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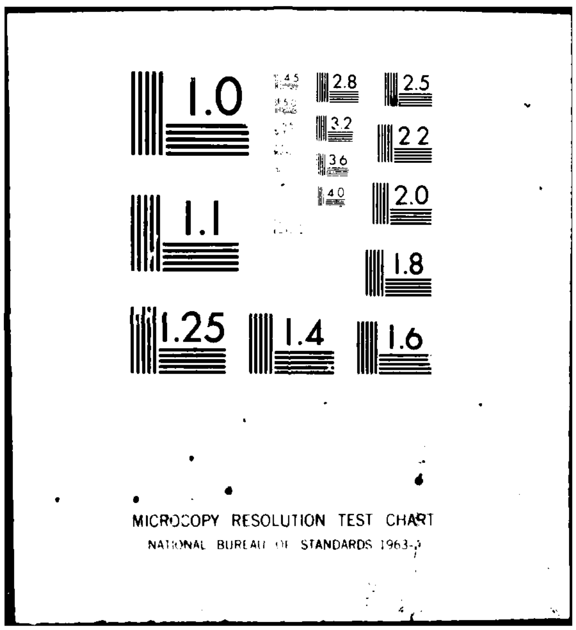
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ULTRAVIOLET ABSORPTION CROSS SECTIONS OF HO_2NO_2 VAPOR

Mario J. Molina
Principal Investigator

APRIL 1980
Final Report

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16. Abstract

The ultraviolet absorption cross sections for gas phase HO_2NO_2 have been measured between 190 and 330 nm, at 298K and 1 atm total pressure. The HO_2NO_2 vapor was prepared in a flowing N_2 stream in the presence of H_2O, H_2O_2, HNO_3, and NO_2. The composition of the mixture was established by visible and infrared absorption spectroscopy and by chemical titration after absorption in aqueous solutions. The HO_2NO_2 cross sections range from $\sim10^{-17}$ cm^2/molecule at 190 nm to $\sim10^{-21}$ cm^2/molecule at 330 nm. The experimental uncertainty (one standard deviation) ranges from 5% at 200 nm to 30% at 330 nm, and mainly falls in the 10% range. The solar photodissociation rate in the troposphere and lower stratosphere is estimated to be about 10^{-5} sec^{-1} for 0° solar zenith angle.

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INTRODUCTION

Pernitric acid (also called peroxynitric acid), HO_2NO_2, is formed in the atmosphere by recombination of HO_2 and NO_2 radicals:

$$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2 \qquad (1)$$

This reaction was proposed, among others, by Johnston (1972) but it received little attention until Niki et al. (1977) identified HO_2NO_2 for the first time in the gas phase through Fourier-transform infrared spectroscopy; Hanst and Gay (1977) and Levine et al. (1977) further corroborated Niki et al.'s findings. Actually, HO_2NO_2 was first characterized by Schwarz (1948) in liquid solutions through its strongly oxidizing properties, i.e., release of Br_2 from KBr solutions.

The importance of HO_2NO_2 is now well established; the potential role of this species for stratospheric chemistry has been discussed, for example, by Jesson et al. (1977) and by Graham et al. (1978a,b).

Howard et al. (1977) have measured the rate constant for reaction (1), and the HO_2NO_2 thermal decomposition rate--the reverse of reaction (1)--has been studied by Graham et al. (1978a):

$$HO_2NO_2 \xrightarrow{M} HO_2 + NO_2 \qquad (2)$$

In the atmosphere, HO_2NO_2 may be destroyed by reaction (2), by reaction with OH radicals (reaction 3), or by photolysis (reaction 4):

$$HO_2NO_2 + OH \rightarrow H_2O + O_2 + NO_2 \quad (3)$$

$$HO_2NO_2 + h\nu \rightarrow \text{products} \quad (4)$$

Photolysis is likely to be the dominant atmospheric sink (Jesson et al., 1977; Graham et al., 1978b). An upper limit of 3×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} for the rate constant for reaction (3) has been established by Graham et al. (1978a), and by Barker and co-workers (private communication). Reaction with O and Cl atoms is also possible, but almost surely of little importance in the stratosphere.

There are now three studies of the UV spectrum of HO_2NO_2: Jesson et al. (1977) measured the spectra of equilibrium mixtures of HNO_3, H_2O_2, and HO_2NO_2 in concentrated aqueous solution between 300 and 360 nm; Cox and Patrick (1979) obtained absorption cross sections in the 195-265 nm range using a static system containing HO_2NO_2 vapor in the millitorr range; there is, however, only one study--that of Graham et al. (1978b)--of the HO_2NO_2 gas phase spectrum in the critical wavelength range for atmospheric photodissociation, i.e., at wavelengths longer than 290 nm. Graham et al. prepared HO_2NO_2 vapor in a static system at a concentration of a few millitorr, and their cross section values are about a factor of 5 larger than those of Jesson et al.

We report here measurements of the absorption cross sections of HO_2NO_2 vapor in the 190-330 nm region. HO_2NO_2 was prepared in a flow system at concentrations approaching 1 torr, in the presence of 1 atm N_2 and of NO_2, H_2O_2, H_2O, and HNO_3 in the subtorr range. The composition of the mixture was established by Fourier-transform infrared spectroscopy, by chemical titration of the flowing gas after absorption in aqueous solutions, and by the absorption spectrum in the visible.

EXPERIMENTAL

Instrumentation

The ultraviolet and visible spectra were recorded with a Cary 219 double beam spectrophotometer interfaced to a Nova 3 computer equipped with a 10 megabyte storage disk, a Tektronix 4006-1 display terminal and a Versatec 1200A printer/plotter. Two quartz absorption cells fused with suprasil windows were used: a 10 cm long, 2.5 cm diameter cell and a 90 cm long, 3.5 cm diameter cell with folded optics giving an optical path length of 180 cm. The Cary 219 spectrophotometer has a limiting resolution of 0.07 nm and is capable of measuring reproducibly absorbances in the 0.002-4 range. To achieve rapid data collection, the present study used a sampling rate of 10 Hz and a scan rate of 1 nm s^{-1} with a spectral bandwidth of 0.1-0.2 nm at the long wavelength region (500-300 nm) and 0.3-0.5 nm at wavelengths below 300 nm. A total of about 100 spectral files (HO_2NO_2, H_2O_2, HNO_3, NO_2, and background spectra) consisting typically of 3000 data points each were recorded and stored in the computer for later manipulations.

