fib CCOL

CMA

CHEMICAL MANUFACTURERS ASSOCIATION

FLUOROCARBON RESEARCH PROGRAM

Effect of Chlorofluorocarbons on the Atmosphere

Revision No. 21

The Fluorocarbon Research Program, sponsored and funded by the industry, is summarized in Revision 21, June 1, 1985. Underscoring indicates developments since Revision No. 20.

For additional information, please contact the investigator or CMA.

Sincerely,

Elizabeth Festa Gormley

Elizabeth Festa Gormley
Program Manager
Fluorocarbon Program
Telephone: 202/887-1194

Attachment: Revision No. 21
June 13, 1985

CODE: 36-B

For Distribution by CMA
SPECIAL PROGRAMS DIVISION
From E. FESTA GORMLEY
Ref. No. EPP 106-AQ
Date 6/14/85

SUMMARY

Research Program on

EFFECT OF CHLOROFLUOROCARBONS ON THE ATMOSPHERE

Sponsored by the Chlorofluorocarbon Industry

Prepared by: B. Peter Block
Hillel Magid
Richard B. Ward

Distributed by: Chemical Manufacturers Association
2501 M Street, N.W.
Washington, D. C. 20037

(Originally Issued: September 26, 1975)

Revision No. 21: June 1, 1985

TABLE OF CONTENTS

Tables:

SUMMARY

Research Program on

EFFECT OF CHLOROFLUOROCARBONS ON THE ATMOSPHERE

Sponsored by the Chlorofluorocarbon Industry
Administered by the Chemical Manufacturers Association

(Originally Issued: September 26, 1975)
Revision No. 21: June 1, 1985

This summary describes work supported by the manufacturers of chlorofluorocarbons (CFCs, sometimes called fluorocarbons) in an attempt to assess the possible impact of these chemicals on the environment and, in particular, on the stratospheric ozone layer.

Summary and Recommendations

In 1972 the CFC manufacturers began supporting a program to investigate the effects of CFCs on the environment. This program has been expanded greatly to help determine the extent, if any, to which these compounds may affect the stratospheric ozone layer. Industry- and government-sponsored scientists working on the halogen-ozone problem have cooperated effectively. Continuation of this cooperation is essential, with special attention to providing periodically updated summaries of research priorities, programs, and results, together with critical analyses of the reliability and significance of the data.

The programs now under way to develop methods for determining the ozone changes that are actually occurring (as opposed to hypothetical or calculated ozone changes) and to resolve important questions about key stratospheric species--O_3, ClO, total chlorine--will lead to a progessively better understanding of the effect of the CFCs on stratospheric ozone.

The industry position continues to be:

- The ozone depletion theory warrants serious concern and continuing investigation.
- The international scientific consensus necessary to resolve this issue must be based on convincing measurements and evaluations, not theory alone.
- Convincing experimental evidence can be obtained to verify or disprove the theory quantitatively.
- There is time to perform these necessary experiments without significant risk to the health and welfare of the population.

The Industry-Sponsored Program

In July of 1972, E. I. du Pont de Nemours & Company issued to CFC manufacturers worldwide an invitation to a "Seminar on the Ecology of Fluorocarbons." Its purpose was to establish a technical program because, as stated in the invitation,

> "Fluorocarbons are intentionally or accidentally vented to the atmosphere worldwide at a rate approaching one billion pounds per year. These compounds may be either accumulating in the atmosphere or returning to the surface, land or sea, in the pure form or as decomposition products. Under any of these alternatives, it is prudent that we investigate any effects which the compounds may produce on plants or animals now or in the future."

Representatives of 15 companies attended the meeting, agreed that such a program was important, and established and funded a CFC research program under the administration of the Chemical Manufacturers Association (CMA). Thus, in 1972, with no evidence that CFCs could harm the environment, the producers of these chemicals agreed that there was a need for more information and proceeded to act.

The CFC producers supporting this program represent almost the total production of CFCs in the Americas, Western Europe, Japan, and Australia. The research is directed by the CMA Fluorocarbon Program Panel (FPP) with one voting member from each supporting company. This Panel meets regularly to review progress on current research, evaluate new proposals, and exchange data with contractors, with government agencies, and with other scientists.

Publication of the Rowland-Molina hypothesis in 1974 identified a potentially serious problem, so the CMA FPP research program was expanded considerably. The CFC-ozone relationship attracted the attention of many scientists in academic and government laboratories, legislative and regulatory bodies, and the press. The CMA FPP program is concentrating on research most likely to answer the critical question: to what extent will human activities affect the stratospheric ozone layer, and, if they are a factor, to what extent are CFCs involved?

To strengthen the overall effort to find the answer, CMA FPP has coordinated its efforts with others working on the possible effects of emission of CFCs and other trace gases. These problems concern the federal government, and interactions with a number of agencies have been especially helpful in:

1. Taking advantage of the knowledge and experience gained in the Climatic Impact Assessment Program;
2. Coordinating funding of programs addressing the environmental effects of trace gases;

3. Planning joint experiments with government research groups; and
4. Helping to set priorities for industry-sponsored research.

About 580 research proposals have been reviewed to date, and projects totaling about \$16.9 million have been funded (see Table 2). Calendar 1985 commitments are expected to total almost \$1.8 million, and total expenditures through 1985 will be approximately \$18.9 million.

Assessments of the Science

The Clean Air Act Amendments of 1977 (U. S. Public Law 95-95) established the U. S. Environmental Protection Agency (EPA) as the agency responsible for assessing the probable effect of CFCs on the ozone layer. Other U. S. agencies are given various responsibilities in the scientific effort required to support any decisions, and the EPA is required to rely on the National Academy of Sciences (NAS) for advice on the status of the science. The NAS has issued several reports. The latest, by its Committee on Causes and Effects of Changes in Stratospheric Ozone: Update 1983, was released in February, 1984.* The present state of knowledge has also been assessed by the National Aeronautics and Space Administration (NASA)[+] and the United Nations Environment

---

*Committee on Causes and Effects of Changes in Stratospheric Ozone: Update 1983, National Research Council, "Causes and Effects of Changes in Stratospheric Ozone: Update 1983," National Academy of Sciences, Washington, D.C., 1984. The pages in the reference where the research recommendations appear are identified by square brackets [ ].

[+] Present State of Knowledge of the Upper Atmosphere An Assessment Report, National Aeronautics and Space Administration, January, 1984.

Programme Coordinating Committee on the Ozone Layer (CCOL),[++] the EPA has reported to Congress on the status of regulations in the Unitd States to protect stratospheric ozone,[x] and the United Kingdom Royal Commission on Environmental Pollution has commented on the current status of the CFC-stratospheric ozone issue.[xx]

Efforts to Resolve Current Uncertainties

The emphasis of the CMA-administered industry program has been overwhelmingly in the major areas recommended for further study by the different groups assessing the issue. The industry-sponsored program, therefore, aims to fill in the most important gaps in existing scientific knowledge. The following research recommendations identified by NAS* are, in whole or in part, the subject of projects funded and cofunded by FPP and member companies.

- More rate and photochemical parameters must be measured with high accuracy and with careful attention to the identification of product channels.
- The rapid progress in experimental techniques must be maintained, new methods for the detection of reactive species developed, and larger ranges of temperature and pressure variation investigated. [Page 30]

[++] Environmental Assessment of Ozone Layer Depletion and its Impact as of November, 1981, Bulletin No. 7, United Nations Environment Programme, January, 1982. The recommendations for future work were revised at meetings of CCOL April 5-8, 1983, and October 15-18, 1984.

[x] Report to Congress on the Progress of Regulation to Protect Stratospheric Ozone, U.S. Environmental Protection Agency, April, 1983.

[xx] Tackling Pollution - Experience and Prospects, Royal Commission on Environmental Pollution, Tenth Report, February, 1984.

See p. 4 for footnote.

- The long-term monitoring of the atmospheric concentrations of the source gases must be supported, because the worth of such data depends strongly on the continuity of the record. Particular emphasis should be placed on the integrity of standards, international intercomparison, and publication of the data, accompanied by documentation of the methodology. [Pages 48-9]
- Instrumentation should be developed to measure ozone concentrations at 40 km with accuracy of a few percent so that there can be early detection of trends at the altitude where the percentage ozone changes due to anthropogenic perturbations are calculated to be the largest relatively. A monitoring program should then be instituted. The thrust should be toward a combination of balloon and satellite sensors.
- The development and field testing of instrumentation to measure a variety of stratospheric trace species should be supported strongly since many of the important species remain unmeasured or poorly measured. The primary goals should be the radical and reservoir species.
- The discrepancies between ClO measurements taken with different techniques should be resolved as soon as possible.
- Rigorous, double-blind intercomparisons of instruments in the field should be continued to assess the reliabilities of current technology, since this is the best way to assess accuracy. Support is critical during the difficult phase of this endeavor, namely, after differences have been demonstrated and rationalizations are then sought.
- Intensive measurement campaigns should be mounted to deploy a group of multiple-species instruments that can determine the full data set required to test a proposed

hypothesis. The campaigns should include ground-based, balloon, aircraft, and satellite configurations. [Page 49]

- The lower stratosphere. Efforts to evaluate the effects of transport and variability on the ozone budget of the lower stratosphere must be increased. In light of the importance of this region in compensating for calculated ozone decreases in the photochemically controlled upper stratosphere, a quantitative understanding of the interaction of transport and chemistry in the lower stratosphere should be given very high priority. [Page 64]
- It is important to validate and calibrate more accurately the existing 2-D models, since they should be able to simulate the seasonal and latitudinal behavior of ozone and other trace species in the current atmosphere. [Page 93]
- The detection and prediction of trends in ozone are a focus of this report. It is now clear that efforts at verifying perturbations to the atmosphere should be directed toward the detection of changes in ozone in the upper stratosphere. The importance of tropospheric ozone, however, should not be ignored; we must also continue to model and observe significant changes in the lower atmosphere. [Pages 93-4]
- The overall effort at comparison of theory with observation must continue. Especially promising are those studies that attempt to remove the noise in observational data that is associated with spatial variations. A more accurate calibration of local ozone concentrations of models with observations is important, especially as an aid to understanding the chemistry and dynamics of the lower stratosphere, an area of great uncertainty in the current models.

- A prime focus of the validation of photochemical models must continue to be the systematic collection of observational data that can define the local chemical systems within the stratosphere. In this framework we regard as essential the simultaneous observation of several long- and short-lived species, for example, O_3, O, OH, H_2O, HNO_3, NO, NO_2, Cl, and ClO. [Page 94]
- Emissions, inventories, and lifetimes should be defined for the key species that affect ozone, directly or indirectly, such as halocarbons, N_2O, NO_x, CH_4, and CO_2.
- Models that couple radiation, dynamics, and photochemistry in comparable detail should continue to be developed. Both the dynamical and the chemical mechanisms that couple the trace gases of the stratosphere and troposphere need to be examined.
- The observational evidence for changes in stratospheric ozone over the past decade need to be evaluated and attempts to define similar trends in important background gases, such as N_2O, NO_x, CH_4, and other hydrocarbons, CO, and stratospheric H_2O should be continued.
- Techniques need to be developed for the quantitative analysis of uncertainties in theoretical models, particularly their sensitivity with regard to the chemical kinetic scheme and the parameterization of dynamical transport. [Page 112]
- Predictions of basal cell carcinomma and squamous cell carcinoma incidence based on epidemiological data must take into account social and demographic factors as well as changes in UV-B insolation. [Page 167]

The FPP also supports many of the areas of research included in the CCOL recommendations for future work,[++] which overlap the

---

[++] See p. 5 for footnote[++].

NAS recommendations to a considerable extent, as well as areas of research not identified in either the NAS or CCOL recommendations (see Table 3).

Details on the CMA FPP program are given in Tables 3, 4A, and 4B. Table 3 lists summaries of the projects by type of research activity. Table 4A lists completed projects, and Table 4B lists active projects in chronological order of funding. Table 5 lists refereed publications resulting from industry-sponsored work, plus selected reports issued by CMA. Additional written information is, in some cases, available from the individual investigators.

In addition to the work supported by the CFC industry at universities and other laboratories, there are studies underway in the laboratories of individual member companies who have scientists able to make significant contributions to the resolution of the problem. Problems receiving particular attention by industry scientists include: the application of statistical methods to detect abnormal trends in stratospheric ozone concentrations, the evaluation and development of modeling techniques, and the study of the sensitivity of models to various input parameters.

Table 1

CHLOROFLUOROCARBON MANUFACTURERS
represented on the
CMA FLUOROCARBON PROGRAM PANEL

Akzo Chemie bv (Holland)
Allied Corporation (U.S.)
Asahi Glass Co., Ltd. (Japan)
ATOCHEM (France)*
Australian Fluorine Chemicals Pty. Ltd. (Australia)
Daikin Kogyo Co., Ltd. (Japan)
Du Pont Canada Inc. (Canada)
E. I. du Pont de Nemours & Company, Inc. (U.S.)
Essex Chemical Corporation (Racon) (U.S.)
Hoechst AG (West Germany)
Imperial Chemical Industries PLC (England)
I.S.C. Chemicals Ltd. (England)
Kaiser Aluminum & Chemical Corporation (U.S.)
Kali-Chemie Aktiengesellschaft (West Germany)
Mitsui Fluorochemicals Co. Ltd. (Japan)
Montefluos - Gruppo Montedison (Italy)
Pennwalt Corporation (U.S.)
Showa Denko K. K. (Japan)
Societe des Industries Chimiques du Nord de la Grece, S.A. (Greece)
Union Carbide Corporation (U.S.)**

June 1, 1985

---

*Has taken over chlorofluorocarbon activities of CHLOE Chemie and Ugine Kuhlmann.

