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TEMPERATURE DEPENDENT ABSORPTION CROSS-SECTIONS OF HNO₃ AND N₂O₅

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Abstract

Absorption cross-sections for HNO_3 and N_2O_5 have been measured in the wavelength region 220-450 nm, using a dual beam diode array spectrometer with a spectral resolution of 0.3 nm. The results for both compounds are in good agreement with recommended values at room temperature. However, the cross-sections of both HNO_3 and N_2O_5 show a marked reduction with decreasing temperature in the range 295-233 K. The calculated photolysis rate of HNO_3 at the low temperatures and high solar zenith angles characteristic of the polar winter and spring is significantly lower than previously estimated.

1. Introduction

Nitric acid and di-nitrogen pentoxide are important reservoir compounds for stratospheric nitrogen oxides. Both compounds sequester stratospheric NO_x, and consequently they play an important role in determining the extent to which high levels of active chlorine oxides are available for ozone destruction in the low stratosphere during polar winter-time (S. Solomon, 1990). The release of NO_x from HNO_3 and N_2O_5 occurs mainly by photodissociation:

$$HNO_3 + h\upsilon \Rightarrow OH + NO_2 \qquad (1)$$
$$N_2O_5 + h\upsilon \Rightarrow NO_2 + NO_3 \qquad (2)$$
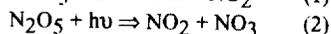
In the stratosphere, ozone absorption strongly attenuates solar radiation in the spectral region 220-290 nm. Consequently at high altitudes (above 30 km) the photodissociation of HNO_3 and N_2O_5 is caused principally by light of wavelengths around 200 nm whereas in the lower stratosphere (below 20 km) wavelengths longer than 300 nm become more important (F. Biaume, 1973/74). It is in these spectral regions and at temperatures typical of the low-stratosphere that it is particularly important to know the absorption cross-sections of HNO_3 and N_2O_5.

There have been few previous investigations of the cross-sections of these species. Currently recommended values (DeMore *et al.*, 1990; Atkinson *et al.*, 1989) are based on the work by Molina and Molina (1981) for HNO_3 and Yao *et al.*, (1982) for N_2O_5. The recommended data for HNO_3 are in good agreement with the earlier results of Biaume (1973/74) and Johnston and Graham (1973) except in the long wavelength tail of the absorption where uncertainties are rather large. There are no previous reported studies of the temperature dependence of the HNO_3 cross-sections. Values of cross-sections for N_2O_5 presented by Yao *et al.*, (1982) are higher than those in the previous studies of Jones and Wulf, (1937) and Johnston and Graham, (1974). The only temperature dependent measurement of the cross-sections for N_2O_5 is reported by Yao *et al.*, (1982) and the data show large scatter in the wavelength region above 340 nm.

We have therefore reinvestigated the ultraviolet absorption spectra of HNO_3 and N_2O_5, with particular emphasis on the determination of the temperature dependencies of the cross-sections in the longer wavelength regions.

2. Experimental Details

Absorption cross-section measurements were made using a dual beam diode array spectrometer which has been described in detail previously (Rattigan *et al.*, 1992). N_2O_5 was produced by the reaction of NO (B.O.C. special gases) with ozonised oxygen, produced by the action of a discharge ozoniser (Argentox GL10) on a flow of O_2 (Distillers M.G.). HNO_3 was prepared by vacuum distillation of a 3:2 mixture of previously cooled sulphuric acid (98%) and nitric acid (70%) held at 273 K, into a trap cooled to 203 K. NO_2 (Cambrian Gases) was mixed with N_2 (Distillers MG) to give a sample suitable for producing NO_2 reference spectra in the ultraviolet

region. The concentration of NO_2 in the mixture was established using the recommended absorption cross-sections for NO_2 at room temperature (DeMore et al., 1990).

The major impurity in the HNO_3 was found to be NO_2. N_2O_5 samples were contaminated with both NO_2 and HNO_3. At low temperatures, in both cases significant association of NO_2 into N_2O_4 was expected to occur and the effects of this were also taken into account. Corrections for any NO_2 present in the samples were performed by the scaled subtraction of NO_2 reference spectra, using the characteristic vibrational structure of NO_2 in the region above 320 nm. The effect of N_2O_4 in samples of HNO_3 was taken into account by recording NO_2 reference spectra at each temperature at pressures as close as possible to that of the NO_2 present in the samples. The assumption being that the quantities of N_2O_4 were equal in both samples. In the experiments on N_2O_5 the correction for N_2O_4 was calculated at each temperature using the known equilibrium constant for the self reaction of NO_2 and the measurements of NO_2 reference spectra at different partial pressures. The amount of HNO_3 impurity in the samples of N_2O_5 was calculated using its characteristic infrared absorption bands. Subtraction of the contribution of HNO_3 to the ultraviolet absorbance was then performed using the values of HNO_3 cross-section recommended in this paper.

