


The net quantum yield of destruction of N<sub>2</sub>O<sub>5</sub> varies with mechanism; im, zero; jkmm, zero; jl, 2; jhop, 2. Holmes and Daniels (7) observed a quantum yield for loss of N<sub>2</sub>O<sub>5</sub> at 280 nm in the absence of NO<sub>2</sub> of about 0.6. Murphy (11), as reported by Hampson (12), found inert-gas dependent quantum yields between 0.3 and 0.6 at 280 nm. Although these low, pressure-dependent quantum yields may be interpreted in terms of long-lived photo-excited N<sub>2</sub>O<sub>5</sub>, it is also possible (and, we think, more probable) that it is a matter of complex secondary thermal reactions such as (k) through (p).

The primary processes in the photolysis of N<sub>2</sub>O<sub>5</sub> are not understood at this time, nor are the secondary reactions of oxygen atoms with N<sub>2</sub>O<sub>5</sub> well understood.

The radical NO<sub>3</sub>.--The NO<sub>3</sub> radical was prepared in steady state relationship to N<sub>2</sub>O<sub>5</sub> and excess O<sub>3</sub>. The chemistry of NO<sub>3</sub> in this system has been reviewed in a text book (13).

There are four elementary chemical reactions



The steady-state concentration of  $\text{NO}_3$  is

$$[\text{NO}_3] = (Kq/2r)^{1/3} [\text{O}_3]^{1/3} [\text{N}_2\text{O}_5]^{1/3}$$

At 300°K, the equilibrium constant  $K$  is  $1.2 \times 10^{11}$  molecules  $\text{cm}^{-3}$ , and the ratio  $q/2r$  is 1.7. Thus in units of molecules  $\text{cm}^{-3}$ , the concentration of  $\text{NO}_3$  is

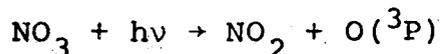
$$[\text{NO}_3] = \{1.9 \times 10^{11} [\text{O}_3] [\text{N}_2\text{O}_5]\}^{1/3}$$

The absorption spectrum for  $\text{NO}_3$  in the visible region (450 to 680 nm) was obtained in a flow system at one atmosphere total pressure. The input gases were nitrogen containing 0.1%  $\text{NO}_2$  (and a small amount of  $\text{NO}$ , which was separately measured and accounted for) and nitrogen plus ozone, as degassed from silica gel. Ozone was present in excess, so that  $\text{NO}$  and  $\text{NO}_2$  were converted to  $\text{N}_2\text{O}_5$ . The amount of residual ozone was determined by its absorption spectrum, corrected for overlapping  $\text{N}_2\text{O}_5$ . For the spectrum presented in Table 2 and in Figure 4, the cell concentrations at 22°C were:  $\text{O}_3$ ,  $5.2 \times 10^{16}$ ;  $\text{N}_2\text{O}_5$ ,  $7.2 \times 10^{14}$ ;  $\text{NO}_3$ ,  $1.6 \times 10^{14}$  molecules  $\text{cm}^{-3}$ . The  $\text{NO}_3$  spectrum has been corrected for the absorption of visible light by ozone.

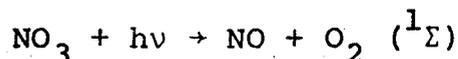
The absorption spectrum of  $\text{NO}_3$  as presented in Table 2 and Figure 4 is estimated to be uncertain by  $\pm 50\%$ . This large uncertainty arises from the rate constants  $q$  and  $r$  entering the expression for the steady-state concentration of  $\text{NO}_3$  and in a 15% loss of  $\text{N}_2\text{O}_5$  that reacted with water in the flowing gases to form nitric acid.

Schott and Davidson (14) measured the absorption coefficient at 652 nm of  $\text{NO}_3$  at high temperatures in a shock-tube experiment. They extrapolated their results to 300°K to obtain  $8.4 \times 10^{-19} \text{ cm}^2$  as the cross section at 652 nm. We find  $2.1 \times 10^{-19}$  at this wavelength.

To photolyze  $\text{NO}_3$  to nitrogen dioxide and a ground state oxygen atom

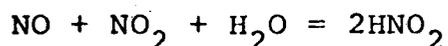


requires a wave length of 578 nm or shorter, and the peaks of maximum absorption lie at longer wave lengths. The radical  $\text{NO}_3$  has only slightly less energy (about 5 or 6 kcal mole<sup>-1</sup>) than ground state  $\text{O}_2$  and NO. The absorption spectrum in Figure 4 has enough energy to proceed as



although the state of the products has not been identified. By a molecular modulation technique, we found (work still in progress) that above 600 nm  $\text{NO}_3$  dissociates to form NO; and we were unable to detect any fluorescence, which would indicate a low quantum yield. Ramsey (15) found the high resolution spectrum of  $\text{NO}_3$  to show predissociation <sup>at all wavelengths.</sup> Thus above 578 nm,  $\text{NO}_3$  is photodissociated to NO and to some form of  $\text{O}_2$ , probably (but not necessarily) with a large quantum yield; but below 578 nm it is not known whether the products are  $\text{NO}_2 + \text{O}$  or  $\text{NO} + \text{O}_2$ .

