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

information concerning gases and low boiling liquids produced in large quantities by industry.

This paper presents some preliminary results of the photolysis of C_2H_5Cl (Freon 160) at 147 nm. The extinction coefficient at this wavelength is of the order of $10^3 \, l \, mol^{-1} \, cm^{-1}$ and the molecule readily photolyzes to give C_2H_4 and $1,4$-$C_4H_8Cl_2$ as the two major products at conversions of $< 1\%$. Other photolysis products observed, in decreasing order of yield relative to C_2H_4, were: C_2H_6, n-C_4H_{10}, 1-C_4H_9Cl, C_2H_3Cl, C_3H_8, C_3H_6, C_2H_2, CH_4, 1-C_4H_8, cis 2-C_4H_8, trans 2-C_4H_8 and CH_3Cl. The yields, relative to C_2H_4, of n-C_4H_{10}, C_2H_6, C_2H_2 and CH_4 did not vary with photolysis time at a fixed pressure of ethyl chloride. In the presence of nitric oxide, ethane was no longer observed and the relative yield of n-C_4H_{10} was significantly suppressed as were the relative yields of most of the other minor products.

The results are interpreted in terms of primary processes where molecular elimination is not a major contributor. The principal reaction pathway appears to be carbon–chlorine bond fission from an electronically excited state of ethyl chloride, followed by rapid decomposition of the highly energised $C_2H_5{}^{**}$ radical to C_2H_4. Subsequent hot atom and radical reactions account for the majority of the remaining observed products.

A comparison of these results with those obtained in the 147 nm photolysis of C_2H_5F suggests different modes of excitation and reaction channels in C_2H_5Cl and C_2H_5F. In the case of ethyl fluoride the observed major products were C_2H_3F and C_2H_2 and it was concluded that molecular eliminations were the major primary processes. Molecular orbital calculations have now been carried out and the molecular orbital descriptions of the first electronic excited states for both halides were found to be antibonding with respect to the carbon–halogen bond (σ^* c–x). This should lead to carbon–halogen bond fission in both cases at 147 nm which is observed in the case of C_2H_5Cl, but does not occur to any significant extent in the case of C_2H_5F. It would therefore seem that

C_2H_5F undergoes an internal conversion to a highly vibrationally excited ground electronic state prior to decomposition.

-It is apparent that the C_2-Freons exhibit a spectral specificity of photodecomposition which is not readily predicted.

V7
Experimental Study of the NO$^+$ + e → N + O Recombination in the Vacuum UV Flash Photolysis of Nitric Oxide

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The main result from this study is the first experimental determination of the $N(^2D)$ branching ratio $f = [N(^2D)]/\{[N(^2D)] + [N(^4S)]\}$ in a laboratory experiment.

Nitric oxide was irradiated with a fast flash lamp ($t = 10 \, \mu s$), separated by a LiF-window from the reaction chamber. The type of flash lamp used has been described earlier [1]. In short, it consisted of a $0.5 \, \mu F$ capacitor, charged to 25 kV. The discharge took place between copper electrodes 15 mm apart in nitrogen at atmospheric pressure. The reaction chamber was a stainless steel tank of approximately 50 l volume. The flash lamp light entering the chamber at one side of the tank was focused by a large concave mirror to the center of the tank yielding a very high photon flux density in a volume of about 1 cm^3. NO, typically at densities of about 10^{14}/cm^3, mixed with argon or nitrogen at a total pressure of 10 Torr was continuously pumped through the chamber.

Nitrogen atoms in either ^4S or ^2D state, the products of the photolysis and ion-electron recombination were detected by resonance absorption with a calibrated resonance lamp, shining through the tank's focal plane, dispersed by a vacuum UV monochromator and recorded on a multi-channel analyzer.

At wavelengths shortward of 1340 Å, nitric oxide is photodissociated and photoionized. The products of the ion-electron recombination