A Digilab FTS-12A Fourier-transform infrared (FT-IR) spectrometer equipped with a standard Digilab data handling system and a liquid-N_2 cooled HgCdTe detector was employed for the infrared analysis. A 50 cm long, 2.5 cm diameter pyrex absorption cell fitted with germanium windows was used in single-pass mode. The spectra were taken at 1 cm^{-1} resolution and each spectrum was computed from the average of 64 interferograms. About 100 FT-IR spectra were recorded simultaneously with the UV-VIS spectra. The concentrations of the various components of each mixture were obtained by subtraction of reference spectra.

Synthesis of Pernitric Acid

Two methods were used to prepare pernitric acid. The first one was a modification of the original method of Schwarz (1948): HO_2NO_2 was generated continuously by mixing 70% nitric acid with 90% H_2O_2 in a porous glass bubbler. The pernitric acid vapor was carried by a stream of nitrogen gas which was forced through the bubbler into the absorption cells. The bubbler was immersed in a water bath maintained at constant temperature to within 0.2°C while the absorption cells remained at room temperature (25°C). This method produced typically $\sim$0.5 torr HO_2NO_2 in the presence of $\sim$1 torr HNO_3 and $\sim$0.1 torr H_2O_2. A small amount of NO_2 ($\sim$0.05 torr) was also present. Once the cells were conditioned, the concentration of HO_2NO_2 could be maintained constant over a period of 1-2 hr.

The second technique--a modification of our first method by Kenley and Barker (private communication)--employed nitronium tetrafluoroborate (NO_2BF_4) instead of HNO_3 as a nitrating agent. Solid NO_2BF_4 was slowly added to a solution of 90% H_2O_2 which was stirred with a magnetic stirring bar at 0°C. This preparation was carried out in a nitrogen atmosphere glove cabinet due to the hygroscopic nature of NO_2BF_4. The final solution was then transferred to the glass bubbler as in the first method. This technique produced a very high concentration of HO_2NO_2 vapor (~1-2 torr) in the presence of small amounts of HNO_3 (~0.2 torr), H_2O_2 (~0.5 torr), and NO_2 (~0.05 torr), but it had the disadvantage that HO_2NO_2 was formed all at once at the beginning and its concentration decreased rapidly during the course of the experiment. A small amount of HF--detected indirectly in the IR as SiF_4 (<0.05 torr)--was also generated in this system. These two techniques provided independent means of deducing the absorption spectra of HO_2NO_2 from chemical titrations and spectral analysis of mixtures containing widely different concentrations of HO_2NO_2, HNO_3, and H_2O_2.

After flowing the mixture through the cell for 10-30 min, the first UV and IR spectra were measured; successive spectra were recorded every 10 min and chemical titrations were carried out at 2 min intervals. The average residence time of the flowing gaseous mixture was about 30 sec in the IR cell, 100 sec in the 90 cm UV cell and 4 sec in the 10 cm UV cell.

Nitrogen dioxide (99.5%, Matheson Gas Products), hydrogen peroxide (90%, FMC Corporation), and nitric acid (70%, Mallinckrodt) were used without further purification.

Chemical Titration and Spectral Analysis

The reference spectra employed for spectral subtractions were obtained by introducing each sample individually into the UV and IR cells. The absorption spectra of ~0.05-0.5 torr of NO_2 in

N_2 (total pressure: 1 atm) were recorded by introducing the mixture into the absorption cells using a greaseless vacuum line. All pressure measurements were carried out with two MKS capacitance manometers (0-10 torr range and 0-1000 torr range). The procedure used in the absorption measurements of H_2O_2 has been described previously (Molina et al., 1977). Briefly, N_2 gas was forced through a bubbler containing concentrated H_2O_2 solution, the concentration of H_2O_2 in the N_2 carrier gas being determined by bubbling the gas through a measured volume of standard $KMnO_4$ solution. The gas phase concentration of H_2O_2 was controlled by varying the temperature of the bubbler between 8°C and 18°C. Titration of the gaseous stream before and after passage through the cells (connected in series, from IR to UV, or UV to IR) indicated that after an initial conditioning period, less than 10% of the H_2O_2 decomposed in the cells. A similar flow technique was employed in the spectral measurements of HNO_3. In this case, the concentration of HNO_3 in the N_2 carrier gas was determined by titration with standard NaOH solution and the concentration of HNO_3 vapor was controlled by varying the bubbler temperature between 3°C and 16°C.

The concentration of HO_2NO_2 in the N_2 carrier gas was determined by bubbling the gas through a measured volume of KBr solution and by measuring spectrophotometrically the Br_2 liberated. Usually, it took 30 to 60 sec to observe an absorbance of 0.5. A Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer was used for this measurement. The amount of Br_2 was determined by comparing the measured absorbance at 417 nm against a calibration curve obtained from standard $KBrO_3$/KBr solutions. Control experiments showed that H_2O_2 or HNO_3 alone do not oxidize KBr. Furthermore, when H_2O_2 or HNO_3 were placed in two separate bubblers and the gaseous streams from the two bubblers (with N_2 carrier gas) were introduced into a solution of KBr, it took about 10 times longer to observe a noticeable color change. A second independent determination of HO_2NO_2 concentration was provided by titration with standard NaOH solution. The total acidity measured is the sum of HNO_3, NO_2 and HO_2NO_2. After correcting for HNO_3 and NO_2, the calculated pressure of HO_2NO_2 agreed with that obtained from the KBr analysis. The concentrations of H_2O_2 and HNO_3 in the HO_2NO_2 sample were determined from the IR spectral analysis and the NO_2 concentration was measured from its structured spectrum in the 400-500 nm region.