Nitrous acid.--HNO<sub>2</sub> was prepared from mixtures of NO, NO<sub>2</sub>, H<sub>2</sub>O, and He. The concentration of HNO<sub>2</sub> present was calculated from thermochemical data (16) for the equilibrium



$$K = [\text{HNO}_2]^2 / [\text{NO}][\text{NO}_2][\text{H}_2\text{O}]$$

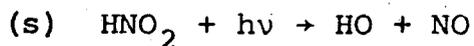
The reactant gases NO and NO<sub>2</sub> were measured from their pressure in small glass pipets, and they were added to the large (46 liter) cell. Helium saturated with water vapor was added. There was a large excess of NO. The actual residual concentration of NO<sub>2</sub> was measured in terms of its known spectrum above 400 nm. The spectrum of N<sub>2</sub>O<sub>3</sub> between 300 and 400 nm was obtained in separate experiments, and it was subtracted from the observed total spectrum. Thus the observed relatively weak spectrum of HNO<sub>2</sub> was corrected for the spectrum of NO<sub>2</sub> and the intense continuous spectrum of N<sub>2</sub>O<sub>3</sub>.

The absorption spectrum of HNO<sub>2</sub> is presented in Table 3 and Figure 5. It was obtained with the following conditions: NO,  $2.6 \times 10^{18}$  molecules cm<sup>-3</sup>; NO<sub>2</sub>,  $3.0 \times 10^{15}$  molecules cm<sup>-3</sup>; N<sub>2</sub>O<sub>3</sub>,  $8.0 \times 10^{12}$  molecules cm<sup>-3</sup>; H<sub>2</sub>O,  $8.9 \times 10^{15}$  molecules cm<sup>-3</sup>; HNO<sub>2</sub> (calc),  $6.1 \times 10^{15}$  molecules cm<sup>-3</sup>; 294°K; 8.6 meter optical path; 1.3 nm resolution. In other experiments several aliquots of He and H<sub>2</sub>O were added to a similar mixture of gases. Beer's law was obeyed over the experimental range of HNO<sub>2</sub>,  $(2 \text{ to } 8) \times 10^{15}$  molecules cm<sup>-3</sup>. The position of the peaks in the spectrum agreed within 0.1 nm of those of King and Moule (17) whose high resolution study of

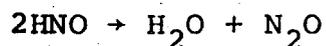
the  $\text{HNO}_2$  spectrum revealed no additional structure. The values of the cross sections in Table 3 and Figure 5 are regarded as uncertain by  $\pm 20\%$ , on the basis of uncertainties in the corrections for  $\text{N}_2\text{O}_3$ .

A study of the quantum yield and primary photolysis products of nitrous acid is underway in this laboratory. Preliminary results are given here. Since  $\text{HNO}_2$  is unstable in the gas phase, it is necessary to have excess of  $\text{NO}$ ,  $\text{H}_2\text{O}$ , and  $\text{NO}_2$  present in the system, with attendant small concentrations of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_3$  also present. The substances  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_4$  all absorb radiation in the same region as  $\text{HNO}_2$ . Thus it is desirable to minimize  $\text{NO}_2$  as much as possible.

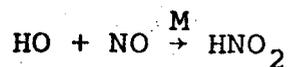
The possible primary products of  $\text{HNO}_2$  photolysis include



The third alternative would lead to nitrous oxide

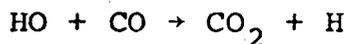


The second alternative would probably be followed by  $\text{H} + \text{NO}_2 \rightarrow \text{HO} + \text{NO}$ , and thus be indistinguishable from the first. The reaction of  $\text{HO}$  with  $\text{NO}$  to reform nitrous acid is rapid



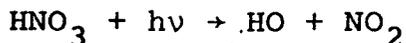
so that no net change would be observed in a static system.

By addition of excess carbon monoxide to the system, the presence of hydroxyl radicals can be identified



A few experiments have been carried out in which  $\text{HNO}_2$  has been photolyzed at 355 nm, and the products have been analyzed by a high resolution mass spectrometer, which could differentiate between  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . In the absence of added CO, no  $\text{N}_2\text{O}$  was observed. One run was made with the following composition: CO,  $8.8 \times 10^{18}$ ; He,  $1.0 \times 10^{19}$ ; NO,  $4.4 \times 10^{17}$ ;  $\text{H}_2\text{O}$ ,  $4.4 \times 10^{17}$ ;  $\text{NO}_2$ ,  $3.2 \times 10^{16}$ ; and  $\text{HNO}_2$ ,  $7.0 \times 10^{16}$  molecules  $\text{cm}^{-2}$ . Photolysis was carried out in a quartz cell  $3.5 \times 10$  cm. No  $\text{N}_2\text{O}$  was observed but a large amount of  $\text{CO}_2$  was found. The apparent quantum yield (no correction for the reaction  $\text{HO} + \text{NO} \xrightarrow{\text{M}} \text{HNO}_2$ ) was 0.5. The indication is that either reaction (s) or reaction (t) occurs with a quantum yield of the order of magnitude of unity. Further work is being carried out.

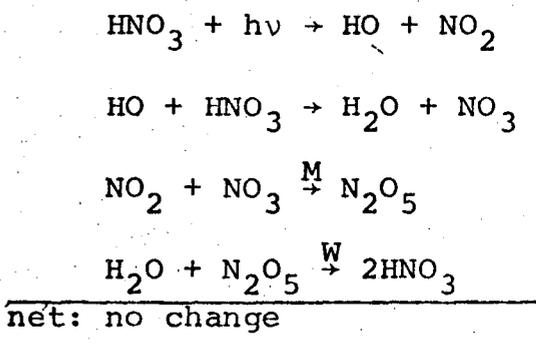
Nitric acid.--The cross sections for absorption of ultraviolet radiation by nitric acid have been published by Johnston and Graham (1), and the values are entered in Table 1 and Figures 3 and 5. Quantum yields for the process



were determined by Johnston and Chang (18) in quartz cylinders with long exposure times to weak beams of monochromatic radiation and these results are reviewed here. Also, we photolyzed  $\text{HNO}_3$

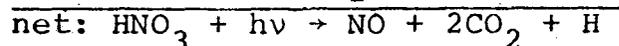
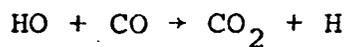
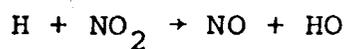
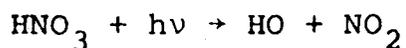
at 253.7 nm and observed the phase shift of NO<sub>2</sub> produced. The phase shift method (19) gave one molecule of NO<sub>2</sub> formed for one photon of 253.7 radiation absorbed by HNO<sub>3</sub>, and the phase corresponded to a primary photochemical product. Thus at this one wave length we have a direct determination of unit quantum yield for NO<sub>2</sub> production from photolysis of HNO<sub>3</sub>.

