

## Short Communication

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### The Vacuum Ultra-violet Absorption Spectrum of Anhydrous Nitric Acid

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The presence of nitric acid in the stratosphere was demonstrated by Murcray *et al.* [1] and Harries [2] has recently measured a mixing ratio above 15 km of  $3 \times 10^{-9}$  by volume. Nitric acid is an important trace constituent of the stratosphere since it may take part in the catalytic chains which partly determine atmospheric ozone concentrations. The production of HNO<sub>3</sub> removes [3] and its photolysis can regenerate [4], OH and NO<sub>2</sub>. A knowledge of the absorption spectrum of nitric acid, together with information about quantum yields, is therefore essential for accurate photochemical modelling of the stratosphere. Johnston and Graham [5], Biaume [6] and Schmidt *et al.* [7] have measured the absorption spectrum down to 170 nm. While absorption by HNO<sub>3</sub> of shorter wavelengths is unlikely to be significant in the lower stratosphere, at high altitudes dissociation to a variety of energetically accessible fragments becomes possible. The present communication reports an extension of the measurements to 120 nm.

Source lamps were mounted on the entrance slit of a McPherson 218 monochromator; an absorption cell was mounted on the exit slit, and consisted of a Pyrex tube with a lithium fluoride window attached at each end. The path length was 5 cm. The lamps used contained high pressure (~ 200 Torr) Ar, Kr, or Xe (depending on the wavelength range) and were powered by an EMS Microtron 200 source (2450 MHz). Radiation was detected at the end of the absorption cell by a Mullard B318 BL channel electron multiplier, and recorded by conventional pulse counting equipment. The instrument band pass was 1.5 nm. The HNO<sub>3</sub> used was anhydrous, contained less than 0.5% NO<sub>2</sub>, and could be kept as a white solid indefinitely at 78 K in the dark [8]. Pressures were measured using a capacitance manometer (MKS Baratron). Since the HNO<sub>3</sub> decomposed slowly on the metal in this device, the gas pressure was measured immediately after filling the cell, and the manometer was then isolated from the cell. After initial "ageing" of the system, the HNO<sub>3</sub> vapour underwent no detectable decomposition in it.

No systematic deviations from the Beer-Lambert law were observed over the pressure range 0.05 - 0.2 Torr, and average molar decadic extinction coefficients,  $\epsilon$ , were therefore calculated at each wavelength by application of this law. The results are shown in Fig. 1.

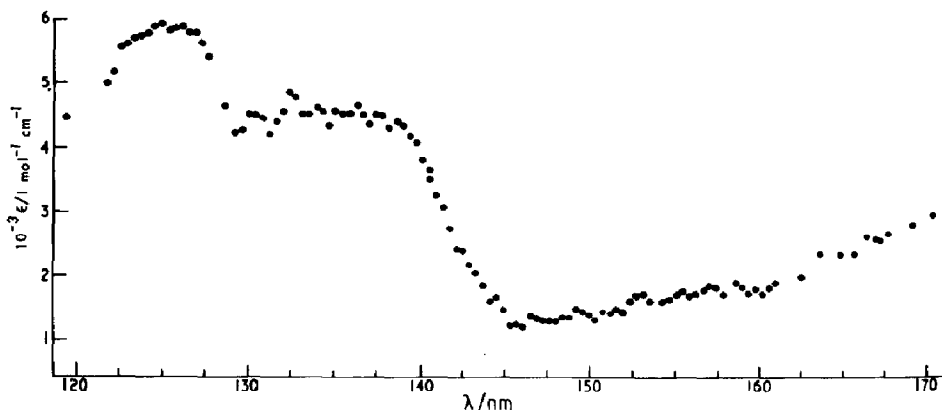


Fig. 1. The molar decadic extinction coefficient ( $\epsilon$ ) as a function of wavelength.

The only overlap of our spectrum with other published work is at  $\lambda = 170$  nm. Schmidt *et al.* [7] quote an extinction coefficient which is a factor of 1.41 lower than our value. Their extinction coefficient at  $\lambda = 200$  nm is lower than that of Johnston and Graham [5] by almost exactly the same factor. The data of Biaume and of Johnston and Graham agree quite well over the range 185 - 320 nm (and do not give evidence of the strong absorption between 320 and 440 nm reported by Schmidt *et al.*). It could be argued, therefore, that there is a systematic error of about 1.4 - 1.5 in the extinction coefficients of Schmidt *et al.* [7], but it should also be emphasized that in our own work the random errors at  $\lambda = 170$  nm are relatively high because of the fall-off in response of the channeltron detector. Table 1 summarizes the points of the preceding argument.

TABLE 1

Comparison of extinction coefficient ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ) for  $\text{HNO}_3$

Reference	$\lambda/\text{nm}$				
	170	200	230	325	365
This work	3000				
Schmidt <i>et al.</i> [7]	2121	973	15.4	1.28	55.9
Johnston and Graham [5]		1430	14.6	0.0052	<0.026
Biaume [6]		1609	13.9	0.0016	0.083

The only recent theoretical studies of the spectroscopy of  $\text{HNO}_3$  appear to be those of Harris [9, 10]. He predicts absorptions at  $\lambda = 278$  and 296 nm, which may correspond with the absorption centred on  $\lambda = 260$  nm found by Johnston and Graham [5]. A further expected transition at  $\lambda = 198$  nm may correspond to the maximum observed by Schmidt *et al.* [7] at  $\lambda = 185$  nm. At higher energies, the only transitions predicted by Harris lie at

$\lambda = 146$  and  $163$  nm. Our data provide no evidence for such transitions; further work is clearly needed to reconcile the observations with theory.

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