3. Results

Measurements of HNO_3 absorption spectra from 200-344 nm were made in the temperature range 238-297 K. Figure 1 illustrates the temperature dependence of the cross-section in the region 270-320 nm, using the data at 295 K, 263 K and 238 K. The spectra show a definite decline in the cross-section throughout the region, the effect being particularly noticeable near the long wavelength tail.
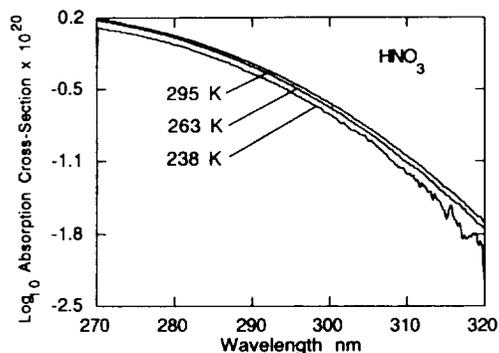

Fig. 1 Temperature dependence of nitric acid absorption cross-section in the wavelength range 270-320 nm.

N_2O_5 absorption spectra were measured in the region 230-450 nm at temperatures from 295 K to 233 K. At each temperature, spectra were measured at several pressures up to the maximum somewhat less than the vapour pressure at that temperature. After the contribution of impurities to the spectra had been removed, the Beer-Lambert law was found to be obeyed by HNO_3 and N_2O_5 providing the absorbance was less than 0.80.

Errors (expressed as one standard deviation) in HNO_3 cross-sections measured at room temperature were approximately 2.5% for wavelengths below 300 nm, increasing to approximately 95% near the limit of detectable absorption at about 335 nm. At the lowest temperature used, HNO_3 cross-sections had errors of 6.5% at 300 nm increasing to 95% at 320 nm. Errors in values of cross-sections for N_2O_5 were calculated from the combined effect of systematic and random errors where random errors are calculated as 95% confidence limits. The errors are 11% for the region 260-360 nm, 12% for 360-380 nm, and 35% for 380-410 nm.

4. Discussion

4.1. Comparison with previous work

The HNO_3 absorption cross-sections measured at 294 K in the present work are in very good agreement with those values reported by Molina and Molina, (1981), Biaume, (1973/74) and Graham and Johnston, (1973) at wavelengths below 300 nm, see Figure 2.
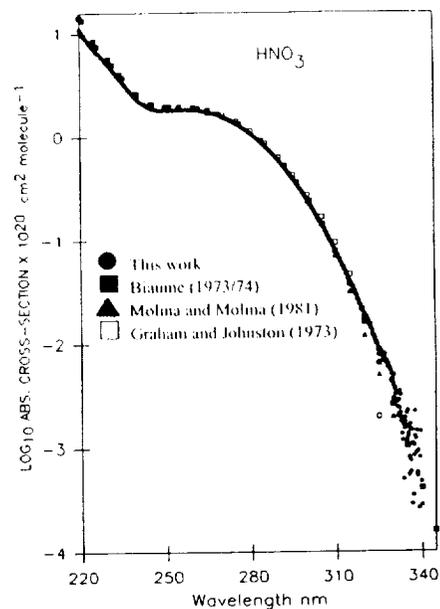

Fig. 2 Comparison of HNO_3 cross-sections at room temperature with previous measurements.

The large uncertainties in the long wavelength region are due to the difficulties involved in correction for the absorbance of NO_2. The present technique provides more spectral information for making this correction, but our samples contained more NO_2 than those measured by Biaume, (1973/74). Molina and Molina, (1981) did not report details of any corrections made for NO_2. The consistency of the cross-sections determined here with differing amounts of NO_2 gives us confidence in the values we report, which are slightly higher above 310 nm than those recommended by both the NASA (DeMore et al., 1990) and IUPAC (Atkinson et al., 1989) evaluations.

The cross-sections for N_2O_5 from the present work show good agreement with the values of Yao et al.(1982), Table 1. However their NO_2 reference spectra were recorded on a different instrument to that which was used for the N_2O_5 work and the different instrument functions gave rise to a wide scatter in the results above 340 nm where spectral subtraction of NO_2 must be performed. The values of Jones and Wulf, (1937) are lower than those measured here probably due to the presence of HNO_3 in their samples which was not accounted for.

Table 1.
Absorption cross-sections for N_2O_5 /10^{-20} cm^2 molecule^{-1}

| Wavelength nm | 295 K | | 273 K | |
	Present work.	Yao et al. (1982)	Present work	Yao et al. (1982)
280	10.5	10.1	9.95	10.0
290	6.46	6.80	6.03	6.44
300	3.76	3.84	3.43	3.43
310	2.10	2.15	1.88	1.83
320	1.17	1.20	0.970	0.98
330	0.645	0.67	0.470	0.52
340	0.347	0.37	0.246	0.28
350	0.198	0.21	0.131	0.15
360	0.115	0.12	0.071	0.080
370	0.068	0.066	0.041	0.043
380	0.040	0.037	0.023	0.023

4.2 Temperature Dependence

The best fit to the temperature dependence of the HNO_3 cross-sections measured here was obtained by plotting log_{10} (cross-section) versus temperature and by performing a linear least squares analysis fit to the data. This function allowed the extrapolation of absorption cross-sections to any chosen temperature in the range 200-300 K. Table 2 shows recommended cross-sections at 298 K, which were obtained by averaging the data from the present work together with those of Biaume, (1973/74), Molina and Molina, (1981) and Johnston and Graham, (1973), together with the recommended temperature coefficients from the present work. Cross-sections

at any temperature can then be calculated from the following expression: $log_{10}(\sigma_T) = log_{10}(\sigma_{298}) + B[T-298]$.