In a small quartz cylinder with long-term exposure <sup>of pure HNO<sub>3</sub></sup> to monochromatic radiation, the quantum yield of NO<sub>2</sub> production is very low, about 0.1. The reason for this low quantum yield is that the products of nitric acid photolysis reform nitric acid under these conditions; the sequence of reactions is

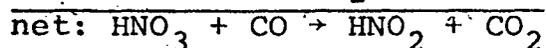
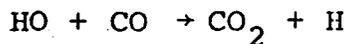


where M refers to energy-transfer catalysts in the gas phase and W refers to the walls of the apparatus. The small degree of reaction that is observed is caused by thermal and photochemical reactions involving N<sub>2</sub>O<sub>5</sub> before it has a chance to react with water to reform HNO<sub>3</sub>. Thus, long-term photolysis of pure nitric acid (20) vapor is an unsatisfactory method for studying the primary quantum yield for HNO<sub>3</sub> photolysis.

Upon addition of excess carbon monoxide to the nitric acid, the hydroxyl radical reacts with CO to produce CO<sub>2</sub>

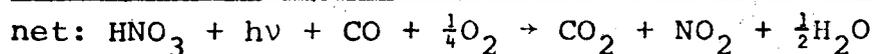
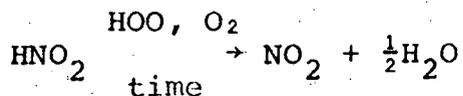
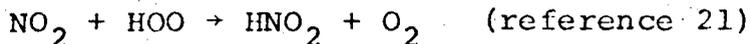
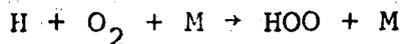
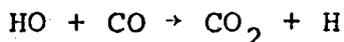
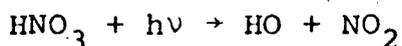


The interpretation of data in this system is somewhat ambiguous, since the fate of the final hydrogen atom is not known. If the second hydrogen atom does not react with nitric acid, the quantum yield to form carbon dioxide is two, and the primary quantum yield for nitric acid destruction can be inferred. On the other hand, if the hydrogen atom attacks nitric acid, for example,

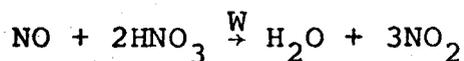


then the secondary processes represent a chain reaction with an indeterminate relation between observed  $\text{CO}_2$  and primary quantum yield.

Upon addition of excess carbon monoxide and excess oxygen, the hydrogen atom is converted to the HOO radical, any nitric oxide formed is converted to nitrogen dioxide, and the significant secondary processes are



For large degrees of reaction, secondary photolysis of  $\text{NO}_2$  forms  $\text{NO}$ , which reacts heterogeneously with nitric acid



Another role of added excess oxygen is to suppress this reaction. Extensive model calculations (18) with up to 40 elementary reactions confirmed that no known secondary reaction destroyed  $\text{HNO}_3$  or  $\text{NO}_2$ . With added  $\text{CO}$  and  $\text{O}_2$ , the quantum yield of  $\text{CO}_2$  and  $\text{NO}_2$  were each 1.0 at 200 nm, and that for  $\text{NO}_2$  was 1.0 at 255 and 300 nm.

#### Acknowledgement

The preliminary studies of the formation of  $\text{CO}_2$  in the photolysis of  $\text{HNO}_2$  were carried out by Dr. Shih-Ger Chang and Mr. Ed Quitevis. This work was supported by the Climatic Impact Assessment Program by means of an interagency agreement between the Department of Transportation and the <sup>U. S.</sup> Atomic Energy Commission through the Inorganic Materials Research Division, Lawrence Berkeley Laboratory.

Table 1. Absorption cross sections,  $\sigma$  cm<sup>2</sup>, for N<sub>2</sub>O, NO<sub>2</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, and N<sub>2</sub>O<sub>5</sub> at 5 nanometer intervals from 190 to 420 nm.

