

a $^4\Sigma_u^-$ state, whose origin lies about 1100 cm^{-1} above the B state. Both the vibrational relaxation rate (strongly temperature and isotopic mass dependent) and $v' = 0$ lifetime of a $^4\Sigma_u^-$ are monitored in this manner. A superficially random variation of B state lifetimes among $^{12}\text{C}^{12}\text{C}^-$, $^{12}\text{C}^{13}\text{C}^-$, and $^{13}\text{C}^{13}\text{C}^-$ reflects accidental coincidences with high levels of the $\text{A}^2\Pi$ state. The purely radiative lifetimes are near 65 ns in Ne, 40 ns in Ar, 38 ns in Kr, and 34 ns in Xe.

The formation of "stable" ions in 1216 \AA photolyzed, acetylene doped rare gas lattices is shown to be consistent with single photon ionization schemes using dielectric physics ideas. A long range electron tunnelling from the excited B state of C_2^- in Ne to a nearby (*ca* 10 - 15 Å) cation is observed. The rate is $K_1 \approx 10^3\text{ s}^{-1}$ and increases with vibrational level.

Fluorescence and radiationless transitions in Br_2 and Cl_2 have also been studied. In Br_2 , the emitting state is identified by its excitation spectrum as the $\text{B } ^3\Pi(\text{O}_u^+)$, and the lifetimes in different matrices suggest a gas phase $v = 0$ radiative lifetime of $11 \pm 1\text{ }\mu\text{sec}$. In Cl_2 , the emission following either $\text{B } ^3\Pi(\text{O}_u^+)$ or $^1\Pi_1$ excitation occurs from a long-lived ($\sim 100\text{ ms}$) electronic state lying 620 cm^{-1} below the B state. We tentatively assign this state as $^3\Pi_2$.

V1 (Invited Lecture)

Chlorocarbon Compounds and Stratospheric Ozone

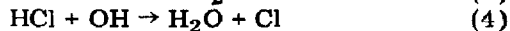
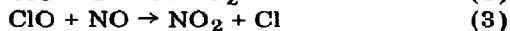
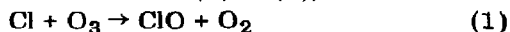
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Two chlorofluoromethane compounds, CF_2Cl_2 and CFCl_3 , are widely used in current technology as aerosol propellants, refrigerants, solvents and in the blowing of polyurethane foam. These uses led in 1974 to the release to the atmosphere of approximately 5×10^5 and 3×10^5 tons, respectively, of these gases. Since the molecules are normally inert chemically, biologically unreactive, insoluble in water and transparent and visually near u.v. radiation, they have long environmental lifetimes and are accumulating in the earth's atmosphere.

The present levels are in the vicinity of 1 part in 10^{10} by volume for each.

Both molecules are decomposed by ultraviolet light with λ less than about 2200 \AA , releasing one Cl atom; the subsequent reaction of the residual radical with O_2 releases another chlorine entity (either ClO or Cl). Since such hard u.v. radiation is absorbed well by both O_2 and O_3 in the atmosphere, the chlorofluoromethanes must rise into mid-stratosphere ($> 20\text{ km}$) before any appreciable photodecomposition occurs in the atmosphere. The chlorine atoms released between 20 - 35 km initiate a chain reaction with O_3 in which the most important reactions are (1) to (5),



and for which the chain-length before eventual termination is $> 10^4$. Detailed calculations indicate a present average depletion of the ozone layer approaching 1%, and future steady-state depletions of 10% or more for continued release of CF_2Cl_2 , CFCl_3 , and other halocarbons at the 1973 rates. Depletion of the O_3 layer has many possible biological and climatic consequences.

The slow upward diffusion of molecules in the stratosphere ensures a delay between ground-level release and the full effect on the ozone layer — the maximum depletion for molecules released in 1974 will occur in 1985 - 1990. In addition, the estimated atmospheric lifetimes for these molecules are so long (40 - 150 years) that approximately a century will be required for the ozone depletion to decrease to one-half its maximum value.

Other halocarbon compounds are also present in the atmosphere, some of natural (*e.g.* CH_3Cl) and many of anthropogenic origin. In general, molecules containing C - H bonds or C = C bonds have much less stratospheric hazard per molecule because they are largely removed by tropospheric reactions with OH radicals. Molecules such as CCl_4 , CCl_3F_3 , etc., also are expected to react predominantly in the stratosphere.

Current estimates indicate that the average ozone level of the stratosphere will

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.

- 1 G. Pannetier and A. G. Gaydon, *Nature*, 161 (1948) 242
- 2 G. Porter, *Disc. Faraday Soc.*, 9 (1950) 60.
- 3 M. J. Molina and F. S. Rowland, *Nature*, 249 (1974) 810.
- 4 R. A. Durie and D. A. Ramsay, *Can. J. Phys.*, 36 (1958) 35.
- 5 T. Amano, S. Saito, E. Hirota, Y. Morino, D. R. Johnson and F. X. Powell, *J. Mol. Spectrosc.*, 30 (1969) 275.
- 6 A. Carrington, P. N. Dyer and D. H. Levy, *J. Chem. Phys.*, 47 (1967) 1756.

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