RESULTS AND DISCUSSION

HNO_3, H_2O_2, and NO_2 Spectra

The ultraviolet absorption spectra of ten samples of H_2O_2 and fifteen samples of HNO_3 were measured using the flow technique and chemical titration. The results are shown in Figures 1 and 2 and Table 1. The absorption cross sections for HNO_3 are in very good agreement with the measurements of Johnston and Graham (1973) except at both ends of the spectrum. In fact, Biaume (1973) observed the same discrepancies in these two regions, and our values agree better with those reported by Biaume. In the case of H_2O_2, our present values are slightly lower than our earlier ones (Molina et al., 1977) as well as those reported by Lin et al. (1978) but fall within the experimental uncertainties cited in these earlier studies.

The UV-VIS absorption spectra of NO_2 over the pressure range 0.05-0.5 torr were stored in the computer and were used to correct the HO_2NO_2 spectra for the NO_2 contribution. The amount of NO_2 was determined from its structured spectrum between 400 and 500 nm, and it was found to be less than 0.05 torr in most cases. The maximum amount of N_2O_4 present under these conditions can be calculated to be less than 1% of the NO_2 present.

HO_2NO_2 Spectra

Figures 3 and 4 show some typical IR and UV-VIS spectra of an HO_2NO_2-HNO_3-H_2O_2-NO_2 mixture prepared by the first of the two

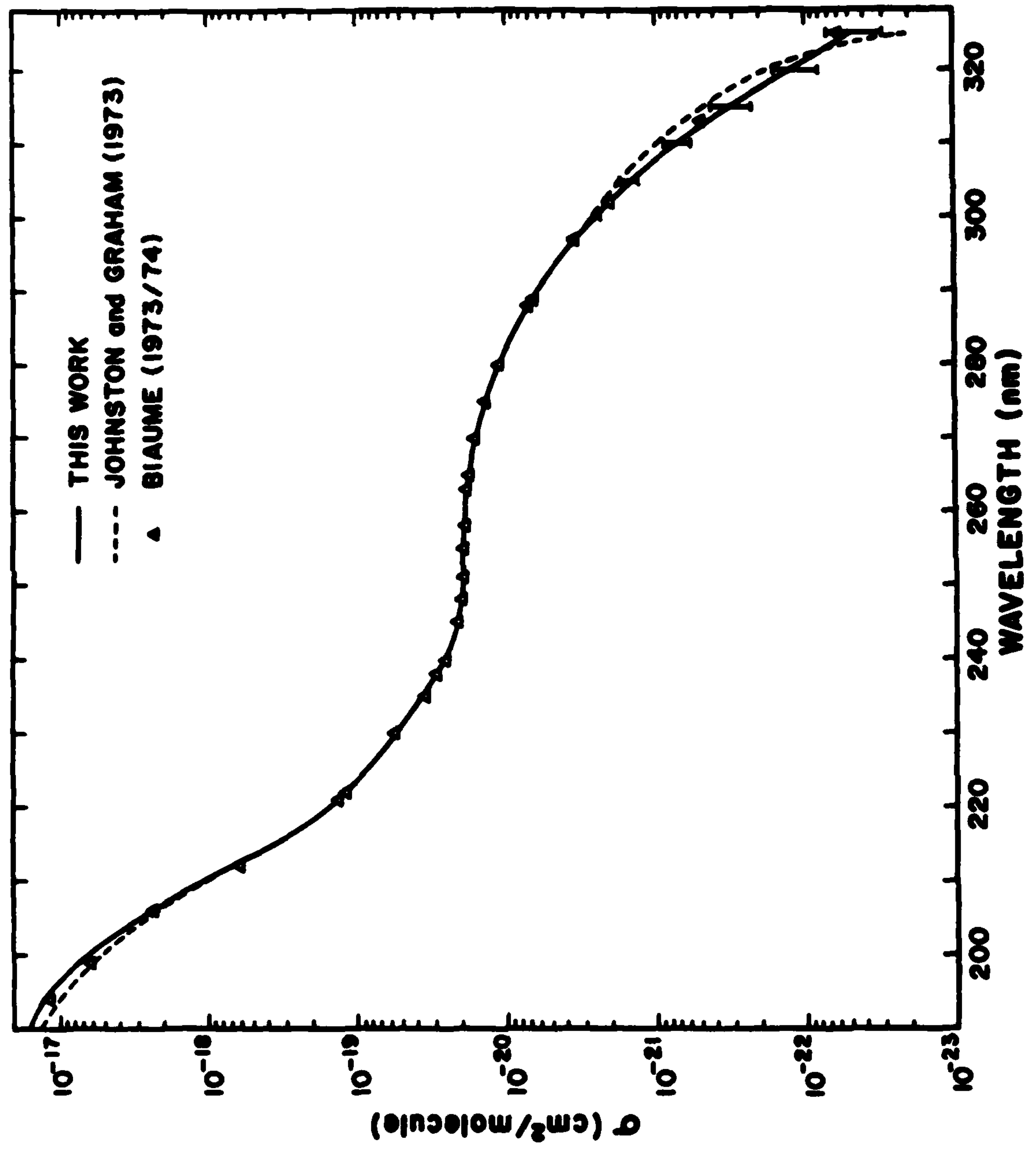

FIGURE 1. UV Spectrum of HNO_3 Vapor.