$\lambda$ nm	N <sub>2</sub> O	NO <sub>2</sub> 10 <sup>19</sup> $\sigma$	HNO <sub>3</sub>	N <sub>2</sub> O <sub>4</sub> 10 <sup>19</sup> $\sigma$	N <sub>2</sub> O <sub>5</sub>
190	1.26(-19)	6.12	1.32(-17)		
195		3.64	9.10(-18)		
200	4.46(-20)	3.19	5.50(-18)		
205		4.27	2.55(-18)		6.5(-18)
210	5.37(-21)	4.52	9.70(-19)		4.4(-18)
215		4.65	3.28(-19)		2.8(-18)
220	7.08(-22)	4.38	1.44(-19)		1.7(-18)
225		3.71	8.51(-20)		1.2(-18)
230	8.90(-23)	2.52	5.63(-20)		8.4(-19)
235		1.36	3.74(-20)		
240	1.90(-23)	0.90	2.60(-20)	10.7	5.2(-19)
245		0.39	2.10(-20)		
250	6.6(-24)	0.34	1.95(-20)	8.54	3.4(-19)
255		0.16	1.94(-20)		
260	4.67(-24)	0.18	1.90(-20)	7.97	2.1(-19)
265		0.24	1.80(-20)		
270	5.12(-24)	0.33	1.63(-20)	7.11	1.2(-19)
275		0.42	1.40(-20)		
280	6.02(-24)	0.57	1.14(-20)	5.69	<u>6.3(-20)</u> (a)
285		0.72	8.77(-21)		4.8(-20) (b)
290	5.0(-24)	0.88	6.34(-21)	4.12	4.2(-20)
295		1.07	4.26(-21)		
300	5.0(-24)	1.33	2.76(-21)	3.02	2.45(-20)
305		1.65	1.68(-21)	2.85	
310	3.2(-24)	1.97	9.50(-22)	3.02	1.3(-20)
315	1(-24)	2.24	4.70(-22)		
320		2.61	1.80(-22)	4.27	7.5(-21)
325		2.94	2(-23)		
330		3.38		6.12	4.0(-21)
335		3.61			

Table 1 (Con't.)

$\lambda$ nm	$N_2O$	$NO_2$ $10^{19} \sigma$	$HNO_3$	$N_2O_4$ $10^{19} \sigma$	$N_2O_5$
340		4.17		6.90	2.7(-21)
345		4.30			
350		4.48		5.69	1.8(-21)
355		5.53			
360		4.96		3.20	1.0(-21)
365		5.84			
370		5.70		1.42	4.7(-22)
375		5.74			
380		6.52		0.57	1.3(-22)
385		6.45			
390		6.51		0.14	
395		6.08			
400		6.68			
405		6.52			
410		6.59			
415		6.03			
420		6.24			
425					
430					

(a) This work, 205-280 nm.

(b) Reference (10), 285-380 nm.

Table 2. Absorption cross section,  $\sigma$  cm<sup>2</sup>, for the NO<sub>3</sub> radical at one nanometer intervals from 450 to 680 nm.

$\lambda$	$10^{19} \sigma$						
450		480	2.26	510	3.12	540	4.60
451	.51	481	2.24	511	3.80	541	4.44
452	.72	482	2.34	512	4.26	542	4.34
453	.57	483	2.24	513	4.08	543	3.54
454	.73	484	2.37	514	4.02	544	2.98
455	.61	485	2.33	515	3.79	545	3.70
456	.40	486	2.68	516	3.73	546	4.57
457	.51	487	2.73	517	3.57	547	6.13
458	.51	488	2.64	518	3.36	548	7.12
459	.56	489	2.73	519	3.35	549	6.53
460	1.03	490	2.87	520	3.77	550	6.13
461	1.07	491	2.87	521	4.21	551	6.13
462	1.19	492	2.76	522	4.53	552	6.06
463	0.92	493	2.84	523	4.62	553	6.21
464	0.67	494	2.61	524	4.06	554	6.47
465	0.95	495	2.65	525	3.72	555	7.02
466	1.06	496	2.89	526	3.64	556	7.52
467	1.16	497	3.20	527	3.79	557	7.74
468	1.32	498	3.22	528	4.62	558	7.99
469	1.34	499	3.16	529	5.51	559	8.41
470	1.60	500	2.97	530	5.80	560	8.43
471	1.99	501	2.81	531	5.39	561	7.65
472	2.13	502	2.71	532	5.01	562	7.17
473	2.00	503	2.63	533	4.67	563	6.94
474	1.82	504	2.97	534	4.61	564	6.74
475	2.01	505	3.19	535	5.14	565	6.69
476	2.27	506	3.29	536	6.18	566	6.77
477	2.48	507	3.25	537	6.53	567	6.84
478	2.60	508	3.04	538	6.08	568	6.90
479	2.38	509	2.81	539	5.13	569	6.88

Table 2 (Con't.)

$\lambda$	$10^{19} \sigma$						
570	6.79	600	6.83	630	14.9	660	12.0
571	6.73	601	6.45	631	12.6	661	23.3
572	6.69	602	6.71	632	8.73	662	34.7
573	6.65	603	7.76	633	6.00	663	40.2
574	6.67	604	8.92	634	4.59	664	29.1
575	6.95	605	9.78	635	3.57	665	18.5
576	7.42	606	9.05	636	3.29	666	13.4
577	7.80	607	6.90	637	3.87	667	8.59
578	7.81	608	4.98	638	4.26	668	5.46
579	7.67	609	4.09	639	4.03	669	3.96
580	7.67	610	3.82	640	3.10	670	3.34
581	8.01	611	4.06	641	2.86	671	2.58
582	8.10	612	4.47	642	2.79	672	2.50
583	7.42	613	5.33	643	2.28	673	2.25
584	6.79	614	5.67	644	2.31	674	2.14
585	6.61	615	5.46	645	2.20	675	2.17
586	6.96	616	4.87	646	2.20	676	2.07
587	8.30	617	4.44	647	2.31	677	2.21
588	10.3	618	4.47	648	2.22	678	2.71
589	12.4	619	4.89	649	2.20	679	2.55
590	13.4	620	5.67	650	2.17	680	2.63
591	12.8	621	8.35	651	2.11		
592	11.9	622	12.9	652	2.08		
593	10.8	623	22.0	653	2.31		
594	10.0	624	26.3	654	2.35		
595	9.44	625	21.1	655	2.59		
596	9.81	626	17.2	656	3.31		
597	10.0	627	15.4	657	4.10		
598	9.42	628	15.5	658	4.72		
599	7.94	629	15.3	659	6.73		

Table 3. Absorption cross section,  $\sigma$  cm<sup>2</sup>, for nitrous acid vapor, HNO<sub>2</sub>, at one nanometer intervals from 300 to 400 nm.

