Title
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DISCLAIMER

NEW CROSS SECTIONS FOR THE ABSORPTION OF NEAR ULTRAVIOLET RADIATION BY NITROUS OXIDE (N_2O)

by

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ABSTRACT

A re-investigation of the ultraviolet absorption spectrum of nitrous oxide (N_2O) agrees with previous results in the range 210 to 235 nm, but contrary to previous results it indicates a vanishingly small cross section above 260 nm. The absence of the relatively long wave length absorption implies a negligible rate of photolysis of nitrous oxide in the troposphere. These results plus the previously estimated atmospheric mean residence times of N_2O indicate that there is a large, unknown tropospheric sink for nitrous oxide.

In a review of atmospheric nitrous oxide, Bates and Hays (1967) presented the photo-dissociation cross section of nitrous oxide (N_2O) from 170 to 320 nm. They reported a moderately strong absorption with a peak at about 180 nm, and a very weak absorption with a peak at 280 nm. The weak absorption extended to about 320 nm, which is above the ozone cut-off of sunlight, and this portion of the spectrum leads to a slow but significant photolysis of nitrous oxide in the troposphere. On the basis of the observed quantity of atmospheric nitrous oxide and the rate of photolysis, Bates and Hays calculated a 70 year atmospheric average residence time.

There are two arguments that lead to the conclusion that the atmospheric residence time of nitrous oxide is much less than 70 years: (1) Schuetz et al (1970) studied the seasonal, geographical, and vertical variations in atmospheric nitrous oxide and concluded that nitrous oxide is destroyed in the troposphere much faster than by photolysis as given by Bates and Hays; (2) Junge and Hahn (1971) and Hahn (1974) estimated the source of nitrous oxide from bacterial reduction of nitrates and nitrites in the ocean and from soils; although there remains a substantial uncertainty in extrapolating those observations to the entire globe, the results strongly imply a source strength such that the atmospheric residence time is short, about 12 years. Junge and coworkers thus argue that there is a large unknown process that removes or destroys N_2O in the troposphere. By stretching every uncertainty to its utmost limit in the direction of minimizing the source strength of nitrous oxide, it can be argued that such a minimum source strength might be balanced by the photolysis of nitrous oxide, using Bates and Hays' cross sections.

The results of this study is that the reported weak absorption of N_2O that extends above the ozone cut-off at 300 nm does not exist; it presumably is due to an impurity in the original spectroscopic studies. In the absence of the long wavelength absorption by N_2O, we calculate the atmospheric residence time based on photolysis and chemical reaction in the stratosphere to be between 100 and 200 years. Thus there must be an unknown process that destroys nitrous oxide in the troposphere. The suggestions made by Junge and coworkers should be accepted as the best current estimate of the situation, subject, of course, to subsequent modification as more measurements are made.

Since there must be some unknown process that destroys nitrous oxide in the troposphere, its possible nature and magnitude can be examined. It may be a surface reaction, occurring on soil surfaces, vegetation, or possibly certain regions of the ocean. On the other hand it may be a homogeneous gas-phase chemical reaction

$$X + N_2O \rightarrow \text{products}$$

for which the rate constant $\underline{k}$ times the concentration of the unknown species x would be about 3×10^{-9} sec^{-1}. If x is an ionic species and $\underline{k}$ has the upper limit for ion-molecule reactions (about 3×10^{-7} cm^3 $molecule^{-1}$ sec^{-1}), then the concentration of x could be as low as 0.1 molecules cm^{-3}. If $\underline{k}$ has the upper bound value for molecular reactions (about 3×10^{-10}), then the concentration of x could be as low as 100 cm^{-3}. If x is present at about 10^6 molecules cm^{-3}, then $\underline{k}$ would be about 3×10^{-15}. Similarly, pairs of possible values of x and k are respectively: 10^9, 3×10^{-18}; 10^{12}, 3×10^{-21}; 10^{18}, 3×10^{-27}. This approach suggests how to look for the

unknown reaction, but it does not identify it.