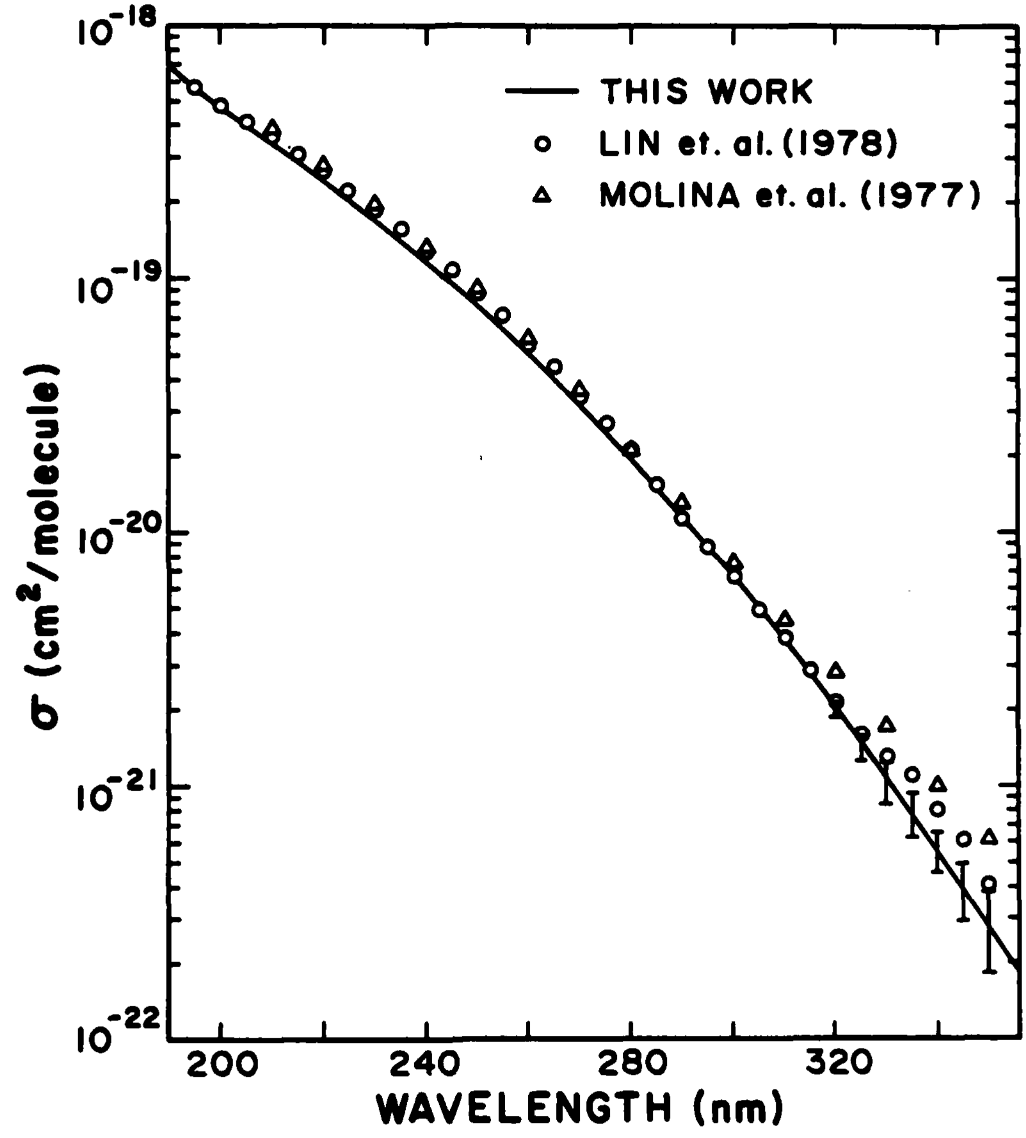

FIGURE 2. UV Spectrum of H_2O_2 Vapor.

Table 1

ABSORPTION CROSS SECTIONS OF HNO_3 AND H_2O_2

	σ (10^{20} cm^2/molecule)	
λ (nm)	HNO_3	H_2O_2
190	1560	67.2
195	1150	56.2
200	661	46.7
205	293	39.5
210	105	33.6
215	35.6	28.7
220	15.1	24.5
225	8.62	20.6
230	5.66	17.1
235	3.72	14.0
240	2.57	11.5
245	2.10	9.42
250	1.91	7.69
255	1.90	6.23
260	1.88	4.94
265	1.71	3.86
270	1.59	3.11
275	1.35	2.42
280	1.10	1.87
285	.848	1.46
290	.607	1.12
295	.409	.870
300	.241	.663
305	.146	.493
310	.071	.364
315	.032	.280
320	.012	.200
325	.005	.140
330	.002	.105
335		.078
340		.055
345		.04
350		.03