$\lambda$	$10^{20} \sigma$						
300	0.26	325	1.44	350	3.07	375	1.67
301	0.34	326	0.88	351	5.22	376	1.40
302	0.21	327	1.41	352	5.50	377	1.58
303	0.25	328	2.95	353	5.65	378	1.86
304	0.29	329	2.36	354	11.1	379	2.09
305	0.46	330	2.59	355	14.0	380	2.69
306	0.57	331	4.73	356	6.97	381	3.48
307	0.40	332	3.62	357	4.06	382	4.64
308	0.40	333	2.31	358	4.08	383	6.17
309	0.62	334	2.65	359	3.72	384	7.38
310	0.58	335	2.93	360	3.11	385	6.96
311	0.60	336	2.40	361	2.52	386	5.10
312	0.92	337	1.69	362	2.62	387	3.27
313	0.94	338	2.39	363	2.84	388	2.23
314	1.23	339	4.93	364	3.89	389	1.54
315	1.39	340	4.17	365	4.87	390	1.04
316	1.17	341	4.28	366	5.70	391	0.67
317	1.47	342	9.43	367	8.03	392	0.52
318	2.14	343	7.34	368	13.4	393	0.47
319	1.93	344	3.66	369	14.4	394	0.31
320	1.55	345	3.21	370	8.67	395	(0.14)
321	1.94	346	3.40	371	4.69	396	(0.13)
322	1.42	347	3.28	372	3.39	397	(0.12)
323	1.09	348	2.77	373	2.88	398	
324	1.54	349	2.61	374	2.10	399	

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Figure Captions

Figs. 1-5. Absorption cross sections,  $\sigma_{\text{cm}^2}$ , as a function of wavelength with principal, energetically possible primary dissociation fragments.

Fig. 1. Nitrous oxide,  $\text{N}_2\text{O}$ .

Fig. 2. Nitrogen dioxide,  $\text{NO}_2$ , and portions of the  $\text{N}_2\text{O}$  spectrum.

Fig. 3. Dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , ----, Jones and Wulf;  
——, this study. Nitric acid,  $\text{HNO}_3$ .

Fig. 4.  $\text{NO}_3$  radical and the visible spectrum of ozone,  $\text{O}_3$ , for comparison ( $\text{NO}_3$  is prepared from  $\text{N}_2\text{O}_5$  plus excess  $\text{O}_3$ ).

Fig. 5. Nitric acid,  $\text{HNO}_3$ , and nitrous acid,  $\text{HNO}_2$ .