**Does not currently manufacture chlorofluorocarbons. Supported the CMA program through June, 1977.

Table 2

CHLOROFLUOROCARBON RESEARCH PROGRAM

Administered by
Chemical Manufacturers Association

Financial Summary

Type of Activity[a]	Completed Projects	Active Projects	Total
A. Investigation of Reaction Rates, Products, and Mechanisms	$ 1,354,665	$ 915,782	$2,270,447
B. Source and Sink Studies	2,361,245	422,971	2,784,216
C. Laboratory Studies Related to Potential Atmospheric Measurements	1,483,500	507,090	1,990,590
D. Tropospheric and Stratospheric Measurements	2,893,936	2,491,451	5,385,387
E and F. Modeling and Other Projects	3,229,285	822,693	4,051,978
G. Consulting	306,208	148,189	454,397
SUBTOTAL	$11,628,839	$5,308,176	$16,937,015
Administrative Expenses			1,381,693
TOTAL			$18,318,708

[a] Individual projects are summarized in Table 3.

June 1, 1985

Table 3*

Chlorofluorocarbon Research Program

Types of Research Activities, Summaries

A. Investigation of Reaction Rates, Products, and Mechanisms

Dr. R. ATKINSON -- University of California at Riverside -- 84-531. Reactions of Gas-Phase Chlorine Nitrate with Water Vapor and Hydrogen Chloride.

Atmospheric modeling calculations show that the title reactions could be important in the stratosphere even if they proceed at a relatively slow rate. Available gas-phase reaction rate data are limited and subject to uncertainties because both reactions appear to be strongly catalyzed by solid surfaces. In this study interference by such wall reactions will be minimized by the use of large reaction chambers with a low surface-to-volume ratio.

Dr. K. H. BECKER -- University of Wuppertal, F.R.G. -- 83-455. Pressure and Temperature Dependence of the Reaction of OH with HO_2NO_2 (completed).

The reaction of OH with HO_2NO_2 was studied at temperatures from 256 to 295 K at total pressures of N_2 or air ranging from 1 to 300 torr. Over the range of conditions investigated and within experimental error the reaction was found to be temperature and pressure independent. A value of $(5.5 \pm 0.5) \times 10^{-12}$ cm^3/s was obtained for the rate constant for the reaction. Product studies using wet chemical and photolytical methods for producing HO_2NO_2 suggest that its reaction with OH radicals leads to formation of H_2O, O_2, and NO_2 with greater than 90% yield.

Dr. J. W. BIRKS -- University of Illinois -- 75-1, 76-117A, 76-117B. Measurement of Reaction Rates Relevant to the Fluorocarbon-Ozone Problem; Studies of Heterogeneous Reactions (completed).

Reaction rate constants were measured using the discharge flow technique in combination with mass spectrometry for detection. The reaction $NO + O_3 \rightarrow NO_2 + O_2$ was studied

---

*Significant changes since the last revision are underscored.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

over the temperature range 203-361 K. The resulting Arrhenius expression is $k = (2.34 \pm 0.23) \times 10^{-12} \exp(-1450+50/T)$ $cm^3 molec^{-1}s^{-1}$ and predicts $k = 1.80 \times 10^{-14}$ at 298 K in excellent agreement with previous determinations. The activation energy, however, is 12% higher than the previously accepted value. A slight curvature in the Arrhenius plot was observed, the activation energy increasing with increasing temperature.

The rate constant for the reaction $ClO + NO_2 + M \rightarrow ClNO_3 + M$ was measured over the temperature range 250-356 K and the pressure range 1-5 torr by detecting the loss of ClO in a large excess of NO_2. The reaction was found to be third order with N_2 being twice as effective a third body as He. The low-pressure, third-order rate constant in N_2 is given by the expression $k = (4.40 \pm 0.66) \times 10^{-33} \exp(1087 \pm 70/T)$ $cm^6 molec^{-2}s^{-1}$.

No reaction of $ClONO_2$ with NO, NO_2, O_3, or HCl could be observed. Upper limits of 4×10^{-17}, 2×10^{-17}, 7×10^{-17}, and 1.2×10^{-15} $cm^3molec^{-1}s^{-1}$ for the respective bimolecular reaction rate constants rule out these reactions as significant sinks for $ClONO_2$ in the stratosphere.

The possibility of successive oxidation of ClO to perchloric acid was investigated. The reaction of ClO with O_3 was too slow to measure. An upper limit of 1×10^{-16} $cm^3molec^{-1}s^{-1}$ was established for the reaction $ClO + O_3 \rightarrow OClO + O_2$, and an upper limit for the reaction $ClO + O_3 \rightarrow ClOO + O_2$ was found to be 5×10^{-14}. Not only is OClO formed slowly; the absorption spectrum was obtained, and the photolysis constant calculated to be $7.6 \times 10^{-2}s^{-1}$, corresponding to a photolytic lifetime of 13 s. Furthermore, the reaction $OClO + O_3 \rightarrow ClO_3 + O_2$ is extremely slow, $k << 1 \times 10^{-18}$ $cm^3molec^{-1}s^{-1}$ at 298 K. These results rule out the importance of successive oxidation of chlorine to higher oxides as a path to the photochemically stable species, perchloric acid.

Exploratory studies of the heterogeneous reactions $ClONO_2 + HCl \xrightarrow{w} Cl_2 + HONO_2$ and $ClONO_2 + H_2O \xrightarrow{w} HOCl + HONO_2$ on sulfuric acid coated walls resulted in heterogenous rate constants that are too small to be of significance in the stratosphere.

> Dr. J. W. BIRKS -- University of Colorado -- 77-192, 78-244, 79-276, 80-321, 80-329, 82-425, 83-490; Drs. J. W. BIRKS and R. E. SIEVERS -- University of Colorado -- 81-358. Studies of Reactions of Importance in the Stratosphere.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

The rate constant for the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ was measured by following the appearance of the HOCl product. The rate constant is independent of pressure over the range 2-6 torr, the result being $k = (4.5 \pm 0.9) \times 10^{-12}$ $cm^3 molec^{-1} s^{-1}$ at 298 K. An upper limit of 2% for the branching ratio to the alternative products, $HCl + O_3$, was established by attempting to detect ozone as a reaction product. The measured rate constants for this reaction at the elevated temperatures of 318 K, 338 K, and 358 K are 3.8×10^{-12}, 4.0×10^{-12}, and 3.8×10^{-12}, respectively.

The reaction $Cl + HOCl \rightarrow$ Products was studied over the temperature range 243-365 K by detecting the loss of HOCl in a large excess of Cl atoms. The temperature-dependent rate constant is given by $k = (3.0 \pm 0.5) \times 10^{-12} \exp[-(130 \pm 60)/T]$ $cm^3 molec^{-1} s^{-1}$. Both sets of products, $HCl + ClO$ and $Cl_2 + OH$, are possible. The products $Cl_2 + OH$ are favored by consideration of the equilibrium constant for the reaction forming these products and the measured rate constant for the reverse reaction. Even if the reaction branches totally to $HCl + ClO$, however, this reaction becomes important in the stratosphere only when the total ClX exceeds 10 ppbv.

Upper limits for the reactions $HOCl + NO \rightarrow$ Products and $HOCl + O_3 \rightarrow$ Products at 300 K were established to be 1×10^{-17} and 4×10^{-16} $cm^3 molec^{-1} s^{-1}$, respectively.

A new method for determining activation energies over temperature intervals as small as 10 K has been developed and applied to the reaction $NO + O_3 \rightarrow NO_2 + O_2$. The activation energy for this reaction was found to vary by ∼650 calories between 200 and 350 K. The best expression for fitting both the rate constants and the activation energies was found to be $k = 9.43 \times 10^{-19} T^{2.19} \exp[-(764/T)]$ $cm^3 molec^{-1} s^{-1}$.

It has been found that singlet-oxygen, $O_2(^1\Delta_g, {}^1\Sigma_g)$ is produced in the reaction between Cl and O_3. Although probably not of significance in the stratosphere, this reaction is frequently used to generate ClO radicals for kinetic studies. In such studies, singlet oxygen can react with O_3 to produce O atoms. The singlet oxygen produced in the reaction between Cl and O_3 is a possible explanation for the O_2-quenching effect on the quantum yield for ozone destruction in the photolysis of $Cl_2/O_3/O_2$ mixtures, an effect first discovered in 1934 by Norrish and Neville.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

The kinetics of chemiluminescence associated with the reactions of chlorine atoms with Cl_2O, ClO_2, and O_3 have been investigated. In all three reactions the chemiluminescence could be attributed to the $B^3\pi(0_u^+) \rightarrow X^1\Sigma_g^+$ transition of Cl_2. For the $Cl + Cl_2O$ reaction the emission is totally attributed to the formation of excited state Cl_2 in the disproportionation reaction of ClO. The reactions of Cl with ClO_2 and O_3 are more complicated. The $Cl + ClO_2$ reaction may form excited state Cl_2 directly, or alternatively, ClO_2 may serve as a good chaperon in the recombination of Cl to form $Cl_2(B)$. The kinetic behavior of the $Cl + O_3$ reaction is best explained by a mechanism involving the chlorine peroxide dimer (ClOOCl) and $O_2(^1\ _g)$.

A new source for HOCl in which dilute chlorine gas in helium is bubbled through a suspension of $CaCO_3$ in water has been developed. The HOCl so produced, which has been found to be relatively free of Cl_2O impurity, has been used in the measurement of the rate constant for the reaction of OH with HOCl, the product distribution for the reaction of Cl with HOCl, and the UV absorption cross section of HOCl.

The reaction rate constant for OH + HOCl was measured to be $(1.8 \pm 1.3) \times 10^{-13}$ $cm^3molec^{-1}s^{-1}$ at 298 K, which indicates that this reaction does not contribute significantly to loss of stratospheric OH or HOCl. The primary products of Cl + NOCl were determined to be Cl_2 and OH (91 ± 6%) at 298 K. Although the measured HOCl cross sections are considerably different from previously recommended values, cancelling effects cause the calculated stratospheric photolysis rates for HOCl below 35 km to be only slightly different from those currently used in models.

The rate constant for the reaction $O + NO_2 \rightarrow O_2 + NO$ has been measured by the discharge flow technique with chemiluminescence detection of the loss of O atoms. At 298 K the rate constant is 1.0×10^{-11} $cm^3molec^{-1}s^{-1}$, in good agreement with the previous results. In the same experiments the rate constant for the reaction $O + ClO \rightarrow Cl + O_2$ has also been measured. The rate constant for this reaction was measured to be $(3.5 \pm 0.16) \times 10^{-11}$ $cm^3molec^{-1}s^1$ at 298 K.

Drs. J. P. BURROWS and R. A. COX -- Atomic Energy Research Establishment, Harwell, England -- 80-334. 1R Laser Investigation of Halogen Species (completed).

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

In this investigation infrared diode laser spectroscopy was used to determine the products formed in the reaction of ClO with NO_2. Chlorine nitrate, $ClONO_2$, is the only stable end product of this reaction at room temperature. These measurements gave a value of $(1.8 \pm 0.4) \times 10^{-31}$ cm^6 $molec^{-2}s^{-1}$ for the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ at 295 K and an upper limit of 5 ms for the lifetime of any isomeric products at this temperature.

> Dr. R. A. COX -- Atomic Energy Research Establishment, Harwell, England -- 82-400. IR Diode Laser Study of the Chemistry of Halogen Species (completed).

This study confirmed the conclusion of the previous project 80-334 that, at laboratory temperatures and pressures, the chlorine nitrate molecule, $ClONO_2$, is the only stable product of the reaction $ClO + NO_2 + M$. The apparent rate of reaction decreases at high $OClO$ concentrations.

The photolysis products from $OClO$ were studied by UV absorption spectroscopy.

> Dr. R. A. COX -- Atomic Energy Research Establishment, Harwell, England -- 83-483. Halogen Species Chemistry by IR and UV Spectroscopy.

The kinetics of the reaction $Cl + HO_2$ has been studied over a range of pressures and temperatures. The major product channel gave $HCl + O_2$. The ultraviolet absorption cross section for chlorine nitrate has been measured in the range 200-400 nm, and some preliminary kinetic studies of reactions involving chlorine nitrate with HCl, HBr, and H_2 have been made.

> Drs. D. E. FREEMAN, K. YOSHINO, and W. H. PARKINSON -- Harvard University -- 82-412, 83-486. Photoabsorption Cross Section of O_2 in the 197-240 nm Region.

Measurements of the Herzberg continuum cross section of O_2 in the 193.5-204.0 nm region have been made. The measurements confirm values derived from recent data from balloon-borne instruments for the 193.5-204 nm region, and preliminary analysis of the laboratory data for the 204-240 nm region yields values consistent with the in situ data. These new values of the Herzberg continuum cross section are considerably smaller than previously measured values that had been accepted for use in photochemical models.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 76-100. Laser Magnetic Resonance Study of HO_2 Chemistry (completed).

HO_2 reactions of stratospheric importance were measured using a laser magnetic resonance technique. The rate constant for the reaction $HO_2 + NO_2 + M \rightarrow HOONO_2 + M$ is 1.5 to 2.0 x 10^{-31} $cm^6 molec^{-2} s^{-1}$. The major pathway is the production of peroxynitric acid, a species not previously considered in the models.

The rate constant for the reaction $HO_2 + NO \rightarrow NO_2 + OH$ is 8 ± 2 x 10^{-12} $cm^3 molec^{-1} s^{-1}$ at room temperature, a value about 30 times faster than the previously accepted value. The temperature dependence of this reaction has been measured.

The rate constant for the reaction between HO_2 and O_3 is 1.4 x 10^{-14} exp(-580/T) $cm^3 molec^{-1} s^{-1}$.

The reactions of HO and HO_2 with N_2O_5 appear to be very slow and consequently not important in the atmosphere.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 77-223. Study of ClO Chemistry by Laser Magnetic Resonance (completed).

