

eventually be depleted by 1% for every 30,000 to 50,000 tons of anthropogenic chlorine atoms released in the stratosphere per year. Accurate estimates of the Stratospheric Hazard Index are required for all chlorine-containing molecules in order to establish appropriate world-wide legal limitations on the atmospheric release of the various volatile anthropogenic chlorocarbon molecules. Similar estimates will also be required for bromine-containing molecules, although current technological levels for these are much lower than for the chlorocarbons.

V4

High Resolution Emission Spectrum, Molecular Constants and Franck-Condon Factors for the $A^2\Pi - X^2\Pi$ system of ClO

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The ClO radical, first identified [1] in 1948 by observation of the $A^2\Pi - X^2\Pi$ system in emission, is an important intermediate in photochemical systems. For example, it is readily observed [2] in the flash photolysis of $Cl_2 + O_2$ mixtures, and is a chain carrier in the photodecomposition of the chlorine oxides. It has recently been suggested [3] that ClO will play an increasingly important part in stratospheric chemistry, and considerable effort is already being made to detect low concentrations of ClO in the stratosphere. The technique of laser-induced fluorescence is being evaluated in several laboratories. However, a rotational constant for the $X^2\Pi$ ground state is known [4, 5] only for the $v'' = 0$ level and rotational constants and vibrational term values are not available for the lowest vibrational levels of the A state. Hence it is not possible at present to perform calculations of realistic potential energy curves and accurate vibrational transition probabilities.

The $A^2\Pi - X^2\Pi$ emission spectrum of ClO from a $H_2/O_2/Cl_2$ diffusion flame at atmospheric pressure has been recorded at high resolution. Preliminary rotational

analyses have been made for several bands, and rotational constants for $v' = 0$ and for several ground state vibrational levels have been found for the first time. The analysis is being extended to other bands of the system.

The interpretation of the high resolution absorption data [4] on ClO is known [6] to be in error. In the present work, new assignments are made which lead to a rotational constant B''_0 in good agreement with the result from microwave spectroscopy [5].

The accepted vibrational numbering in the $A^2\Pi$ state is based on the band-head analysis of Pannetier and Gaydon [1]. Evidence will be presented to show that this numbering requires revision.

RKR potential energy curves and numerically calculated Franck-Condon factors for the $A \leftrightarrow X$ system of ClO are reported for the first time.

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V5

Photolysis of Ethyl Chloride At 147 nm

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The current interest in the photodecomposition of Freons 11 and 12 leading to the possible large scale removal of ozone from the stratosphere has stimulated this laboratory to investigate the primary processes in the C_2 -Freons, not because they pose the same environmental threat as the C_1 -Freons, but because it has become apparent that there is a definite need for photochemical