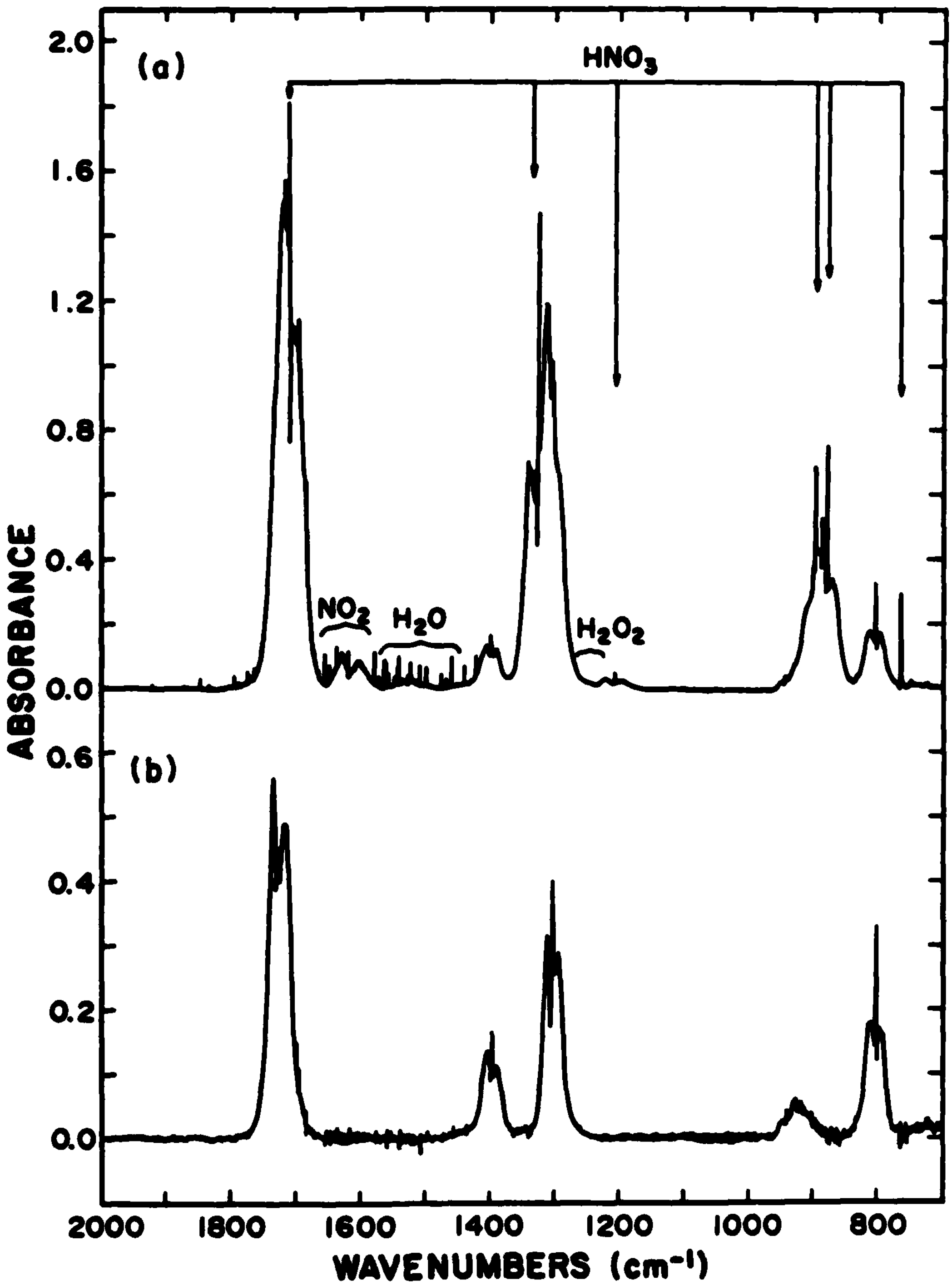

FIGURE 3. Typical IR Spectra of a Mixture Containing HO_2NO_2 Formed Via H_2O_2 + HNO_3.

(a) Product spectrum from H_2O_2 + HNO_3 reaction.
(b) Residual spectrum (HO_2NO_2) after subtraction of HNO_3, H_2O_2, NO_2, and H_2O.

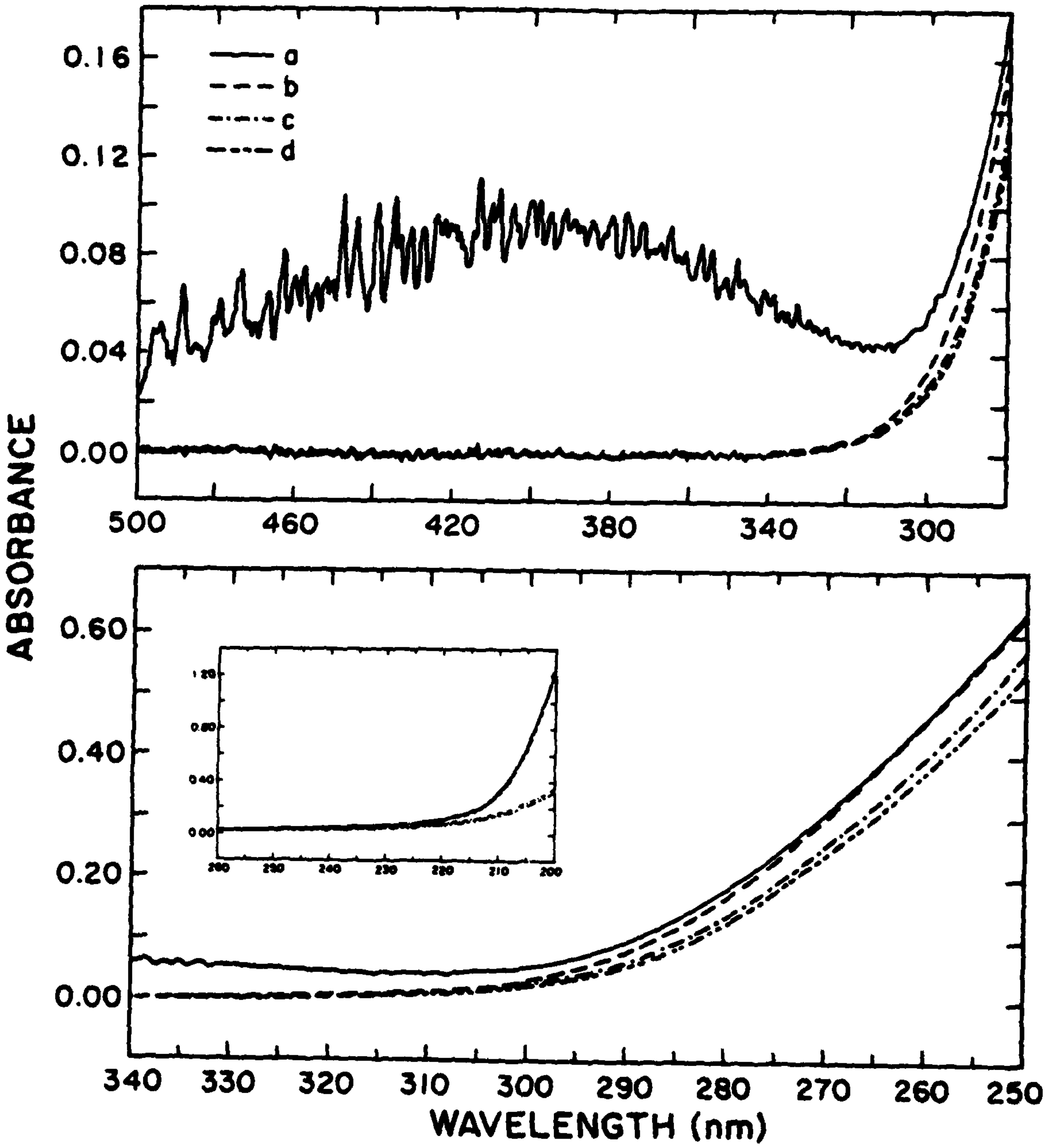

FIGURE 4. Typical UV-VIS Spectra of a Mixture Containing HO_2NO_2 Formed Via H_2O_2 + HNO_3.