The far-infrared Zeeman spectrum of ClO has been observed and analyzed. Five observed transitions of wavelengths between 444 and 713 μm have been compared with values predicted with spectroscopic constants from the literature. These measurements provide the basis for Laser Magnetic Resonance detection of ClO radicals.

The rate constant for the reaction HO_2 + ClO was measured over the temperature range 235-393 K. The result does not fit a normal Arrhenius expression, $k = 3.3 \times 10^{-11} \exp[-850/T] + 4.5 \times 10^{-12} (T/300)^{-3.7}$ $cm^3 molec^{-1} s^{-1}$. At temperatures below room temperature the reaction has a negative temperature dependence.

The temperature dependence of the reaction of ClO with NO has been investigated. The results are k = (7.1 ± 1.4) x

10^{-12} exp[(270 ± 50)/T] $cm^3molec^{-1}s^{-1}$ for the range 202 to 393 K. These data are in good agreement with other direct studies.

The ClO + NO_2 + M recombination reaction has been studied as a function of temperature and in three different gases, He, O_2, and N_2. The results are k(M = He, T = 250-387 K) = (2.8 ± 0.6) x 10^{-33} exp[(1090 ± 80)/T], k(M = O_2, T = 250-416 K) = (3.5 ± 0.6) x 10^{-33} exp[(1180 ± 80)/T], and k(M = N_2, T = 297 K) = (2.09 ± 0.3) x 10^{-31} cm^6molec^{-2} s^{-1}. This was the first measurement of this reaction in oxygen. The other results agree with previous studies.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 79-289, 82-424. Kinetic Studies of Stratospheric Chlorine Chemistry.

A trace gas detection system using a tunable infrared diode laser and a multipass absorption cell has been assembled. This system was used to measure the concentration of N_2O in air, 0.298 ± 0.005 ppmv. This result indicates that there is an error in the calibration standards used by some measurement groups.

The heat of formation of HO_2 radicals was determined by measuring the rate constants in the forward and reverse directions for the equilibrium reactions: HO_2 + NO = OH + NO_2. The value, $\Delta H_{f_{298}}$ = 2.5 ± 0.6 kcal mol^{-1}, significantly revises the previous recommendation, 0.5 kcal mol^{-1}.

The rate constants and branching ratio for the reaction of HO_2 and Cl radicals have been measured as a function of temperature. A new product path OH + ClO (b) is observed in addition to the previously accepted path HCl + O_2 (a). k_a = (1.8 ± 0.5) x 10^{-11} exp[(170 ± 80)/T] $cm^3molec^{-1}s^{-1}$ and k_b = (4.1 ± 0.8) x 10^{-11} exp[-(450 ± 60)/T] cm^3molec^{-1} s^{-1}. The total rate constant k = (4.2 ± 0.7) x 10^{-11} is independent of temperature for T = 250-420 K. This value is in reasonable agreement with the average of all previous measurements, which were all made at room temperature and cover a range of about a factor of four.

The temperature dependence of the rate constant for the reaction OH + HNO_3 has been measured in a discharge flow system. The results indicated that the reaction has a

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

strong negative temperature dependence below room temperature, k = (2.0 ± 0.4) x 10^{-14} exp[(430 ± 60)/T] cm^3molec^{-1} s^{-1}. Between room temperature and 400 K the rate constant changes only slightly, with measured values falling between 7 and 9 times 10^{-14}. Although these results are similar to some other studies, they do not agree well with them. No satisfactory explanation for the differences has been found. A study of the products of the OH + HNO_3 reaction indicated NO_3 and H_2O are dominant.

The rate constant for the $HO_2 + HO_2$ reaction is 2.0 ± 0.6 x 10^{-13} exp[(595 ± 120)/T] $cm^3molec^{-1}s^{-1}$ between 253 and 390 K, and that for the reaction OH + ClO is 8.0 ± 1.4 x 10^{-12} exp[(235 ± 46)/T] $cm^3molec^{-1}s^{-1}$ between 219 and 373 K. The branching ratio $k_a/(k_a + k_b)$ for the products (a) HO_2 + Cl and (b) HCl + O_2 is 0.86 ± 0.14 for the reaction of OH with ClO.

The rate constant for the NO_3 + NO reaction is (1.55 ± 0.3) x 10^{-11} exp [(195 ± 50/)T] $cm^3molec^{-1}s^{-1}$ for temperatures lower than 300 K. For temperatures above 300 K the value is 2.9 x 10^{-11} $cm^3molec^{-1}s^{-1}$ and shows very little change with temperature.

Dr. M. J. KURYLO -- National Bureau of Standards -- 78-233. Rates of Reaction of Cl Atoms with the Primary Products of Alkane Photooxidation (completed).

Flash photolysis resonance fluorescence (FPRF) has been used to establish a limiting rate constant for the reaction of Cl with OCS (k ≦ 1 x 10^{-13} $cm^3molec^{-1}s^{-1}$; 220-323 K). Similarly the rate constant for the reaction Cl + H_2CO has been measured as (1.09 ± 0.40) x 10^{-10} exp[-131 ± 98)/T] cm^3 $molec^{-1}s^{-1}$ over the temperature range 223 to 323 K. In other FPRF experiments the rate constant for OH + CH_3CCl_3 was found to be (5.41 ± 1.8) x 10^{-12} exp[-(1810 ± 100)/T] $cm^3molec^{-1}s^{-1}$ (253-363 K). This markedly lower value leads to revised model calculations of CH_3CCl_3 tropospheric lifetimes and then to the prediction of higher tropospheric OH concentrations. An upper limit to the rate constant for the reaction $CH_3 + O_2 \quad OH + H_2CO$ has been set at 3 x 10^{-16} $cm^3molec^{-1}s^{-1}$ at 368 K based on the sensitivity of monitoring the OH product by resonance fluorescence. The temperature dependence of the rate constant for the ozone formation reaction O + O_2 + M (M = N_2, O_2, Ar), which has been measured by FPRF, provides the first detailed analysis for M = N_2

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

and O_2 and indicates a weaker temperature dependence than previously assumed for M = O_2. The recommended value for ozone formation in air [$(6.3 \pm 0.9) \times 10^{-34}\ (T/300)^{-(1.9 \pm 0.5)}$ $cm^6 molec^{-2} s^{-1}$] is in good agreement with current NASA recommendations. Studies of the atmospheric quenching of $O_2(^1\Delta, v > 0)$ indicate that vibrational deactivation dominates over reaction with O_3. Other experiments indicated an upper limit of 15% on the production of $O_2(^1\Sigma)$ by the reaction of $O(^1D)$ with O_3.

Dr. M. J. KURYLO -- National Bureau of Standards -- 80-307. Reactions within the HO_x Cycle (completed).

A steady-state photolysis experiment utilizing mass spectrometric detection was used to investigate the reaction $H^{18}O + HO_2$. The results do not support the existence of a linear adduct reaction intermediate as suggested by the proposed pressure dependence of the reaction. Modeling analysis of the experiments best duplicates the product observations for rate constant values ($OH + HO_2$) in the range $1\text{-}2 \times 10^{-10}$ $cm^3 molec^{-1} s^{-1}$ at atmospheric pressure. The temperature dependence of the $OH + H_2O_2$ reaction was determined by FPRF over the temperature range 250-370 K, resulting in a recommended value of $(2.91 \pm 0.30) \times 10^{-12}$ $\exp[-(161 \pm 32)/T]$ $cm^3 molec^{-1} s^{-1}$. Computer simulations of this and other investigations indicate significant problems in the pre-1980 studies of the $OH + H_2O_2$ reaction. Experimental modifications to an existing kinetic spectroscopy apparatus are being made to permit measurement of the HO_2 self reaction. This work is being continued under project 82-402.

Drs. M. J. KURYLO and A. H. LAUFER -- National Bureau of Standards -- 82-402. Reactions within the HO_x, NO_x, ClO_x, and SO_x Cycles.

Rate constants for the reaction between Cl atoms and $HONO_2$ were measured by FPRF between 243 and 298 K. The data can be fit to the Arrhenius expression $5.1 \times 10^{-12} \exp(-1700/T)$ $cm^3 molec^{-1} s^{-1}$, indicating the lack of any importance of the reaction in stratospheric Cl removal. A reinvestigation of the Cl atom reaction with chlorine nitrate by FPRF over the temperature range 220-296 K yielded the rate constant expression $7.3 \times 10^{-12} \exp(165/T)$ $cm^3 molec^{-1}$ s^{-1}. These results supersede earlier measurements from this laboratory, which are thought to have been complicated by O atom interference. The rate constants for the reactions of Cl and OH with CH_3CN have been measured by FPRF. At room temperature an upper limit for the rate constant of the reaction between Cl and CH_3CN is 2×10^{-15} $cm^3 molec^{-1} s^{-1}$. The temperature dependence between 250 and 363 K for the rate constant of the OH + CH_3CN reaction is $6.28 \times 10^{-13}(-1030/T) cm^3 molec^{-1} s^{-1}$.

The rate constants for the $HO_2 + HO_2 + M$ and $HO_2 + NO_2 + M$ reactions have been determined by flash photolysis kinetic absorption spectroscopy. In the presence of N_2 and O_2 as third bodies the rate constants for the $HO_2 + HO_2 + M$ reactions are, respectively, 5.95×10^{-32} $cm^6 molec^{-2} s^{-1}$ and 4.53×10^{-32} $cm^6 molec^{-2} s^{-1}$. Likewise for the $HO_2 + NO_2 + M$ reaction, the values using N_2 and O_2 as third bodies are, respectively, 1.5×10^{-31} $cm^6 molec^{-2} s^{-1}$ and 1.3×10^{-31} $cm^6 molec^{-2} s^{-1}$.

Dr. G. LE BRAS -- Centre de Recherches sur la Chimie de la Combustion et des Hautes Temperatures, CNRS, Orleans, France -- 83-488. Study of OH + ClO.

Kinetics parameters, rate constant, and branching ratio of the reaction

$$\begin{aligned} OH + ClO &\longrightarrow HO_2 + Cl \quad (1a) \\ &\longrightarrow HCl + O_2 \quad (1b) \end{aligned}$$

have been studied in a discharge flow reactor at 298 K and 1 torr. The final data are $k_1 = 1.94 \pm 0.18 \times 10^{-11}$ $cm^3 molec^{-1} s^{-1}$ and $k_{1a}/k_1 = 0.98 \pm 0.07$.

Dr. G. LE BRAS -- Centre de Recherches sur la Chimie de la Combustion et des Hautes Temperatures, CNRS, Orleans, France -- 85-545. Kinetic Study of the Reactions of N_2O_5 with ClO, OH, and HO_2,

This study is just getting started.

Dr. Y. P. LEE -- Tsing-Hua Universty, Taiwan -- 83-480. Product Determination of Atmospheric Reactions.

The matrix isolation technique is being combined with a discharge-flow system to determine the products of some important stratospheric reactions. The matrix-isolated products will be analyzed by infrared absorption spectroscopy

The technique will be applied to the reactions OH + NO_2 + M, OH + ClO, and HO_2 + ClO.

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 74-2. Atmospheric Reactions of Fluorocarbons (completed).

Reaction rate constants have been measured for the reactions of $O(^1D)$ with CFCs 11, 12, 22, 113, and 114 and of OH with CFCs 11, 12, and 22. The results indicate that in the stratosphere the reaction of $O(^1D)$ atoms with CFCs 11 and 12 is secondary to photolysis, whereas the reaction of OH with CFC 22 is much more important than photolysis. The photooxidation products of 11, 12, and 22 at 184.9 nm, i.e., COFCl and COF_2 as appropriate, are also observed to be the products for reaction with $O(^1D)$.

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 77-190. Atmospheric Chemistry of Peroxynitric Acid (completed).

The HO_2NO_2 cross sections vary smoothly from 1.6 x 10^{-17} cm^2 $molec^{-1}$ at 190 nm to ∿ 2 x 10^{-20} cm^2molec^{-1} at 330 nm. The infrared cross sections for the 802.7 and 1303.9 cm^{-1} Q branches of HO_2NO_2 at 0.06 cm^{-1} resolution are 2.1 x 10^{-19} and 1.8 x 10^{-18} cm^2molec^{-1}, respectively.

Dr. A. R. RAVISHANKARA -- Georgia Institute of Technology -- 80-295. A Study of the Reaction of OH with ClO (completed).

The overall rate of the reaction OH + ClO has been measured in a discharge flow system by resonance fluorescence detection of OH: $k = (1.17 \pm 0.33) \times 10^{-11}$ $cm^3molec^{-1}s^{-1}$ nearly independent of temperature for $248 < T < 335$ K. This result includes a correction for the reaction of product HO_2 with Cl, which produces OH and is responsible for an earlier underestimation of the rate constant. Attempts to develop a microwave interferometry system to measure the yield of HCl in this reaction proved unsuccessful because of difficulty in generating an adequate 625 GHz signal.

Dr. A. R. RAVISHANKARA -- Georgia Institute of Technology -- 81-368, 83-449; Drs. A. R. RAVISHANKARA and P. H. WINE -- Georgia Institute of Technology -- 84-499. Laboratory Studies of Stratospheric Reactions.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

Several reactions important in stratospheric modeling calculations were investigated. The rate constants for the reactions $NO_3 + NO \rightarrow 2NO_2$, $NO_3 + NO_2 \rightarrow N_2O_5$, $ClO + O(^3P) \rightarrow Cl + O_2$, and $Cl_2 + O(^3p)$ products were determined. The results indicate that some of the prevously accepted kinetic parameters for these reactions may need to be revised. Significant new kinetic data have been obtained for the reactions of chlorine species with $O(^1D)$. Aspects of the photochemistry of N_2O_5 have been investigated, and new absorption cross sections of NO_3 have been determined.

Drs. J. A. SILVER, M. S. ZAHNISER, and C. E. KOLB -- Aerodyne Research, Inc. -- 82-401, 84-494. A Study of the Gas Phase Reaction of Sodium Hydroxide with Hydrochloric Acid.