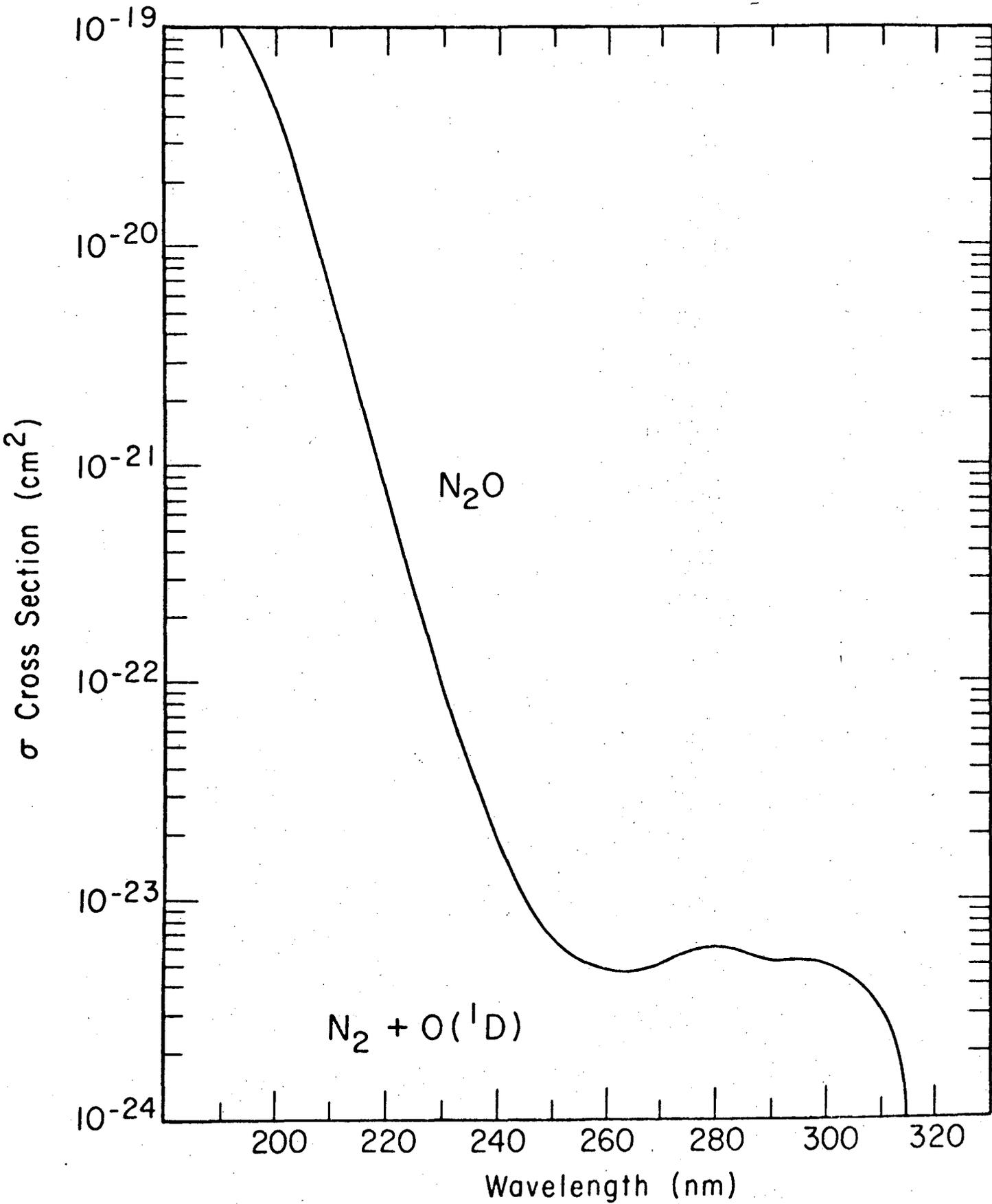


Fig. 1

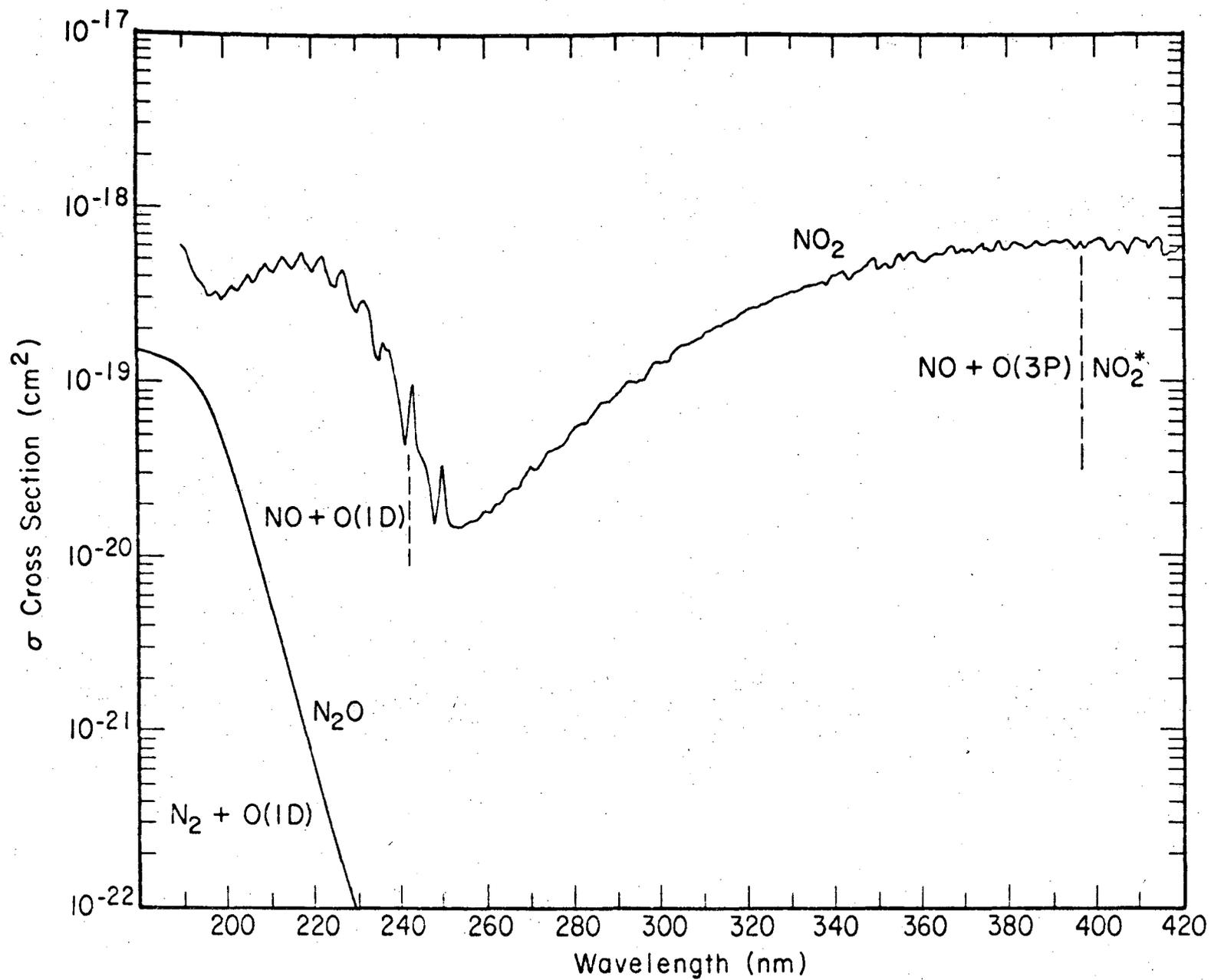


Fig. 2

XBL 738-1680