(a) Original spectrum.
(b) Spectrum (a) after correcting for NO_2.
(c) Spectrum (b) after correcting for HNO_3.
(d) Spectrum (c) after correcting for H_2O_2.

Table 2

INFRARED ABSORPTION CROSS SECTIONS OF HO_2NO_2 AT 1 CM^{-1} RESOLUTION

	σ (10^{18} cm^2/molecule)	
ν (cm^{-1})	This Work[a]	Graham et al.[b]
802.7 (Q)	1.0	1.5
1304.2 (Q)	1.3	1.6
1396.9 (Q)	0.54	0.6
1728.3 (Q)	1.4	1.7
810- 814 (R)	0.56	0.56
1295-1296 (P)	0.90	1.0

[a]Total Pressure: 1 atm.

[b]Total Pressure: 1-20 torr.

techniques described earlier. In Figure 4, the 500-280 nm and 340-250 nm spectra were taken with a 180-cm path length cell while the 260-200 nm spectra were taken with a 10-cm cell. As can be seen in Figure 4, the absorption in the visible is due entirely to NO_2 whereas HNO_3 is responsible for most of the absorption for $\lambda<210$ nm.

The infrared absorption cross sections of HO_2NO_2 at 1 cm^{-1} resolution and 1 atm total pressure are given in Table 2. These were obtained from the spectra of the gaseous mixtures after subtraction of the HNO_3 and H_2O_2 contributions. The HO_2NO_2 pressures were determined from KBr titrations and range from 0.2 to 1.0 torr. Beer's law was shown to hold for the P-, Q-, and R-branches of the four absorption bands. As can be seen in Table 2, our absorption cross sections for the 810-814 cm^{-1} R-branch and 1295-1296 cm^{-1} P-branch are in good agreement with those reported by Graham et al. (1978b) while those for the Q-branches are lower; this is most likely due to pressure broadening effects. We did not include the cross sections for the 3540 cm^{-1} band because of the relatively low signal-to-noise arising from the weak response of our detector in that spectral region.

The UV absorption cross sections of HO_2NO_2 vapor at 298K are presented in Table 3 and Figure 5; for comparison, the cross section values reported by other workers are also included. Our results are based on spectra of approxiately 60 gaseous samples of HO_2NO_2 prepared by the two different methods described earlier and using three different flow rates. Some spectra were taken

Table 3

ABSORPTION CROSS SECTIONS OF HO_2NO_2 VAPOR

	σ (10^{20} cm^2/molecule)			
λ (nm)	This Work	Cox and Patrick	Graham et al.	Jesson et al.[a]
190	1010		1610	
195	816	404	960	
200	563	434	640	
205	367	420	430	
210	241	378	290	
215	164	298	200	
220	120	220	154	
225	95.2	163	123	
230	80.8	120	99	
235	69.8	93	82	
240	59.1	76	68	
245	49.7	65	58	
250	41.8	54	51	
255	35.1	44	45	
260	27.8	30	40	
265	22.4	<10	35	
270	17.8		28	
275	13.4		23	
280	9.3		18	
285	6.3		14	
290	4.0		11	
295	2.6		8.4	
300	1.6		6.2	1.4
305	1.1		5.0	
310	0.7		4.2	0.92
315	0.4		3.6	
320	0.3		3.0	0.59
325	0.2		2.6	
330	0.1		2.2	0.1
340				0.01
350				0.0037
360				0.0016