Experimental method. - The apparatus was a Cary 118 double beam spectrophotometer fitted with an external quartz cell with double pass optics and an optical path length of 252 cm. The reference path was unmodified, 10 cm of air. Results were obtained by measuring the change in absorbance when the cell filled with nitrogen or with helium was refilled by an equal pressure of nitrous oxide. The nitrous oxide used was purified by vacuum distillation for some runs. In an effort to identify the impurity responsible for the peak reported by Bates and Hays, we also used unpurified N_2O from the commercial cylinder (Matheson). No differences could be detected in the spectrum between the purified and unpurified gas, and then most measurements (especially the long wavelength ones) were carried out with unpurified tank nitrous oxide. At maximum sensitivity, the Cary 118 gives a full scale chart reading for absorbance ($\log_{10} I_o/I$) of 0.02. Pen vibration and irreproducibility of the baseline with an evacuated cell was about 3 percent of full scale at this setting, limiting the sensitivity of N_2O cross section to about 2×10^{-25} cm^2. Due to distortions in the cell when it was evacuated, there was a small systematic decrease in absorbance when the evacuated cell was filled with one atmosphere of nitrogen or helium. For this reason, the cell was filled with helium or with nitrogen as reference for N_2O, rather than with a vacuum. On a single day, results had a precision of about 1 to 2 $\times 10^{-25}$ cm^2 for N_2O cross sections. Reproducibility from one day to the next was substantially less than this, indicating "low-frequency" errors associated with the total method. The spread in the apparent N_2O cross sections indicates the extent of both types of experimental error,

Figure 1.

Results - The apparent, observed N_2O cross sections ($\ln I_o/I = \sigma NL$; cm^2/molecule) are given in Figure 1 for the wavelength range 245 - 328 nm. The pressure was 760 torr and the temperature was 294±1K. The solid curve represents the N_2O cross sections read from the first figure in the article by Bates and Hays (1967). It can be seen that the long-wavelength cross sections reported by Bates and Hays are much higher than the results obtained here and are about 10 times greater than the range of experimental error of these measurements. The dashed line in Figure 1 is an estimate of the Rayleigh scattering cross section for nitrous oxide; the observed values for air (Leighton, 1961; Forsythe, 1956) were scaled by the index of refraction function $(n-1)^2$ for air and N_2O. Our results scatter more or less equally about the Rayleigh scattering line above 270 nm, and they indicate no significant absorption by nitrous oxide at room temperature in the troposphere.

Bates and Hays gave two references to the entire absorption spectrum, 170 to 320 nm. The references are not broken down with respect to wavelength, and it is not stated whether these references were reviews of the literature or new data. One reference is to an unpublished doctoral thesis and the other to a private communication. Thus the experimental basis for the long-wavelength absorption reported by Bates and Hays is not clear. Sponer and Bonner (1940) did report a long wavelength absorption of N_2O, but they used unpurified gas and stated that impurities could be the source of this absorption.

With purified nitrous oxide and pressures less than one atmosphere, our cross sections for nitrous oxide are in reasonably good agreement with those reported by Bates and Hays below 230 nm; Figure 2. These results

are preliminary; we have still not done all we intend to do with respect to wavelength calibration and repetition of runs. They do show, however, that there is no major discrepency with respect to the far ultraviolet absorption spectrum of nitrous oxide.

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Acknowledgement

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Titles to Figures

Figure 1 - Observed, apparent cross sections σ for nitrous oxide absorption of near ultraviolet radiation, circles, relative to values reported by Bates and Hays (heavy line) and Rayleigh scattering (dashed line). The cross sections are defined as $\sigma = (\ln I_o/I)\ (N^{-1}\ L^{-1})$ where N is the concentration in molecules cm^{-3}, and L is the optical path in cm, and the logarithm is to the base e. The scatter of points reflects both short term noise and long term irreproducibility of initial conditions.

Figure 2 - Observed N_2O cross sections, circles, and values reported by Bates and Hays, line, for shorter wavelength region.