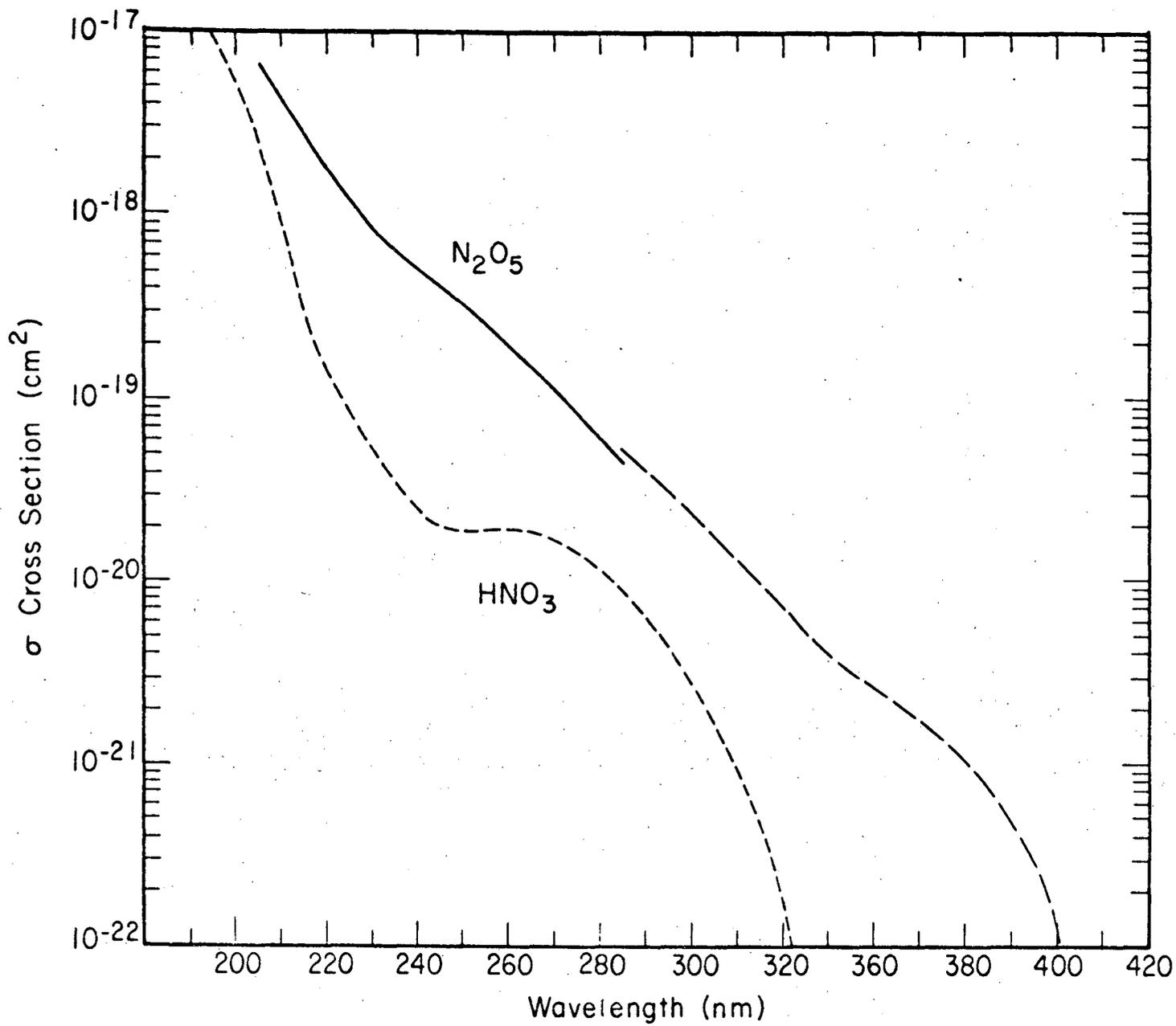


Fig. 3

XBL 738-1682

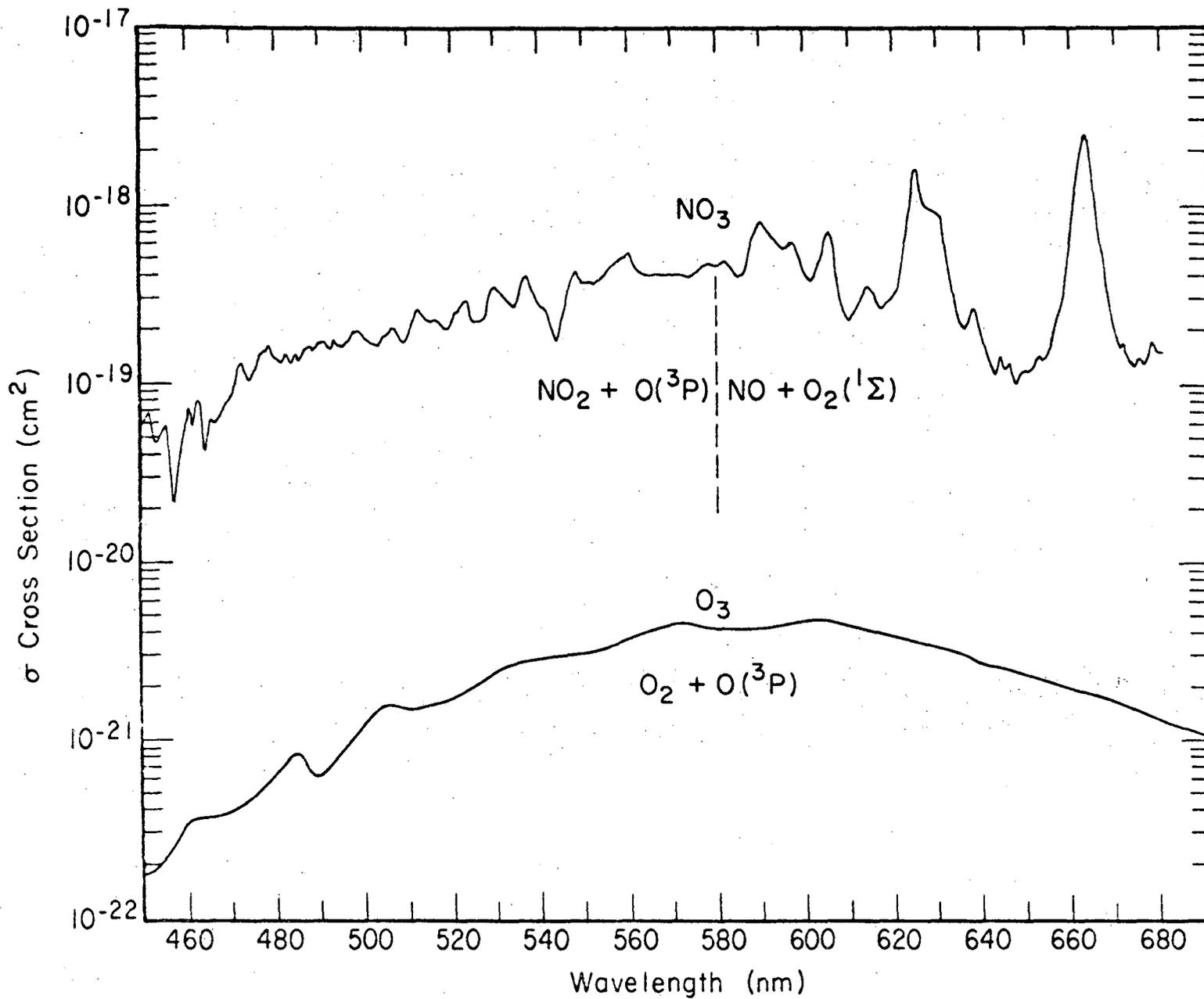


Fig. 4

XBL 738-1683