[a]Aqueous solution

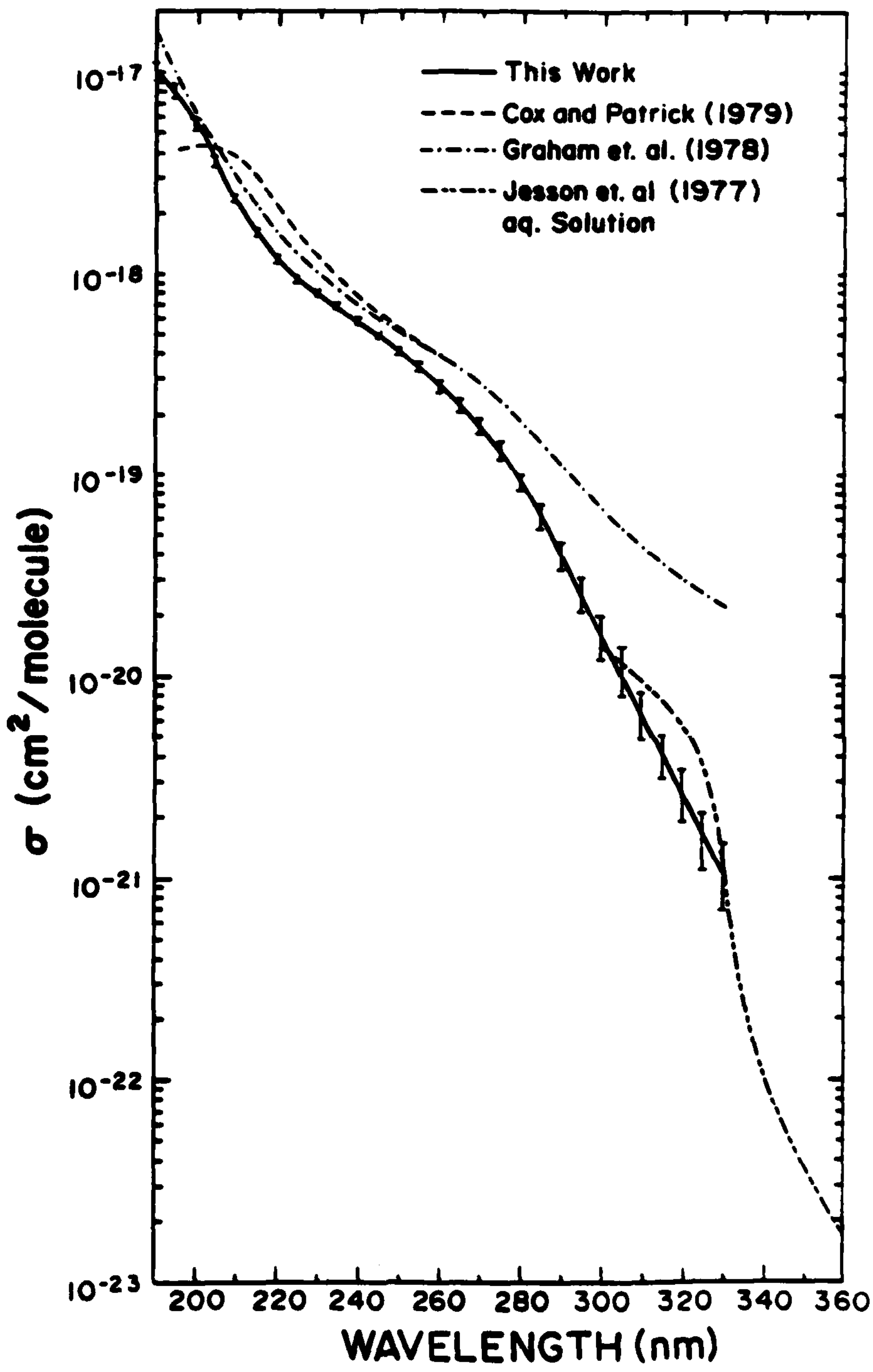

FIGURE 5. UV Spectrum of HO_2NO_2 Vapor.

with the HO_2NO_2 sample flowed through the UV-cell followed by the IR-cell, and some with the two cells in reverse order. Beer's law was obeyed throughout the HO_2NO_2 pressure range used in our absorption measurements, i.e., 0.2 to 1.0 torr. The standard deviation was about 10% around 190 nm, 5% in the 200-270 nm range, and it increased to about 30% at 330 nm.

Chemical Kinetic Considerations

The average residence time of the flowing gaseous mixture in our experiments was of the order of one minute (see experimental section), while the HO_2NO_2 thermal decomposition lifetime is ~10 sec at room temperature and 1 atm pressure (Graham et al., 1978a; Cox and Patrick, 1979). However, the NO_2-HO_2 recombination reaction is fast enough to keep the net rate of homogeneous gas phase decomposition at a negligible level under our experimental conditions, even considering the relatively fast disproportionation of the HO_2 radicals:

$$\frac{1}{[HO_2NO_2]} \frac{d[HO_2NO_2]}{dt} \simeq 2k_3 \frac{k_2}{k_1} \frac{[HO_2NO_2]}{[NO_2]}^2 \lesssim 0.05\%/\text{min}$$

$$HO_2NO_2 \xrightarrow{M} HO_2 + NO_2 \qquad (1)$$

$$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2 \qquad (2)$$

$$HO_2 + NO_2 \longrightarrow H_2O_2 + O_2 \qquad (3)$$

We observed considerably larger decomposition rates--up to 5% per min--presumably due to heterogeneous processes. The procedure employed in our experiment was designed to minimize the latter processes: besides a small germanium surface, only glass and teflon surfaces were present; the flowing mixture conditioned these surfaces and replenished the components of interest, thus eliminating the accumulation of impurities. The relatively high pressure of the inert carrier gas--1 atm N_2--also slowed down diffusion to the walls.

Comparison with Other Measurements

Our measured UV absorption cross sections are in reasonable agreement with those reported by Graham et al. (1978b) except in the critical wavelength range for atmospheric photodissociation, i.e., 290-330 nm, where our numbers are about an order of magnitude smaller (see Figure 4). The maximum HO_2NO_2 concentration was $\sim$50 times larger and the maximum optical path length $\sim$10 times smaller in our work. Thus, the net absorbance due to HO_2NO_2 should be 5 times greater in our UV cell. The discrepancy is well outside the limits of experimental error: the presence of unidentified impurities in our system can only increase the apparent HO_2NO_2 cross sections; we estimate an error of at most 50% from oversubtraction of absorbance due to NO_2, HNO_3, or H_2O_2. We can only speculate that either some trace impurity might have been present in Graham et al.'s work, or the NO_2 absorbance was not subtracted with sufficient accuracy, or perhaps they had complications with the UV instrumentation: a single beam, single monochromator multiple path UV spectrometer does not easily attain the extreme baseline stability required for absorbance measurements in the 0.005-0.02 range.

Our HO_2NO_2 cross section values differ somewhat from those reported by Jesson et al. (1977) (see Figure 4), but fall within their large estimated uncertainty. As may be seen in the figure, between 220 and 265 nm our cross section values are in fair agreement with those of Cox and Patrick (1979), but below 220 nm their values are considerably smaller. We have appreciable experimental uncertainty at these short wavelengths, but not enough to accomodate Cox and Patrick's results. On the other hand, these latter results were obtained through a measurement of the UV spectrum of a static photolysis mixture containing only a few millitorr HO_2NO_2 and containing many additional components, including Cl_2 and O_3. The composition of this complex mixture was inferred solely from the UV spectrum itself and from kinetic considerations, and no infrared or other chemical analysis was attempted; thus, we believe that the uncertainty in Cox and Patrick's UV absorption experiments is considerably larger than the uncertainty in the work we report here.