This project explores the potential role of meteoritic sodium in stratospheric chemistry by examining a reaction that could couple sodium chemistry with chlorine chemistry. The rate constant for the gas-phase reaction of NaOH with HCl is $2.8 \pm 0.9 \times 10^{-10}$ $cm^3 molec^{-1} s^{-1}$. Work is in progress toward measuring the rate constant for the reaction betwen NaO_2 and HCl and the photodissociation cross sections of NaCl.

Dr. T. C. STEIMLE -- University of Oregon -- 82-418. Identification of Photodissociation Products by Resonance-Enhanced Multiphoton Ionization (completed).

In a first effort to identify the products of the photodissociation of peroxynitric acid, HO_2NO_2, the compound was photolyzed in a flow system with UV at 193, 248, and 308 nm. The principal nitrogen-containing product, detected by laser-induced fluorescence approximately 1 s after photolysis, was NO_2. Its high quantum yield suggested that as yet unidentified secondary reactions contributed to its formation.

Dr. T. C. STEIMLE -- University of Oregon -- 84-509. Absorption Cross Section of HO_2NO_2.

Pernitric acid is believed to play an important role in stratospheric chemistry, and more precise measurements of its UV cross sections are needed. In this study, laser techniques will be employed for generation of incident UV over the 260-310 nm range as well as for monitoring HO_2NO_2 in the infrared.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

Dr. F. STUHL -- University of Bochum -- 77-170. Determination of the Photodissociation Process and Absorption Cross Section of FC-11 and 12 in the Near UV (completed).

The absorption spectra of some chlorine-containing methanes (CCl_4, $CHCl_3$, CH_2Cl_2, CFC 13, and CFC 31) and ethanes (CFC 113, CFC 114, CFC 115, CFC 133a, and CFC 142b) and also of N_2O were determined at wavelengths around 220 nm. Some of these spectra were obtained at both 298 and 208 K. A chemical method was used to determine the absorption cross section of CFC 11 at 253.7 nm and the absorption properties at wavelengths greater than 280 nm. It is concluded from these experiments that the tropospheric decay rate of CFC 11 is smaller than 10^{-10} s^{-1} for homogeneous gas phase photolysis.

Dr. G. A. TAKACS -- Rochester Institute of Technology -- 77-196. Photoabsorption Cross Sections for Compounds of Atmospheric Interest (completed).

Ultraviolet-visible absorption spectra have been measured and solar photodissociation rates have been calculated for SO_2Cl_2, CCl_3NO_2, CF_3NOCl, $SOCl_2$, SO_2F_2, SO_2ClF, CH_3SO_2Cl, and CCl_3SCl. A maximum photoabsorption cross section, which indicates a long stratospheric lifetime, has been established for $HClO_4$. Attempts to measure photoabsorption spectra for gaseous $ONO(SO_2)OH$ and $ONO(SO_2)Cl$ were unsuccessful. Photolysis of CFC 11 and CCl_4 in the presence of solid NaCl with wavelengths longer than 300 nm results in maximums of 2.3×10^{-4} and 2.4×10^{-4} molec, respectively, photodissociating per incident photon on the NaCl.

Dr. B. A. THRUSH -- University of Cambridge -- 75-58, 75-58-II. Reactions of the HO_2 Radical Studied by Laser Magnetic Resonance (completed).

The rate coefficient of the reaction O + HO_2 was measured for the first time. The value found, $3.5 \pm 1.0 \times 10^{-11}$ cm^3 $molec^{-1}s^{-1}$ at 293 K, improves the fit of the calculated OH profile with Anderson's recent measurements. The rate coefficient of the reaction OH + HO_2 was measured based on direct measurement of HO_2 and found to be $5.1 \pm 1.6 \times 10^{-11}$ $cm^3molec^{-1}s^{-1}$ at 293 K.

Dr. B. A. THRUSH -- University of Cambridge -- 81-378. Reactions of HO_2 Radicals Studied by Mid Infrared Laser Magnetic Resonance Spectroscopy (completed).

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

Laser magnetic resonance in the mid infrared was used to detect HO_2 in a flow system. Preliminary measurements of the rate coefficient of the reaction $HO_2 + NO \rightarrow HO + NO_2$ gave a value of 7×10^{-12} $cm^3 molec^{-1} s^{-1}$ at 10 torr total pressure.

Dr. J. WIESENFELD -- Cornell University -- 76-128, 77-220. Photochemistry of Small Chlorinated Molecules (completed).

The photochemistry of chlorine nitrate was studied by determining the yields of Cl and ClO from the flash photolysis of $ClONO_2$. The rate of reaction between O and $ClONO_2$ has been measured and is in good agreement with the literature value.

Dr. R. ZELLNER -- University of Goettingen, F.R.G. -- 77-195. Experimental Investigation of the Branching Ratio in the $O(^1D) + H_2O$ Reaction (completed).

The branching ratio in the reaction $O(^1D) + H_2O \rightarrow 2$ HO (1) and $\rightarrow H_2 + O_2$ (1') has been determined at 298 K from direct measurements of HO and H_2 to be 0.01 (k_1'/k_1) (+0.005, -0.01). The main conclusions to be drawn from this result are:

1. Reaction 1' is not an important source of H_2 in the upper stratosphere and mesosphere.

2. The reduction of mesospheric HO_x through the occurrence of reaction 1' is not large enough to account for discrepancies in calculated and measured O_3 concentrations.

DR. R. ZELLNER -- University of Goettingen, F.R.G. -- 80-331. Kinetic Investigations of the Reaction ClO + $O_2(^1\Delta) \rightarrow$ Products and the Equilibrium Constant for the Possible Complex Formation $ClO + O_2 \rightarrow OClO_2$ (completed).

The reaction between ClO and $O_2(^1\Delta)$, possibly forming ClO_3, is too slow to be a significant scavenging process for ClO. The reaction between ClO and $O^2(^3\Sigma)$ is also found to be slow, $(k \sim 1 \times 10^{-17}$ $cm^3 s^{-1})$. Its equilibrium constant however is $\leq 5 \times 10^{-20}$ $cm^3 molec^{-1}$ at 298 K, indicating possible importance at stratospheric temperatures.

DR. R. ZELLNER -- University of Goettingen, F.R.G. -- 83-478. Laboratory Studies of Atmospheric Radical-Radical and Photochemical Reactions Using Laser Photolysis/Laser Line Spectrometry.

Table 3 (continued)

Investigation of Reaction Rates, Products, and Mechanisms

The reaction of ClO with O is being reinvestigated with emphasis on the possible effect of O_2 on the rate constant. This involves a refined determination of the equilibrium constant of $ClO + O_2 \rightarrow ClO \cdot O_2$ over a wider temperature range. Preliminary results do not support a strong O_2 effect on any ClO rate constant.

In another experiment the reaction $ClONO_2 + HCl$ is being studied under wall-free conditions. The $ClONO_2$ is produced in situ by photolysis of ClO_2 in the presence of NO_2 and defined concentrations of HCl. UV absorption spectroscopy is used to monitor the buildup and consumption of $ClONO_2$.

B. Source and Sink Studies

Dr. P. AUSLOOS -- National Bureau of Standards -- 77-186, 78-254. Follow up for Photodecomposition of Chloromethanes Absorbed on Silica Surfaces (completed).

The decomposition of CF_2Cl_2, $CFCl_3$, CH_3Cl, CCl_4, CH_3CCl_3, and CH_2CCl_2 on Tunisian sand at dilute concentrations (100 ppb - 100 ppm) has been investigated in both the presence and the absence of light and/or moisture. Experiments with $^{13}CCl_4$, $^{13}CFCl_3$, and $^{13}CF_2Cl_2$ in the presence of oxygen show that one molecule of $^{13}CO_2$ is produced per halomethane molecule destroyed on the surface. For CH_3CCl_3, surface destruction leads to CH_2CCl_2 rather than CO_2.

Under all conditions relative stabilities were as follows $CF_2Cl_2 > CFCl_3 > CCl_4 > CH_3CCl_3$. Both with and without light the rate of surface-induced destruction decreases rapidly with increasing moisture content. When the chlorofluoromethanes were exposed to sand with a moisture content in equilibrium with laboratory air (35% humidity at 20°C), no decomposition was observed. However, a sudden reduction in moisture content by 40% or more leads to a measurable destruction rate for CCl_4 and CH_3CCl_3.

Dr. J. W. BIRKS -- University of Illinois -- 76-117B. Studies of Heterogeneous Reactions (completed).

See Table 3, Section A.

Table 3 (continued)

Source and Sink Studies

Dr. F. BRUNER -- Urbino University, Italy -- 80-330. Atmospheric Monitoring of F-21 (completed).

The occurrence of CFC 21 suggests the existence of a CFC 11 sink by desert destruction. Two intercalibrated measurement stations capable of detecting the absolute difference in mean daily CFC 11 concentration and the possible simultaneous occurrence of CFC 21 were arranged in a desert region about 500 km apart and oriented along the direction of the prevailing winds -- the upwind station located along the edge of the desert, the downwind station situated in the desert. A sampling campaign at the two stations was carried out during two weeks of favorable winds during May, 1982. The samples collected were analyzed for CFC 11 and 21 by a GCMS procedure. The results show a negligible amount of CFC 21 at both stations but a constant, higher concentration of CFC 11 at the up-wind station. The data were submitted to a statistical procedure to evaluate a possible desert destruction effect for CFC 11 and found to be insufficient to assess the effect.

Dr. M. J. CAMPBELL -- Washington State University -- 75-53. Chlorofluoromethane Destruction by Natural Ionization (completed).

Laboratory measurements at high irradiation levels show large rate constants for removal of CCl4 and CFC 11. The rate constant for CFC 12 is much smaller. The significance of these results with respect to atmosphere sinks for the CFCs is questionable.

Drs. D. M. CUNNOLD, F. N. ALYEA, and R. G. PRINN -- CAP Incorporated -- 77-213, 78-251, 79-281, 80-323, 81-361, 82-422, 83-476. Coordination and Analysis of Data for the Atmospheric Lifetime Experiment (ALE).

CAP is continuing its work on the processing of the raw atmospheric and calibration tank chromatographic analyses received in digital form from ERT. This process includes computation of calibrated atmospheric concentration from the raw data, statistical analyses of the raw and calibrated data, determination of trends in the observed species, and reporting of the calibrated data in graphical and tabular forms.

Table 3 (continued)

Source and Sink Studies

CAP is also using its optimal estimation technique to compute atmospheric lifetimes of CFC 11, CFC 12, methyl chloroform, and carbon tetrachloride from the observed trends in the species.

The three year data set suggests that if any tropospheric sink for CFCs exists it must be very small. If it is assumed to be negligible and the photochemical lifetimes are taken for the species, it is possible to "run ALE in reverse" and hence calculate the trend in release rates for the various species. For CFC 12 the derived releases are significantly higher than the current FPP estimates.

See Lovelock and Simmonds, 77-193, et al., Rasmussen, 77-201, et al., and Rosen, 81-377.

> Dr. R. J. DONOVAN -- University of Edinburgh, Scotland -- 79-286. Reaction of ClO with OH: A Potential Sink for ClO_x (completed).

The reaction between OH and ClO was studied at room temperature using flash photolysis. At a total pressure of 12 torr the rate coefficient is $(3.3 \pm 0.7) \times 10^{-12}$ $cm^3 molec^{-1} s^{-1}$ and the reaction rate increases with pressure.

> Dr. P. J. B. FRASER -- Commonwealth Scientific and Industrial Research Organization (CSIRO), Aspendale, Australia -- 82-415. Atmospheric Lifetime Experiment Participant (completed).

The contract enabled Dr. Fraser to attend ALE data analysis meetings in the USA and UK during the period November, 1982, to April, 1984. It also assisted the continuing collaboration of the Australian Baseline Station in the global CFC monitoring network.

> Dr. P. J. B. FRASER -- Commonwealth Scientific and Industrial Research Organization (CSIRO), Aspendale, Australia -- 85-540. Global Atmospheric Gases Experiment (GAGE).

The contract provides supplemental travel funds to enable the investigator to participate in the 1985 GAGE meetings.

Table 3 (continued)

Source and Sink Studies

Dr. M. KAUFMAN -- Emory University -- 76-126, 77-197. Studies of Compounds of Sulfur, Oxygen, and Chlorine (completed).

The three body recombination rate constant for Cl and SO_2 at 295 K has been found to be 1.3 x 10^{-33} $cm^6 molec^{-2} s^{-1}$ with Ar, 2.3 x 10^{-33} $cm^6 molec^{-2} s^{-1}$ with N_2, and 19 x 10^{-33} $cm^6 molec^{-2} s^{-1}$ with SO_2. At 281 K the first and third values become 2.9 x 10^{-33} and 20 x 10^{-33}, respectively. Ultraviolet cross sections of SO_2Cl_2 and $HOSO_2Cl$ have been determined, and the incorporation of ^{36}Cl into sulfate-type aerosol particles has been studied. Surface effects appear to have dominated the latter experiment.

When OCS is added to a $Cl/Cl_2/Ar$ mixture at room temperature, SCl^+ and SCl_2^+ ions are detected mass spectrometrically. The rate constant for the reaction Cl + OCS   SCl + CO is less than 10^{-16} $cm^3 molec^{-1} s^{-1}$ at 296 K.

Dr. F. KORTE -- Technical University of Munich, F.R.G. -- 77-194. Photodegradation of Chlorofluoromethanes in the Troposphere (completed).

The photodegradataion of CFC 11 and CFC 12 on silica gel and on Mecca sand was studied with the aid of ^{14}C-labelled compounds. Whereas in the dark no change was determined with silica gel, there was significant decomposition on the sand with formation of $^{14}CO_2$ (up to 50%). Irradiation with UV (>290 nm) led to 1-5% decomposition of the CFCs on silica gel also with formation of $^{14}CO_2$. Irradiation with UV was not observed to increase the decomposition rate on sand. The results suggest that decomposition takes place at active sites on the surface.

