ROTATIONAL DISTRIBUTION OF OH ($^2\Sigma$) FLUORESCENCE IN THE PHOTODISSOCIATION OF NITRIC ACID

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The photodissociation of nitric acid in the ultraviolet has recently been studied[1]. The main primary process is

$$HONO_2 \xrightarrow{h\nu} HO + NO_2$$

Thus, the photolysis of nitric acid in the troposphere may be important in smog formation.

The photodissociation of $HONO_2$ in the vacuum ultraviolet leads partially to the formation of OH in an electronically excited state, $^2\Sigma^+$. Although the thermochemical threshold for OH ($^2\Sigma$) production is 6.09 eV, corresponding to 2037 Å, the observed threshold is at 1485 Å, corresponding to the long wavelength limit of the third absorption band. (See Fig. 1.) The fluorescence yield increases towards shorter incident wavelengths and is about 5% at 1236 Å.

The rotational distribution of OH ($^2\Sigma$) in the photolysis of 0.2 torr $HONO_2$ at the Kr (1165, 1236 Å) lines is shown in Fig. 2. For comparison, the rotational distribution of OH ($^2\Sigma$) from the photolysis of H_2O is also presented. The rotational distributions are markedly different in the two cases; the maximum appears at N' = 10 for $HONO_2$ but at N' = 20 for H_2O. Possible reasons for the different distributions will be discussed.

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[1] H. S. Johnston, S. G. Chang, and G. Whitten, J. Phys. Chem. 78, 1 (1974).

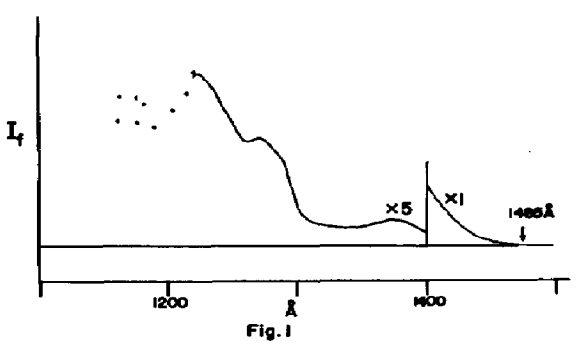

Fig. 1

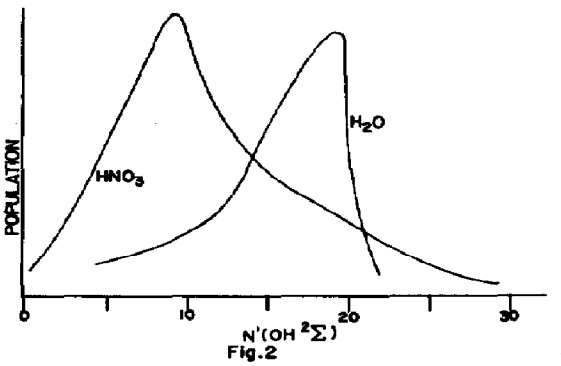

Fig. 2