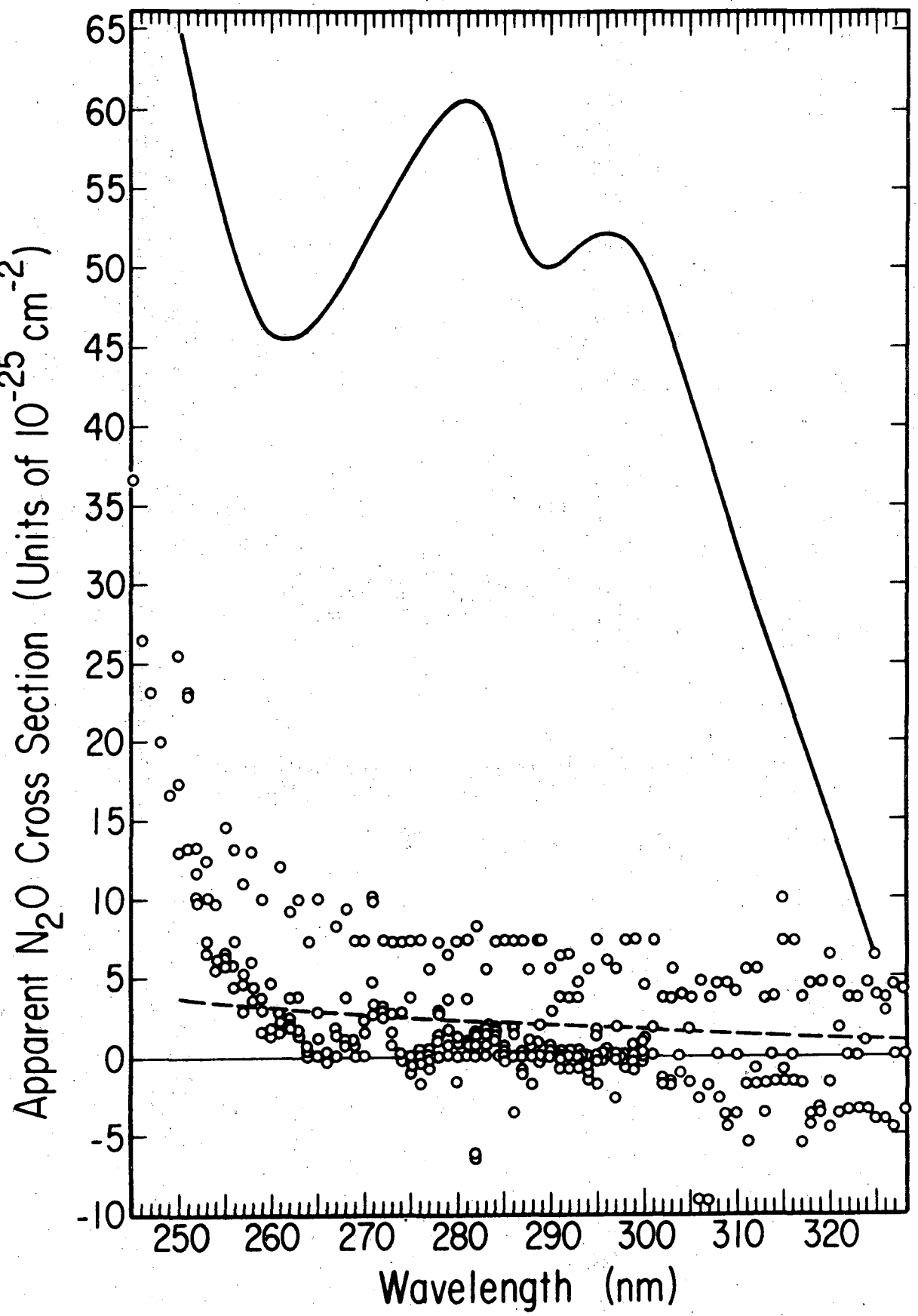

Fig. 1

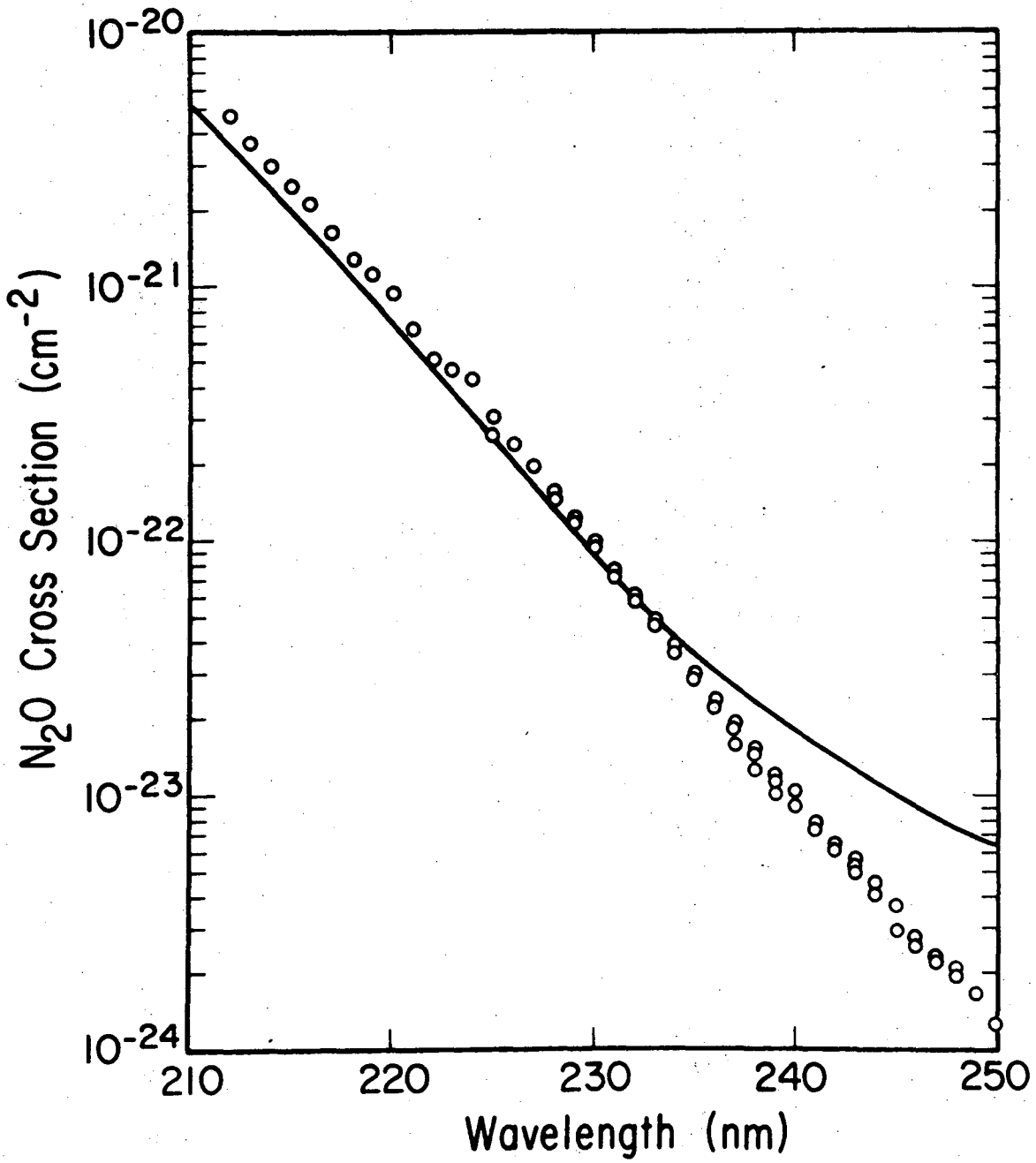
10^{-20}
10^{-21}
10^{-22}
10^{-23}
10^{-24}
N_2O Cross Section (cm^{-2})
210
220
230
240
250
Wavelength (nm)

Fig. 2

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