Dr. M. J. KURYLO -- National Bureau of Standards -- 78-233. Rates of Reaction of Cl Atoms with the Primary Products of Alkane Photooxidation (completed).

See Table 3, Section A.

Dr. J. E. LOVELOCK -- University of Reading -- 75-67, 77-144. Unidentified Factors in the Fluorocarbon-Ozone Problem (completed).

Coarse Saharan surface dust showed an unusual degree of retention for CFC 11 and CCl_4. Investigations were made on the

Table 3 (continued)

Source and Sink Studies

relationship between photochemically produced atmospheric peroxy compounds (e.g., peroxyacetyl nitrate) and the incidence of skin carcinoma.

Observations on dissolved gases in the ocean were made during the April 1977 voyage of RRS Challenger. Concentrations of N_2O in ocean and atmosphere confirmed earlier estimates of N_2O flux from the ocean.

> Drs. J. E. LOVELOCK and P. G. SIMMONDS -- Private -- 77-193, 78-243, 79-280, 80-324, 81-370, 82-421. Operation of Stations in Adrigole and Barbados for the Atmospheric Lifetime Experiment (completed).

Automated long-term ground measurement stations have been operated in Adrigole (continuing the data base already collected there) and in Barbados. Hewlett-Packard electron-capture gas chromatographs were used to collect data for CFCs 11, 12, and 113, CH_3CCl_3, CCl_4, and N_2O, which were processed, tabulated, and forwarded to CAP Associates for analysis.

Both stations operated well with data being processed from March 3, 1978, (Adrigole) and July 12, 1978, (Barbados) up to December 31, 1983. The Adrigole station has been shut down, but the Barbados station continues as part of the GAGE network (see also Simmonds, 84-515).

> Dr. L. R. MARTIN -- Aerospace Corp. -- 75-81, 75-81-II. Laboratory Investigation of the Heterogeneous Interaction of Cl and ClO with H_2SO_4 (completed).

A flowing afterglow apparatus was used to measure the rate of the heterogeneous reactions of Cl and ClO with sulfuric acid, simulating the stratospheric aerosol. The reaction rate of Cl is too slow for its reaction to constitute a significant sink, although rates were markedly increased by the presence of certain metal salts in the sulfuric acid. Even at stratospheric temperatures the HCl formed goes into the vapor phase. The for ClO on H_2SO_4/H_2O substrates is 1×10^{-3} at room temperature. These, the first examples of heterogeneous reactions with stratospheric aerosol, are not in any models.

> Dr. V. A. MOHNEN -- State University of New York, Albany -- 75-64. Ion Molecule Reactions Involving Fluorocarbons (completed).

Table 3 (continued)

Source and Sink Studies

Ion molecule reactions between the equilibrium ion distribution formed in pure air-like gas mixtures and CFC 12 were studied. From these investigations it was concluded that: (1) stable CFC 12 attachments to ions ("cluster formation") of the form $H^{+} \cdot (H_2O)_n$, $O_2^{-} \cdot (H_2O)_n$, $CO_3^{-} \cdot (H_2O)_n$, and $CO_4^{-} \cdot (H_2O)_n$ do not occur; (2) dissociative charge transfer reactions between $H^{+} \cdot (H_2O)_n$ and CFC 12 are not observed for all $n > 2$; (3) approximate rate constants for dissociative charge transfer reactions between CFC 12 and $O_2^{-} \cdot H_2O$ and CFC 12 and CO_3^{-} are 3×10^{-12} cm^3s^{-1} and $<2 \times 10^{-13}$ cm^3s^{-1}, respectively; (4) knowledge of time integrated rate constants for atmospheric negative ions is necessary before the importance of ion reactions with CFCs can be estimated, but the likelihood of substantial importance is small.

Dr. L. F. PHILLIPS -- University of Canterbury, N.Z. -- 78-241. Determination of Atomic Oxygen Yields in the Photolysis of HOCl and ClOO (completed).

The photolysis was studied by looking for prompt O atoms by observation of resonance fluorescence on a nanosecond time scale. Detection limits for ground-state oxygen atoms produced by photolysis of NO_2 were established.

Gaseous mixtures containing HOCl were photolyzed with UV radiation at 337 nm from a nitrogen laser to determine whether the HOCl → HCl + O reaction path occurred. Because the signal to noise ratio was too low, attempts to measure oxygen atoms by resonance fluorescence gave inconclusive results. Recommendations were made for improving the sensitivity of the detection method in future studies.

Dr. L. F. PHILLIPS -- University of Canterbury, N.Z. -- 81-342. Yield of Atomic Oxygen from HOCl Photolysis at 308 nm (completed).

Although the major products from the ultraviolet photolysis of HOCl were known to be Cl and OH, uncertainty remained about the extent of a second product channel yielding HCl and O. Equilibrium mixtures containing HOCl, Cl_2O, and H_2O were therefore photolyzed with a XeCl laser at 300 nm. No oxygen atoms were detected by resonance fluorescence, indicating that the quantum yield for this secondary channel was below 1% and thus not significant.

Table 3 (continued)

Source and Sink Studies

Dr. J. N. PITTS, JR. -- University of California at Riverside -- 75-12. Monitoring and Atmospheric Reactions of Fluorocarbons (completed).

CFCs 11 and 12 are photochemically stable in simulated sunlight, even when irradiated for several weeks. Plant tissues did not absorb measurable quantities of CFCs 11, 12, or 22, and no adverse effects could be measured. CFCs penetrate into the soil atmosphere, and concentrations change in direct relationship with changes in concentration in the atmosphere above ground.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-71. Measurement of Fluorocarbon Content of "Antique" Air Samples (completed).

A sensitive method for the determination of low parts per trillion analysis of CFCs 11 and 12 in small-volume air samples in containers was developed and applied to a wide variety of vessels believed to contain antique air. All samples analyzed showed varying levels of CFCs. Contamination during handling is not a problem, so that either CFCs were present in nature prior to 1930 or the samples were contaminated by leakage during storage.

Dr. R. A. RASMUSSEN -- Rasmussen Associates -- 75-84. Collection and Analysis of Antarctic Ice Cores (completed).

The concentration of halocarbons in air obtained from Antarctic snow shows no enrichment in samples obtained from the Ross ice shelf (mainly -30 F), whereas there is enrichment in samples obtained from the South Pole (-50 to -60 F).

Dr. R. A. RASMUSSEN -- Private -- 76-140. Lower Stratospheric Measurement of Non-methane Hydrocarbons (completed).

Ethane, ethylene, and acetylene are found in the upper troposphere and lower stratosphere at concentrations of 40-820 ppt. Total concentrations of the three species range from 1085 ppt (NH troposphere) to 323 ppt (SH stratosphere).

Table 3 (continued)

Source and Sink Studies

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 77-201, 78-248, 78-263, 79-279, 80-325, 81-376. Operation of Stations in American Samoa, Cape Meares, Oregon, and Tasmania for the Atmospheric Lifetime Experiment (completed).

Automated long-term ground measurement stations were operated in American Samoa and Tasmania as detailed in 77-193, et al. (Lovelock and Simmonds). Data have been processed from May, 1978, (Tasmania) and June, 1978, (American Samoa) up to June, 1982.

The fifth ALE station at Cape Meares, Oregon, became operational early in 1980 and contributed measurement data routinely to the ALE network.

Propagation of the standards for the networks and their referencing back to OGC were part of the program.

The Tasmanian instrument has been moved into the Australian baseline station, and data have continued to be available to the ALE Team. The ALE 5840 and the Australian 5880 instruments were intercompared to make the data consistent.

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 77-215. Kilauea Volcanic Emissions -- Halocarbon Measurements (completed).

Electron capture gas chromatograph analyses were made on fumerolic emissions from two vents on Kilauea at the site of the September, 1977, lava flow. Some 20 halocarbons were observed and compared with local control samples. CFCs 11 and 12, CCl_4, and CH_3CCl_3 were not significantly different from controls. Peaks tentatively identified as N_2O and methyl halides showed elevated concentrations versus controls. The presence of N_2O was confirmed by GCMS.

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 82-416. CFC 11 Release Rate from Rigid Polyurethane Foams.

The rate of release of CFC 11 from rigid polyurethane foams by monitoring the fluorocarbon level in the purge gases from environmental chambers containing samples of PUR boardstock has been determined. The results indicate that the half-life of chorofluorocarbon in undisturbed closed-cell foams can exceed 100 years. Actual residence times will be determined by the service life of the freezer, vehicle, building, or other structure insulated with such foams and will thus be limited to a few decades.

Dr. R. D. ROSEN -- ERT, Inc. -- 81-377. Data Processing for the Atmospheric Lifetime Experiment (ALE) (completed).

The data from the five automated long term ground measurement stations [cf. 77-193, et al. (Lovelock and Simmonds), and 81-376 (Rasmussen)] are received, archived, verified, and converted onto disc storage for transmission to CAP Inc. This contract terminated on March 14, 1982, when Rosen left ERT and joined Atmospheric and Environmental Research, Inc. (AER). The work continued under a NASA contract as part of the NASA-CMA FPP cofunded Atmospheric Lifetime Experiment. See Simmonds, 84-515.

Dr. C. SANDORFY -- University of Montreal -- 73-2. Spectroscopy and Photochemical Changes of Fluorocarbons (completed).

The vacuum ultraviolet and photoelectron spectra of CFCs were measured. The photochemical vulnerability of these molecules was predicted from their spectra.

R. E. SHAMEL -- A. D. Little, Inc. -- 79-275. Analysis of Release of FC-11 from Rigid Plastic Foam Products in the U. S. (completed).

The lifetime for CFC 11 emissions from rigid foam is much longer than previously assumed and will not be a problem for the ALE lifetime calculations.

Dr. P. G. SIMMONDS -- Private -- 84-515. Global Atmospheric Gases Experiment (GAGE), Barbados Station.

The Barbados station, which with other former Atmospheric Lifetime Experiment (ALE) stations now forms part of the GAGE network, is being supported.

Drs. P. G. SIMMONDS and J. E. LOVELOCK -- Private -- 79-269. Determination of Tropospheric Halocarbons and Their Relative Importance (completed).

See Table 3, Section C.

Table 3 (continued)

C. Laboratory Studies Related to Potential Atmospheric Measurements

Dr. J. BALLARD -- Rutherford Appleton Laboratory, England -- 82-444. Laboratory Spectroscopic Studies of Stratospheric Gases (completed).

A very long path (1 km) coolable absorption cell (white cell) was built and linked to a high resolution interferometer. The system was used to investigate the spectrum (0.004 cm^{-1}) of CO_2. Shorter cells were used to investigate the spectrum of NO_2, to measure the temperature dependence of the strength and pressure broadened widths of spectral lines for HCl (3.5), and to assess interferences from H_2O, CH_4, and N_2O in the stratospheric determination of HF.

Dr. J. W. BIRKS; Drs. C. J. HOWARD and F. C. FEHSENFELD -- University of Colorado; National Oceanic and Atmospheric Administration, Boulder -- 77-222. Development of a Technique for Measuring the Total Chlorine Content in Air (completed).

The goal of this project was to develop an analytical instrument for measuring the total chlorine content of air. The technique developed did not have adequate sensitivity to analyze stratospheric air samples for chlorine content.

Drs. A. BONETTI and B. CARLI -- University of Florence, Consiglio Nazionale delle Ricerche, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy -- 80-297. Submillimeter-Infrared Balloon Experiment (completed).

Rotational spectra of key stratospheric molecules have been measured by a submillimeter Polarizing Interferometer that had been employed in the stratospheric flights. Resolution of the instrument is 0.0033 cm^{-1}. Spectra of H_2O_2 have been measured between 10 and 40 cm^{-1}, and the various lines identified. The spectra of the following molecules have been obtained between 10 and 72 cm^{-1}: CO, O_3, H_2O, H_2O_2, N_2O, NO, NO_2, HNO_3, ND_3, SO_2, H_2S, HOCl, NOCl, and HCNO. The positions of the lines have been determined using a peak finder program, which allows a high precision of 2×10^{-4} cm^{-1} with respect to the calculated reference frequencies.

See Bonetti, et al., 76-137, and Trombetti, et al., 83-472.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

DR. F. BRUNER -- Urbino University, Italy -- 81-365. Joint Calibration Study of F-21 (completed).

The presence of CFC 21 in the atmosphere has been detected at two separate locations by two research groups independently, and results differing by an order of magnitude have been obtained.

The intercalibration study between the two groups (see Rasmussen, 81-356) showed excellent agreement between the two different methods used for sampling and measuring.

Dr. H. L. BUIJS -- Bomem, Inc. -- 75-90. Construction of a Fourier Transform Spectrometer (completed).

A spectrometer with a projected resolution of 0.02 cm^{-1} was constructed for use in the simultaneous determination of $ClONO_2$ and either HCl or HF, or of HCl and HF. See Buijs, 75-98 and 77-156.

Dr. H. L. BUIJS -- Bomem, Inc. -- 77-168. Measurement of Halogen Compounds for Determination of Total Chlorine and Total Fluorine in the Stratosphere Using Long-Path Interferometric Spectroscopy (completed).

A library study showed that there were very few published experimental data of sufficient resolution and quality for the interpretation of solar IR spectra.

Dr. H. L. BUIJS -- Bomem, Inc. -- 77-221. Measurement of Infrared Spectra of Selected Stable Molecules (completed).

Fourier transform infrared spectra of methyl chloride in the 3.3 μm region and of phosgene, carbonyl chlorofluoride, and carbonyl fluoride in the 1.3 μm to 5.6 μm region have been recorded at 0.01 cm^{-1} resolution both at room temperature and at stratospheric temperature (∿240 K). The low-resolution spectrum of methyl chloroform from about 2.1 μm to 5.6 μm showed no useful features for detection of this species in the atmosphere.

