escence is entirely within the ultraviolet region and extends to wavelenths as short as 225 nm (127 kcal/einstein). The identity of the emitter and possible mechanisms for the chemiluminescence will be considered.

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## R6

# Recent Measurements of Stratospheric Water Vapor

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A balloon borne frost-point hygrometer is being used to measure the vertical distribution of water vapor to a height of 30 km. The measurements which were begun in 1964 now provide an 11-year record of the vertical distribution of water vapor for the mid-latitude stratosphere in the northern hemisphere and constitute the only continuous series of measurements over a period of several years. The water vapor to air mass mixing ratio for the stratosphere is found to be approximately constant with height. The total accumulation of data for the 11-year period shows a modal distribution of mixing ratio for the lower stratosphere which is centered at 2.7 ppm with 80 percent of the observations within ± 1 ppm of the modal value. The times series shows a trend of increase during the first 6 years followed by a step decrease in 1971 with a level trend thereafter. A seasonal cycle is observed in the lowest stratospheric levels with minimums in late winter. The data record provides a reference base for early detection of significant changes in stratospheric water vapor distribution.

Aircraft measurements and balloon soundings since November 1974 show a pronounced decrease in water vapor concentration in the low stratosphere between 13 and 16 km. The minimum in the vertical distribution of water vapor coincides with the base of a layer of increased aerosol concentration between 15 and 20 km which was first observed by investigators at mid-latitudes in November 1974.

## **R7**

# Laboratory Kinetic Studies of Reactions of Atmospheric Interest Using Resonance Fluorescence Spetroscopy

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The technique of UV resonance fluorescence detection of reactive atoms and radicals has been coupled with a dischargeflow apparatus to study reactions of OH with HNO<sub>3</sub>, HCl, and D, of Cl with O<sub>3</sub>, and of ClO with NO and O. With the exception of the OH + D exchange reaction all of these are of importance in the photochemistry of the earth's stratosphere.

The sensitivity of the resonance fluorescence technique ([OH]  $\ge 2 \times 10^9$  cm<sup>-3</sup>) has permitted the direct investigation of these reactions under conditions where the observed species' disappearance is unambiguously attributed to the corresponding reaction. The study of the OH + D exchange demonstrates the valuable selectivity of resonance fluorescence such that OH decay could be followed without interference by OD.

The rate constants and temperature dependencies of these reactions studied at total pressure of 1 – 10 Torr of He are: OH + HCl  $\rightarrow$  H<sub>2</sub>O + Cl 224  $\leq$  T  $\leq$  460 K  $k = 2.0 \times 10^{-12} \times \times \exp\left[-\frac{620 \text{ cal/mole}}{RT}\right] \text{ cm}^3 \text{ sec}^{-1}$  (1) OH + HNO<sub>3</sub>  $\rightarrow$  H<sub>2</sub>O + NO<sub>3</sub> 295  $\leq$  T  $\leq$  470 K  $k = 0.89 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  (2)