Table 2. Recommended absorption cross-sections for HNO_3.

Wavelength nm	$\sigma_{298}/10^{-20}$ cm^2 molecule^{-1}	$B/10^{-3}$ K^{-1}
190	1560.0	0
200	661.0	0
210	105.0	1.09
220	14.1	1.09
230	5.45	1.52
240	2.44	1.52
250	1.92	1.52
260	1.86	1.52
270	1.59	1.52
280	1.10	1.52
290	0.613	1.95
300	0.243	2.61
310	0.081	3.91
320	0.017	7.82
330	0.003	>7.82

Data for N_2O_5 was collected at 295, 273, 253, and 233 K. Results from 295 and 273 are displayed in Table 1 and the agreement at both temperatures with the recommended values (DeMore et al., 1990 and Atkinson et al., 1989) is good. Analysis of results at the lowest temperatures which require correction for the presence of N_2O_4 has yet to be performed.

4.3 Atmospheric photolysis rates

Atmospheric photolysis rates for HNO_3 were computed using the cross-section values recommended in Table 2. These calculations were carried out using the model of Lary (1991) for a range of temperatures, altitudes and solar zenith angles (SZA). The results illustrated in Figure 3, show that the photolysis rates decrease monotonically with temperature at all altitudes and SZAs, the decline is most prominent at low altitudes and high SZAs. At lower altitudes and high SZAs ozone strongly attenuates the incoming solar radiation at wavelengths below 290 nm. The remaining light intensity available for photolysis is therefore at longer wavelengths where the HNO_3 cross-section shows the greatest temperature dependence.

These results indicate that the photolysis rate for HNO_3 at temperatures appropriate to the low stratosphere is lower than that using the previous recommended values for the HNO_3 cross-sections (DeMore et al., 1990 and Atkinson et al., 1989). Consequently, reactive chlorine released
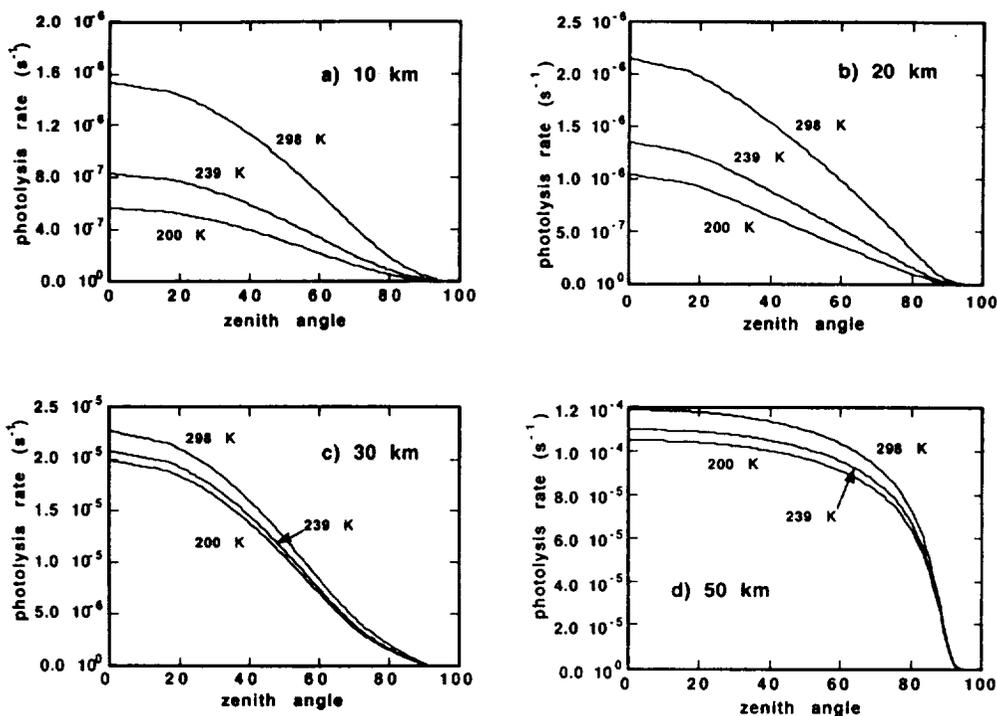
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Fig. 3 Dependence of the photolysis rate of HNO_3 on solar zenith angle and temperature at four different altitudes: a = 10 km; b = 20 km; c = 30 km; d = 50 km.

heterogeneously either on background aerosol or polar stratospheric clouds will be longer lived, and a greater ozone loss might be expected through the established mechanisms involving ClO and BrO (Solomon, 1990).

4.4 Future work

Analysis of the low temperature data for N_2O_5 will allow photolysis rates to be calculated in a similar way. Any likely effects on our understanding of the nitrogen partitioning of the atmosphere will then be considered.

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