Dr. J. A. COXON -- Dalhousie University -- 78-255, 80-315. The $A^2\pi_i \leftarrow X^2\Sigma_i$ Band System of ClO: Absolute Absorption Cross Sections at High Resolution for Bands of Stratospheric Interest (completed).

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

The ultraviolet absorbance of ClO produced at 315 K and 1.0-2.0 torr has been determined with a resolution of 0.0054 nm for all ^{35}ClO v'-0 $A^2\pi_{3/2}$ - $X^2\pi_{3/2}$ sub-bands in the range $3 \leq v' \leq 12$. The experimental absorbance profiles for each sub-band have been reproduced closely by synthetic spectrum calculations with parameters optimized by nonlinear least-squares techniques. The fitted band strengths lead to a well defined electronic transition moment variation for the A-X system of ClO. Absorption cross sections calculated at 222 K have been used as data in calculations of synthetic absorption spectra for a ClO column density of 10^{15} cm^{-2} at two different spectral resolutions (0.02 and 0.15 nm).

Dr. D. D. DAVIS -- University of Maryland -- 74-10. Laboratory Determination of the Sensitivity of Laser-Induced Fluorescence for the Detection of ClO under Atmospheric Conditions (completed).

Ground-state stationary ClO concentrations of about 10^{12} cm^{-3} were scanned at several electronic absorption wavelength regions with a tunable UV laser. Laser-induced fluorescence proved to be unusable for measuring ClO.

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-73. Laboratory Measurement of Spectroscopic Absorption Cross Sections of ClO (completed).

A frequency doubled tunable dye laser with a band width of 0.0015 nm was used to measure the absorption cross sections of ClO as a function of wave length for the $A^2\pi_{3/2}$ 9-0 band. There was overall lack of resolution in the data, and an unassigned peak was observed at 283.06 nm. Simulated spectra indicated that a baseline resolved spectrum is not feasible, that the unassigned peak could be a ^{37}ClO absorption, and that the ^{35}ClO line width is somewhat wider than reported by Coxon and Ramsay. The real cross section attributable to ^{35}ClO at 282.94 nm (the largest peak in the spectrum) is calculated to be $\sigma^{R}_{19.5} = 1.0_4 \times 10^{-16}$ cm^2.

Dr. D. D. DAVIS -- University of Maryland/Georgia Institute of Technology -- 75-87. Development of Instrument for Stratospheric OH Measurement by Laser-Induced Fluorescence (completed).

A miniaturized dye laser module for balloon flights has been built and tested.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Dr. A. E. J. EGGLETON -- Atomic Energy Research Establishment, Harwell, England -- 76-116. Total Chlorine Measurements in the Troposphere and Stratosphere (completed).

The feasibility of measuring total chlorine and fluorine in the atmosphere by neutron activation and photon activation, respectively, after collection of reactive species and particulate material on filters and collection of gaseous compounds on activated charcoal was studied. The proposed method proved unsuitable for the determination of total chlorine and fluorine contained in unreactive organic compounds due to a combination of insufficiently low halogen blank values in the best activated charcoal prepared and to inadequate adsorptive capacity for the more volatile organic compounds.

Dr. J. W. ELKINS -- Natonal Bureau of Standards -- 83-473. Measurement of the Temperature Dependence of the Infrared Band Strengths for CFC 11 and CFC 12.

The temperature dependence of the infrared band strengths for CFC 11 and CFC 12, needed to estimate their effects on surface temperature, will be measured.

Dr. K. M. EVENSON -- National Bureau of Standards, Boulder -- 84-533. Line Broadening and Line Strength Studies Using a TuFIR Spectrometer.

The line broadening parameters of the 118 cm^{-1} line of OH will be measured as a function of pressure using tunable far infrared spectroscopy.

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 75-47. Laboratory Determination of the Feasibility of Laser Magnetic Resonance for ClO Detection and Reaction Studies (completed).

It has been demonstrated that ClO can be detected by laser magnetic resonance with a sensitivity of about 10^{10} molec cm^{-3}. Current maximum model predictions are about 10^{8} molec cm^{-3}, and measurements have approached 10^{9} molec cm^{-3} at 30 km.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Dr. C. J. HOWARD -- National Oceanic and Atmospheric Administration, Boulder -- 80-299. Infrared Spectroscopy of Atmospheric Species.

This measurement program is to provide accurately calibrated high-resolution infrared spectra of shorter lived atmospheric species for the identification and quantification of these constituents in the stratosphere. A Fourier transform infrared spectrometer has been delivered and is operational. The first species to be studied is peroxynitric acid.

Dr. H. D. KNAUTH -- University of Kiel, F.R.G. -- 77-171. Laboratory Study of the UV and IR Spectra of HOCl, $HOONO_2$, and $HClO_4$ in the Temperature Range of the Stratosphere (completed).

It was not possible to obtain partial pressures of HO_2NO_2 greater than 0.1 torr in the N_2O_5/H_2O_2 system in Pyrex vessels. The spectrum for gaseous HOCl was derived from extinction measurements on the Cl_2/H_2O system at 333 K for different values of the equilibrium constant for the reaction $H_2 + Cl_2O \rightarrow 2HOCl$. The results are not in complete agreement with those of Timmons (76-129), so additional work on the absorption centered around 300 nm is required.

Dr. H. D. KNAUTH -- University of Kiel, F.R.G. -- 77-224. Laboratory Study for Determination of the Equilibrium Constant of the reaction $Cl_2O + H_2O \rightarrow 2HOCl$ and the UV Spectrum of HOCl (completed).

The gas phase system $Cl_2O + H_2O = 2HOCl$ has been investigated by UV from 200 to 500 nm at 333 K. Isobestic points were found at 214, 233, 335, and 380 nm. The equilibrium constant 0.132 ± 0.008 and HOCl cross sections were derived from absorbance measurements of the mixtures at equilibrium. The resulting HOCl spectrum shows absorption bands with peaks at 240 and 310 nm. Very clean $Cl_2O/H_2O/$HOCl mixtures proved to be remarkably stable. Thermal decomposition produced Cl_2 with intermediate formation of ClO_2. The absorption cross sections of Cl_2O, ClO_2, and Cl_2 were determined separately at 333 K.

Dr. W. J. LAFFERTY -- National Bureau of Standards -- 84-501. Laboratory Studies to Support the Determination of HOCl in the Stratosphere.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

The ν_2 and ν_3 bands of HOCl will be recorded and the individual rotation-vibration transitions assigned. A line atlas will be produced listing the wave number, rotational quantum number assignment, and the line strength for each transition. Measurements and assignments have been completed for the ν_2 band at under 0.004 cm^{-1} resolution.

Drs. F. J. LOVAS and R. D. SUENRAM -- National Bureau of Standards -- 81-350. Millimeter Measurements and Spectral Predictions of Stratospherically Important Species (completed).

Detailed line positions and line strengths have been determined for HOCl and $ClONO_2$. They will permit the detection of these species in the stratosphere from their microwave emission.

Dr. J. E. LOVELOCK -- Private -- 76-120. The Electron Capture Detector as a Reference Standard for Analysis of Atmospheric Halocarbons (completed).

A theoretical model of the operation of the electron capture detector was developed. Application to the procedure used at the Adrigole station and on the RV Shackleton (1971-2) indicate that measurements at these bases are within 3% of theoretical predictions for CCl_4 and CFC 11. This evaluation was extended to CH_3CCl_3 measurements.

Dr. J. E. LOVELOCK -- Private -- 78-226, 78-264, 80-293. Development of Primary Fluorocarbon Standards (completed).

An exponential dilution technique, using a converted barn as the dilution chamber, has been developed to provide absolute calibration of standards for fluorocarbon concentration measurements.

Two standards from the ALE Program, each containing CFC 11 and CFC 12, have been repeatedly analyzed by exponential dilution and for CFC 11 by coulometry and the results compared with each other and the stated value for the ALE standards. The dilution-chamber and coulometry absolute calibrations agreed to within a few percent and were some 2% (11) and 4% (12) below the stated values, giving high confidence in the absolute calibrations. Extension of the technique to methyl chloroform and carbon tetrachloride was less successful, with

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

the form of the dilution relationship suggesting frequent partial absorption of the less volatile chlorocarbon on the glass ampoule from which it is released into the 50 m^3 chamber.

Dr. J. E. LOVELOCK -- Private -- 81-348. Consulting in Association with the Atmospheric Lifetime Experiment (ALE).

Data collected earlier have been assembled and analyzed to provide an absolute calibration by coulometry for the carbon tetrachloride (CCl_4) concentration in some ALE calibration tanks.

Dr. K. MOE -- Private 78-235. Effect of Aerosol Scattering on Ozone Measurements with the Dobson Spectrophotometer (completed).

The NCAR UV double monochromator (UVDM) and associated computer programs have been shown to be capable of ozone measurements of hitherto unobtainable accuracy, while simultaneously measuring aerosol optical depth as a function of wavelength in the region of strong ozone absorption. An ozone value of 0.328 ± 0.006 cm was obtained at 10:00 h MST for June 8, 1978, compared with a corrected Dobson measurement of 0.340 cm at 12:05 h MST.

The increasing number of UVDMs being deployed could provide accurate ozone data to resolve the discrepancy between predictions of ozone decrease from photochemical models and Dobson measurements, which show no decrease or increase.

Dr. D. G. MURCRAY -- University of Denver -- 75-92, 77-152, 78-265, 81-364, 82-413, 82-423. Laboratory Measurement of High Resolution Infrared Spectra of Molecules of Stratospheric Interest.

High resolution infrared spectra of compounds of interest in stratospheric chemistry have been measured. Statistical-band-model analyses and integrated intensity measurements for the 10.8 μm band of CFC 12 and 11.8 μm band of CFC 11 have been published. A compendium of laboratory IR spectra (resoolution 0.04-0.06 cm^{-1}) has been prepared, and a list of the compounds studied as well as the detailed spectra are available to investigators upon request to CMA, attention Fluorocarbon

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Program Manager. An atlas of spectra for approximately thirty molecules is available from the University of Denver, and a handbook of spectra measured earlier is available from the CRC Press.

Dr. R. W. NICHOLLS -- York University, Canada -- 75-11 and 75-11-II. Experimental and Theoretical Studies on the UV Spectrum of ClO with Stratospheric Applications (completed).

Absolute absorption coefficients and cross sections have been measured for all bands and the photodissociation continuum of the v"=0 progression for ClO. The very complicated emission spectrum that has been excited over the wavelength range 2500-4500 A in discharges through ClO_2 and Cl_2O is currently undergoing measurement, identification, and analysis. Computer-based synthetic spectra of various ClO bands have been calculated. Current work, which emphasizes the (2,0), (3,0), and (4,0) bands, should be of immediate diagnostic application to ground-based and balloon-based stratospheric spectroscopic observations.

Dr. R. W. NICHOLLS -- York University, Canada -- 75-30b. Laboratory Studies of the Infrared Vibration-Rotation Spectrum of ClO (completed).

Work in this area was suspended to allow greater effort in the UV measurements (Nicholls, 75-11).

Dr. R. A. RASMUSSEN -- Private -- 76-142, 78-247. Interlaboratory Comparison of Fluorocarbon Measurements (completed).

A second round of identical samples of rural air has been circulated blind to participating laboratories for analysis for CFCs 11 and 12, $CHCl_3$, CH_3CCl_3, CCl_4, and N_2O. Overall the results obtained showed a spread similar to that obtained in the 1976 NASA workshop. However, as in 1976, there was excellent agreement between Rasmussen and Lovelock, who use two different methods of calibration. A third round of samples was analyzed by 19 laboratories. Good agreement (±5%) was obtained by the 5 laboratories using common primary standards, but the other 14 laboratories showed much larger variations, with mean values considerably lower than those of the 5 laboratories.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 81-356. Joint Calibration Study of F-21 (completed).

Two sets of pressurized tanks have been prepared from clean air and doped with differing amounts of CFC 21 up to 100 ppt. The tanks have been analyzed by Rasmussen's published mass spectrophotometric technique both before and after they were measured by Bruner (See 81-365). Agreement between the two laboratories is excellent and within one standard deviation on the measurements.

Dr. R. J. SAYKALLY -- University of California, Berkeley -- 80-300. Near- and Far-Infrared Spectroscopy (completed).

This project sought to develop far-infrared laser electric resonance as a technique for detection and measurement of transient species, with parallel work in tunable F-center laser spectroscopy. The methods have potential applications in both laboratory kinetics and stratospheric measurements. The apparatus for both experiments was completed.

However, the laser electric resonance project was not pursued under this contract. The color center laser was used to develop a sensitive detection method for NO and OH known as "tone burst modulated infrared laser absorption spectroscopy." The work will be extended to other molecules such as HO_2, HOCl, and HONO under other funding.

Drs. P. G. SIMMONDS and J. E. LOVELOCK -- Private -- 79-269. Determination of Tropospheric Halocarbons and Their Relative Importance (completed).

A routine, practical method for the direct determination of ambient CH_3Cl in 5-ml samples to ±5% has been developed based on a ^{63}Ni electron capture detector with oxygen-doped carrier gas. A special chromatographic column, which is a combination of OV101 silicone and Parasil E coated with SP1000 phase, specifically separates CH_3Cl from all of the anticipated halocarbon interferences in ambient air. Daily measurements of ambient CH_3Cl during January, 1981, ranged from 553 ppt to 2470 ppt. The high values, associated with maritime air, suggest that the overall global budget for CH_3Cl might have been underestimated.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Concentrating 60-ml air samples with silica gel as an absorbent improves the precision of analysis for CH_3Cl to ±1.7%. From retention volume data it has also been demonstrated that 0.5 g of silica gel would be sufficient for the quantitative adsorption of other important halocarbons such as CFC 22 and CFC 114 in a 100-ml air sample.