Atmospheric Photodissociation Rate

Figure 5 shows the atmospheric photodissociation rate of HO_2NO_2 as a function of altitude calculated with the cross section values presented in Table 1 and using Lawrence Livermore

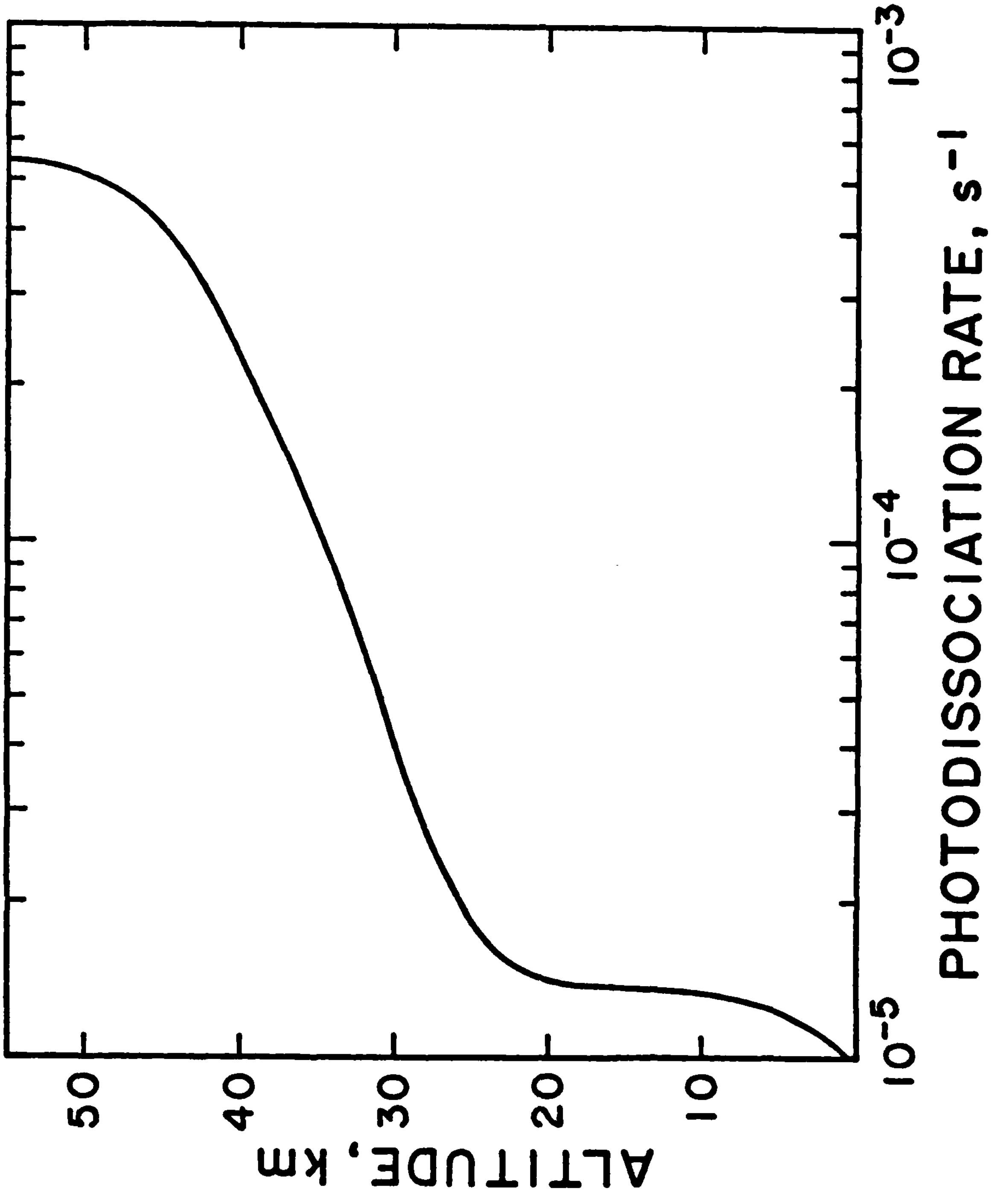

FIGURE 6. Atmospheric Photodissociation Rate of HO_2NO_2.

Laboratory 1-D atmospheric photochemistry model (D.J. Wuebbles, private communication, 1980). The photodissociation rate in the troposphere is $J \approx 10^{-5}$ sec^{-1}, which corresponds to a lifetime, 1/J, of the order of one day. This lifetime might be actually longer in the lower stratosphere due to the lower temperatures prevailing at those altitudes: the cross sections in the wing of an absorption band often decrease with temperature. In the upper stratosphere photolysis will occur much faster and predominantly with radiation in the 200 nm window.

The photodissociation rate calculation assumes unit quantum yield for photodecomposition, as expected from the continuous nature of the HO_2NO_2 absorption spectrum. Also, the calculated rate includes only contributions from wavelengths shorter than 330 nm, since we were unable to measure absorption cross sections beyond this wavelength. The calculated photodissociation rate in the troposphere increases by about 30% if the absorption cross sections beyond 330 nm are computed by extrapolation: the logarithm of the absorption cross sections between 280 and 330 nm changes linearly with wavelength, as can be seen in Figure 4.

Our experiments provide no information on the identity of the primary photolysis products: O atoms, OH and HO_2 radicals are plausible species. This identity is likely to have little effect on predicted HO_2NO_2 profiles (Jesson et al., 1977), but might play some role in overall NO_x chemistry at altitudes where HO_2NO_2 photodissociates rapidly.

If our cross section values were correct, significant HO_2NO_2 concentrations should be present in the lower stratosphere. Murcray (private communication, 1979) has estimated an upper limit to the stratospheric HO_2NO_2 concentration of 0.4 ppb from atmospheric emission spectra in the infrared obtained at 40 km and looking at a depression angle of 3.5°. Only a detailed calculation will establish whether or not Murcray's estimate is compatible with current model predictions and with our HO_2NO_2 cross sections.

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