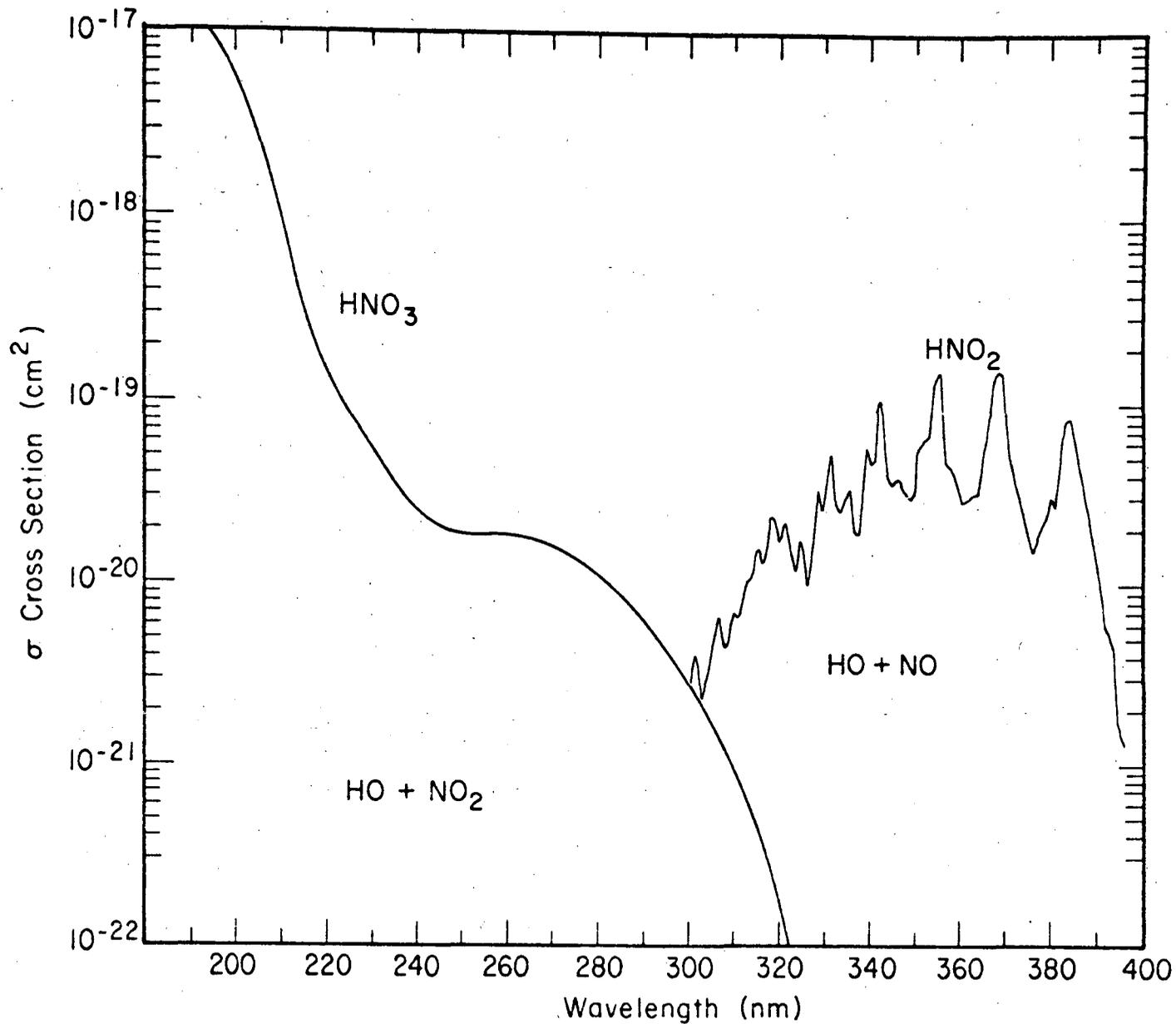


Fig. 5

XBL 738-1786

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