A portable gas chromatograph has been constructed for on-site analysis of river and sea water samples. Initial surveys indicate that the concentration of both CH_3Cl and CH_3I in river water is approximately half that found in sea water, implying that river water is a hitherto unrecognized significant source of alkyl halides.

Chemical conversion methods were in general unsuccessful, and, of a large number of carrier gas dopants explored, only oxygen doping gave sufficient sensitivity for direct ambient analysis. Other potentially useful detectors, such as the photoionization and electrolytic conductivity detector, were also found to have inadequate sensitivity for determining trace levels of ambient halocarbons.

Dr. R. K. SKOGERBOE -- Colorado State University -- 77-206. Development of a Measurement System for the Determination of Total Chlorine in Air (completed).

The technique involves two flame reactions. The first, in a H_2-rich flame, forms HCl, which is treated with indium to yield InCl. The InCl is then excited in an air-rich flame and detected photometrically. Blind analyses of calibration samples proved that the sensitivity of the technique was not sufficient to be of value for stratospheric measurements. However, it is hoped that the system can be put to use in tropospheric monitoring.

Dr. D. H. STEDMAN -- University of Michigan -- 74-7. Atmospheric Determination of ClO Concentration: A Feasibility Study (completed).

Laboratory studies have demonstrated the feasibility for detecting stratospheric ClO by chemical conversion to Cl (by reaction with NO) accompanied by vacuum ultraviolet resonance fluorescence. In-flight use of this technique is being supported by NASA.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Dr. D. H. STEDMAN -- University of Michigan -- 76-132. Absolute Calibration of Fluorocarbon Measurements (completed).

A feed-back flow system for the calibration of CFC samples has been built.

Dr. D. H. STEDMAN -- University of Michigan -- 77-151. Generation and Exchange of Calibrated Samples of Fluorocarbons (completed).

Work on this project was stopped because of feasibility problems.

Dr. R. B. TIMMONS -- Catholic University -- 76-129. Photochemical and Chemical Kinetics Measurements of Stratospheric Importance with Respect to the Fluorocarbon Issue (completed).

HOCl is a possible stratospheric sink the magnitude of which would depend on the absorption cross section. Earlier spectral measurements were inaccurate. Pure HOCl cannot be prepared, for an equilibrium mixture of Cl_2O and HOCl exists. The equilibrium constant for this reaction is $K_p \cong 0.8$. This value and the UV absorption cross sections of Cl_2O have been used to determine the UV absorption cross sections of HOCl between 200-330 nm. The 230-240 nm peak was lower than previously measured, and no peak was found at 320 nm.

Dr. R. B. TIMMONS -- University of Texas, Arlington -- 77-214, 78-258. Photochemical and Chemical Kinetics Measurements of Stratospheric Importance with Respect to the Fluorocarbon Issue (completed).

The UV absorption cross sections of HOCl between 200-330 nm over longer pathlengths have been determined under conditions such that interference by Cl_2O is minimal, i.e., low Cl_2O concentration and excess H_2O. An induction period for the increase in UV absorption at 320 nm was observed, suggesting that the 320 nm absorption may be due to more than one species.

The equilibrium constant for the $Cl_2O + H_2O$ reaction appears to be essentially temperature independent over the temperature range 25 to 57 C.

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

Work was performed using a quadrupole mass spectrometer in an attempt at direct determination of the concentration of HOCl and any other interfering species. This would make the measurement of the UV absorption cross section more accurate. Results obtained with this instrument were not reproducible, and no reliable estimate for the HOCl concentration could be made.

Drs. W. A. TRAUB and K. V. CHANCE -- Smithsonian Astrophysical Observatory at Harvard University -- 80-318, 81-375, 82-445, 83-489, 85-544. Far-Infrared Laboratory Spectroscopy of Stratospheric Species.

Laboratory spectra of HOCl and $ClONO_2$ have been studied at a resolution of about 0.03 cm^{-1} in the region 70 to 250 cm^{-1}, in order to establish the line positions, strengths, and pressure broadening effects of air on the lines and bands. All lines appear too weak to be observed in the stratosphere. Pressure broadening coefficients for HF and HCl are being measured, and a computer program has been developed for simulating observed atmospheric spectra. This work is being done in support of an ongoing balloon measurement program.

Laboratory spectra of the ν_6 and ν_5 bands of $ClNO_3$ in the 20 micron region will be measured and analyzed for use in the balloon-borne measurement of $ClNO_3$.

Upper limits for hydrogen peroxide concentrations in the 22 to 38 km range have been determined from spectra obtained during the first Balloon Intercomparison Campaign. The value at 31 km is a factor of 1.8 lower than a recent calculated value.

Dr. A. TROMBETTI, et al. -- University of Bologna, Italy, and other Italian institutions -- 83-472. Laboratory Measurements of Far-Infrared Spectra of Molecules of Stratospheric Interest.

This project continues activity on laboratory measurements of the spectra of source, temporary reservoir, and radical species in the 5 cm^{-1} to 180 cm^{-1} region. A new model of the flight IROE Fourier Transform Interferometer of higher resolution has been designed and built. The resulting resolution is 0.0018 cm^{-1} in the range 5-80 cm^{-1}, as compared with 0.003 cm^{-1} for the previous model. Similar higher

Table 3 (continued)

Laboratory Studies Related to Potential Atmospheric Measurements

resolution is also expected in the wave number region above 80 cm^{-1}.

See Bonetti, et al., 80-297.

Drs. M. S. ZAHNISER and C. E. KOLB -- Aerodyne Research, Inc. -- 81-355, 83-469. Quantitative Infrared Line Strengths for HO_2.

The absolute infrared absorption coefficients and temperature-dependent collisionally-broadened line shapes for vibrational-rotational bands of HO_2 are being determined with a tunable diode laser. The line positions, line strengths, and overall band strength were determined for the ν_3 band of HO_2. Work is in progress on the ν_2 band of HO2.

D. Tropospheric and Stratospheric Measurements

Dr. J. G. ANDERSON -- Harvard University - 82-428. Detection of Stratospheric OH, HO_2, and H_2O by Copper Vapor Laser.

A newly developed atomic copper vapor laser system, a water vapor detector, and an ozone detector will be employed to obtain profiles of these important species below 30 km. Problems with the computer system, now resolved, have caused the launch date to be postponed to Spring, 1985.

Dr. J. G. ANDERSON -- Harvard University - 82-429. Resonance Fluorescence Measurement of ClO and Related Species Using a Reel-Down Technique.

A platform capable of elevating and descending repeatedly by means of a Kevlar tether when suspended under a helium filled balloon will be employed for multiscannings at critical altitude intervals in order to investigate in detail the concentration of ClO and related species in the stratosphere between 20 and 42 km. The payload has been flown successfully twice.

Dr. J. E. BECKMAN -- Queen Mary College, London, England -- 79-282. Airborne Millimeter-Wave Determination of ClO (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Measurements of the ClO mixing ratio were made with an airborne heterodyne receiver operating in the 230-270 GHz range during six day- and night-time flights over France in 1980. O_3 profiles of moderate height resolution were also derived. The same instrument was used to detect ozone from a ground site at 242 and 481 GHz.

Drs. A. BONETTI and B. CARLI -- University of Florence and Consiglio Nazionale delle Ricerche, Istituto di Ricerca Sulle Onde Elettromagnitiche, Italy -- 85-543. High Resolution Submillimeter Balloon Spectroscopy.

The objective of this project is to optimize the IROE High Resolution FT Spectrometer for further balloon measurements of the rotational (far infrared and submillimeter) emission of selected stratospheric trace constituents. See also Traub and Chance, 84-537.

Drs. A. BONETTI and B. CARLI; Dr. J. E. HARRIES -- University of Florence, Consiglio Nazionale delle Ricerche, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy; National Physical Laboratory, England -- 76-137. Submillimeter-Infrared Balloon Experiment (completed).

Vertical distributions and diurnal variability of H_2O, O_3, NO_2, HNO_3, HCl, CFCs 11 and 12, ClO, $ClONO_2$, and other molecules were determined using the 9 to 15 micron infrared region and submillimeter wavelengths from 200 to 1000 microns. Data from the October, 1978, flight have been reduced for CFC 11 and 12, O_3, $^{16}O^{18}O^{16}O$, HNO_3, H_2O, HDO, $H_2{}^{17}O$, $H_2{}^{18}O$, HF, $H^{35}Cl$, $H^{37}Cl$, HCN, CO, O_2, $^{16}O^{18}O$, and OH.

See Bonetti, et al., 80-297.

Drs. A. BONETTI, B. CARLI, F. MENCARAGLIA, and F. FORNI -- University of Florence and Consiglio Nazionale delle Ricerce, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy -- 82-389, 82-437. Balloon Intercomparison Campaign.

See Ogawa and Iwagami -- 82-391 and 82-438.

Dr. F. BRUNER -- Urbino University, Italy -- 78-256. Determination of F-21 and Other Halocarbons in the Troposphere (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Two analytical methods for the quantitative determination of atmospheric CFC 21 at 1-50 ppt concentration have been set up based on GC separation followed, respectively, by EC and MS. In both methods the permeation tube technique has been adopted as the primary quantitative standard.

A series of samples has been collected from rural and industrial areas in Italy and over the Red Sea and the Indian Ocean. Concentrations of CFC 21 ranged from a few ppt to as great as 40-50 ppt.

> Dr. H. L. BUIJS -- Bomem, Inc. -- 75-90, 75-98. Measurement of HCl and HF in the Stratosphere by Fourier Transform Spectroscopy (completed).

Balloon flights to Alaska (May, 1976) and New Mexico (September, 1976, and March, 1977) have provided profiles for HF and HCl concentrations. The HCl profile (volume mixing ratio), but not the HF profile, appears to show a maximum at 23-25 km, where the volume mixing ratios are 8×10^{-10} (HCl) and 10^{-10} (HF). The HCl value is similar to values obtained by other investigators.

Upper limits on the concentrations of C_2H_6 and CH_3Cl are $\leq 0.6 \times 10^{-9}$ and $\leq 1 \times 10^{-9}$ (mole fraction), respectively.

See Buijs, 75-221.

> Dr. H. L. BUIJS -- Bomem, Inc., Canada -- 77-156. Operational Costing for Flights Planned in 1977 (completed).

HCl and HF profiles were recorded by infrared techniques from a balloon launched in New Mexico on October 27, 1978. The HCl mixing ratio increased from about 2×10^{-10} at 20 km to about 1×10^{-9} at 35 km. Similar values for HF are about 3×10^{-11} and 3×10^{-10}, respectively. The shape of the curve of HF/HCl vs. altitude is in reasonable agreement with that of Farmer and Raper (1977) over the altitude interval 17-27 km but does not agree with the profile calculated from a 2-D model (1981 chemistry), especially below 25 km.

A balloon flight on October 13 was designed to measure HCl, HF, and $ClONO_2$. A failure in the on-board recording system and problems with the telemetry link prevented obtaining usable data from this flight.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Dr. E. B. BURNETT -- Florida Atlantic University -- 85-547. Feasibility Study of ClO Column Measurement from UV Spectra.

The feasibility of using an instrument similar to the OH Pepsios for the measurement of ClO by ground-based absorption of sunlight in the near UV will be investigated.

Drs. H. U. DUETSCH and K. F. KUENZI -- Federal Institute of Technology ETH and University of Bern, Switzerland -- 81-371. Comparison of Umkehr and Microwave Ozone Profiles (completed).

A 30-channel microwave spectrometer at Bern and a Dobson instrument at Arosa were used to measure the same air mass simultaneously. The microwave technique yielded 20-30% higher ozone values than the Umkehr technique. Comparison of standard deviations indicates that the Umkehr technique is more precise for layer 6 (±5-8%), whereas the microwave technique is more precise for layer 9 (±8%). The microwave technique is less affected by aerosols.

Dr. D. H. EHHALT -- Nuclear Research Establishment Juelich, F.R.G. -- 76-145. Electron Spin Resonance Detection of Stratospheric Radicals (completed).

Under a program supported by the German Government's Department of Research and Technology a cryogenic sample was collected at 30.5 km at 1600-1700 hr (conditions of relatively low radical concentration) during Murcray's March, 1977, balloon flight. The frozen sample was analyzed by ESR, showing the following concentrations. NO_2: $\sim 3.5 \times 10^8$; HO_2: $\sim 8.5 \times 10^6$ molec cm^{-3}; ClO: not detected.

Dr. P. A. EKSTROM -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 75-27. Ground-Based Millimeter-Wavelength Observations of Stratospheric ClO (completed).

About 500,000 data points were obtained in the microwave spectra near 93 GHz with the Kitt Peak radiotelescope. Due to excessive noise no ClO signal could be detected.

Dr. A. GIRARD -- Office National d'Etudes et de Recherches Aerospatiales, France -- 75-88. Measurement of HCl, HF, ClO, etc., in the Stratosphere by High Resolution Infrared Spectroscopy (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Vertical profiles of HCl, NO_2, H_2O, and CH_4 between 26 and 35 km have been deduced from two balloon-borne grating spectrometer experiments. There is a hint of a decrease in HCl mixing ratio at the upper limit of the October, 1977, experiment. Laboratory infrared spectra have been obtained for $ClNO_3$, NO_2, HNO_3, and HCHO. The method of infrared limb sun pointing was found to be inadequate for the detection of ClO in the atmosphere.

> Drs. A. GOLDMAN and A. BARBE -- University of Denver; University of Reims, France -- 80-322, 83-457. Collaborative Studies on Atmospheric Spectroscopy.

Groups from the Universities of Denver and Reims are collaborating to develop consistent inversion algorithms to obtain atmospheric concentration data for several trace species (e.g., HCl, HF, O_3) from infrared spectra measured from the ground or balloon platforms. Atmospheric infrared spectra will also be used to gather information on weak lines of molecules such as O_3 and HNO_3 that cannot easily be measured in laboratory systems.

The two groups now get excellent agreement for the ν_2 band of O_3. Work is in progress on the ν_1, ν_3 region of O_3 and on isotopic O_3.

> Drs. D. W. T. GRIFFITH and P. J. CRUTZEN -- Max Planck Institut fuer Chemie, Mainz, FRG -- 84-526. Stratospheric Trace Gas Measurements Using Matrix Isolation--FTIR Analysis.

A promising technique for the detection of nitrogen oxides and other stable and unstable species in the lower stratosphere is being tested. Air is sampled cryogenically at 77 K, the sample taking the form of a CO_2 matrix with trace gases embedded in it, and analysis is done in the laboratory by FTIR absorption spectroscopy of this matrix. Some samples are frozen directly into the cyrostat in which the absorption spectrum is to be measured later in the laboratory. In a second technique the sample is collected by pumping air through a liquid nitrogen cooled glass sampling coil. In the laboratory the sample is briefly evaporated and refrozen into the measurement cryostat.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

The preliminary results of test flights with a Lear jet over northern Europe identified some shortcomings of both collection techniques. Surprisingly, the direct frozen matrix was not firm enough to allow a sensitive analysis by FTIR. Nevertheless, the matrix isolation technique combined with FTIR spectroscopy seems to be a powerful tool for the detection of trace species in the lower stratosphere due to its high sensitivity and selectivity.

> Dr. W. S. HEAPS -- National Aeronautics and Space Administration, Goddard -- 84-508. Balloon Lidar Measurements of OH and O_3.

A balloon-borne Lidar system has been developed for stratospheric measurements of OH and O_3. The FPP funding will permit an additional flight to be made in 1985.

> Dr. P. JOUVE -- University of Reims, France -- 79-290. Measurement of the Vertical Distribution of HCl, O_3, and HCHO and the Ratio HF/HCl (completed).

Ground-based measurements of HCl, HF, NO, COS, O_3, and H_2CO have been made using high resolution infrared spectroscopy. These measurements were made during 1981 from an observatory in Haute Provence, France, by a team from Jouve's group at the CNRS Laboratory located in Reims. The vertical profiles of HCl, O_3, H_2CO, and the ratio HCl/HF have been obtained.

The last series of measurements has confirmed the possibility of obtaining high quality Umkehr measurement for ozone in the upper stratosphere.

> Drs. W. D. KOMHYR, R. D. GRASS, R. D. EVANS, and A. N. CHOPRA -- National Oceanic and Atmospheric Administration, Boulder, and University of Colorado -- 81-363. Umkehr Observations with Automatic Dobson Ozone Spectrophotometers (completed).

Modernization of six Dobson spectrophotometers is underway in order to permit automated Umkehr observations at selected locations worldwide. The automated instruments are expected to provide more frequent and more accurate Umkehr altitude profiles of ozone. Ozone trends at altitudes near 40 km are potentially a more sensitive warning of depletion by chlorofluorocarbons than total ozone trends. The prototype automated unit is installed at Boulder (Colorado). Under this

Table 3 (continued)

Tropospheric and Stratospheric Measurements

project, instruments have been automated and installed in Haute Provence (France), Poker Flats (Alaska), Mauna Loa (Hawaii), and Perth (Australia). An instrument will be installed at Huancayo (Peru) during 1985, and one at an additional Southern Hemisphere location. This project is cofunded by EPA, NOAA, and WMO.

Dr. J. E. LOVELOCK -- University of Reading, England, Private -- 73-1, 74-3, 75-67, 77-144. Fluorocarbons in the Environment (completed).

The electron capture gas chromatograph (ECGC) has been developed and applied to the measurement of several halocarbons in the lower stratosphere and troposphere, particularly over Europe and the Atlantic Ocean. In 1976 levels of CFC 11 were about 130 ppt (U. K.) and 80 ppt (Southern Hemisphere). CH_3Cl, with the ocean and smouldering vegetation as identified sources, was at about 10^{-9} v/v in the Northern Hemisphere but was found to be higher over the southern African continent (2.2×10^{-9} v/v in Kenya) (cf. Rasmussen, 77-181, p. 54). CCl_4 and CH_3CCl_3 were also unexpectedly high. Portable monitoring equipment has been provided and put to use in South Africa and Australia. The levels of CH_3CCl_3 found in the Southern Hemisphere (50 ppt) appeared higher than expected from release and tropospheric lifetime estimates. Northern Hemisphere values were about 100 ppt.

Measurements of CFC 11 in the atmosphere and ocean were made during the April, 1977, voyage of RRS Challenger in the northeast Atlantic Ocean. Average air concentrations of 155 ppt were observed for CFC 11, and it was present at saturation quantities down to depths of 500 m.

See Rasmussen 76-142.

Dr. G. MEGIE -- Service d'Aeronomie, Centre National de la Recherche Scientifique, France -- 84-510. Ozone Monitoring in the 35-45 km Altitude Range by an Exciplex Laser-UV Lidar.

The laser will be received and tested in June. Ground-based measurements will be done in July at "Observatoire de Haute Provence."

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Dr. D. G. MURCRAY -- University of Denver -- 75-13, 76-101, 76-135, 77-166. The Measurement of the Stratospheric Distribution of Fluorocarbons and Other Constitutents of Interest in the Possible Effect of Chlorine Pollutants on the Ozone Layer (completed).

Measurement of stratospheric distribution by balloon-borne, high-resolution, infrared absorption measurement at large solar zenith angles has been achieved using a specially constructed grating spectrometer. The distributions obtained for CFCs 11 and 12 and CCl_4 showed a concentration increase of about 2.5, with a rather wide range of uncertainty, from 1968 to 1975 for CFCs 11 and 12. Subsequent flights also yielded HCl and HNO_3 profiles. A preliminary value of 2 ppbv for the concentration of $ClONO_2$ at 26 km has been calculated. The upper limit for H_2O_2 is 1 ppbv at 20 km.

An October, 1978, balloon flight with an interferometer system instead of a grating system was successful and recorded through sunset with the last record obtained at solar zenith angle > 95°. A strong absorption at 1283 cm^{-1} is due to CF_4 with an estimated mixing ratio of 75 pptv at 25 km. The $ClONO_2$ mixing ratio is 0.8 ppbv from 24 km to 32 km, then falling to 0.4 ppbv at 33.5 km. Several features coincide with some of the HOCl lines, but the agreement appears fortuitous, and no features can be assigned with certainty to HOCl. The upper limit for H_2O_2 is 0.5 ppbv at 20 km and for COF_2 is 0.4 ppbv at 25 km.

The latest flight of the series was performed on October 20, 1981. The float altitude at sunset was 32.3 km. Two interferometer systems and a pressure modulated radiometer were on board. The principal objective of the flight was to obtain measurements of $ClONO_2$, which has been tentatively identified. Mixing ratio profiles of $ClONO_2$ have been determined for flights made October 27, 1978, and March 23, 1981.

Dr. D. G. MURCRAY -- University of Denver -- 77-211. Acquisition of an On-Board Digital Recording System (completed).

The balloon-borne interferometer system has been improved by incorporating into it on-board recording capability.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Advantages are two-fold: a back-up is provided in case the telemetry system malfunctions, and it becomes possible to operate under atmospheric wind conditions that might carry the balloon out of telemetry range. The system was used successfully for balloon flights on October 28, 1978, and October 20, 1981.

Dr. D. G. MURCRAY -- University of Denver -- 78-228. Detection of Selected Molecules by Ground-Based Solar Spectroscopy (completed).

Solar spectra were examined with a resolution of 0.01 cm^{-1}. An atlas of the 775-950 cm^{-1} and 1050-1300 cm^{-1} regions has been prepared.

A workshop on solar spectroscopy was held at the National Bureau of Standards, March 26, 1980.

Dr. D. G. MURCRAY -- University of Denver -- 81-380, 84-497. Ground-Based Observatons of Stratospheric Species.

Ground-based infrared techniques will be used to attempt measurements of temporary reservoir species ($ClONO_2$, N_2O_5, HO_2NO_2) in the stratosphere. Laboratory infrared spectral studies will be made in support of these studies.

Laboratory data have been obtained for $ClONO_2$ and N_2O_5 at a resolution of 0.003 cm^{-1}. Ground-based spectra show a feature at 780.23 cm^{-1} that may be associated with $ClONO_2$. This has been tentatively identified in balloon-based spectra.

Drs. D. G. MURCRAY and H. K. ROSCOE -- University of Denver; Oxford University, England -- 77-219. Stratospheric HCl Measurements Conducted as a Piggy-Back to Murcray's Flight (completed).

Because the vibration problem with the solar-absorption pressure modulator radiometer used for the HCl measurements could not be reasonably solved, this project was cancelled.

Drs. D. G. MURCRAY and H. K. ROSCOE -- University of Denver; Oxford University, England -- 80-328. An Intercomparison of Measurements of Stratospheric HCl (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

The simultaneous measurement of stratospheric $ClONO_2$ (rather than HCl) on a balloon flight with a high resolution IR interferometer (Murcray) and with a pressure modulator radiometer (Roscoe) was planned. Difficulties with encoding prevented obtaining useful results with the latter.

> Drs. T. OGAWA and N. IWAGAMI -- University of Tokyo, Japan -- 82-391, 82-438; Drs. G. M. STOKES, D. W. JOHNSON, and G. J. SCHUSTER -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 82-397; and Dr. P. T. WOODS -- National Physical Laboratory, England -- 82-403, 82-432. Balloon Intercomparison Program (BIC), Phases One and Two.

These three projects form part of an extensive balloon measurement campaign, cofunded with NASA, the Council of European Communities (CEC), and others primarily to take measurements of HCl and NO_x at Palestine, Texas, in the fall of 1982 and the spring of 1983.

The campaign comprised the simultaneous launch of several balloons, each carrying a number of instruments. Measurements were taken simultaneously, in the same air mass, over a period of some hours. Evaluation of the data from these numerous devices will permit a better distinction between atmospheric variability and instrument characteristics.

Projects 82-403 and 82-432 contain subcontracts with Zander, University of Liege (82-395 and 82-435); Bonetti, et al., University of Florence (82-389 and 82-437); Pommereau, CNRS (82-394 and 82-436); Taylor, University of Oxford (82-393 and 82-434); as well as with Woods, et al., NPL (82-394 and 82-433). In all, some 20 investigators flew instruments enabling extensive intercomparisons of different techniques for measuring HCl and NO_x, as well as providing extensive data on other species.

In addition simultaneous measurements were made from the ground and from aircraft. Project 82-397, a ground-based experiment providing for measurement of solar absorption spectra from Kitt Peak during the period of the stratospheric measurements, yielded excellent HCl and HF absorption spectra during the first BIC flight and HNO_3 spectra for the subsequent day.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

The first phase of the BIC campaign, completed in September, 1982, was only partially successful. It was possible to launch four large balloons into the same air mass within a spread of three hours. However, one balloon failed, not all instruments were flown, and some instruments had problems.

Data from this first phase of the campaign have been analyzed by the investigators under the coordination of Seals of NASA Langley, whose group reduced some of the raw data.

The CMA investigators in this program have reported the following results: sunset profiles for HCl and CH_4 and a daytime profile for HF (82-403), a profile for HNO_3 (82-394), qualitative identification of ClO (82-389), total column NO_2 from the ground and an NO_2 profile in the stratosphere during ascent (82-394), and a profile for NO, together with other data on NO_2, N_2O_5, and HNO_3, which are apparently affected by aerosol from the El Chichon eruption (82-393). Efforts will be made to evaluate any effect of aerosol from El Chichon on all the data obtained.

The Spring, 1983, campaign was rescheduled for later in 1983 following two balloon failures during the May, 1983, launch. Additional experiments were included in the campaign to characterise the aerosol layer. These included aircraft-borne instruments for remote sensing, climate observations, in situ sampling, and characterization of composition and size distribution of the aerosols, together with a small balloon-borne instrument on a fifth gondola for aerosol profiling.

In June, 1983, flights were accomplished without mishap by the University of Liege and the JPL-2 gondolas. Unfortunately, the JPL-1 gondola and instruments were totally destroyed following free fall from 110,000 ft. The NPL gondola landed safely but was subsequently damaged when dragged during a storm. Several instruments were damaged and the Oxford PMR destroyed.

As analysis of the results has progressed, it has become evident that the BIC-I data set is somewhat limited for intercomparison purposes. This is not the case for BIC-II, and a remarkable quantity and quality of results have been achieved. The only significant failure was the JPL interferometer.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Several productive data analysis meetings have been held. A set of papers are being drafted for publication.

Dr. J. P. POMMEREAU -- Service d'Aeronomie, Centre National de la Recherche Scientifique, France -- 82-392, 82-436. Balloon Intercomparison Campaign.

See Ogawa and Iwagami -- 82-391 and 82-438.

Dr. J. P. POMMEREAU -- Service d'Aeronomie, Centre National de la Recherche Scientifique, France -- 85-550. Participation in MAP GLOBUS NO_x Campaign.

Supplemental funding will be provided to enable several investigations to participate.

Dr. R. A. RASMUSSEN -- Washington State University -- 75-2, 75-59. Fluorocarbon Research (completed).

An attempt was made to obtain halocarbon concentration measurements as far into the stratosphere as could be reached by an available commercial aircraft. A small portable gas chromatograph was used for on-board measurements, and cannister samples were collected for subsequent detailed halocarbon analysis on the ground. One phase of the study consisted of samples collected over a wide area of the Pacific Northwest, a second of samples collected frequently to the maximum attainable altitude over Alaska. The halocarbon concentrations are either constant or decrease very slowly with altitude in the tropopause, decrease rapidly in the tropopause from the tropospheric concentration to an average value identifiable with the stratosphere, and do not show a clear pattern of concentration gradients above the tropopause.

A trans-Pacific flight from 80°N to 60°S has been completed, and the air samples collected have been analyzed for halocarbons. Most of the samples were collected at 39,000 to 43,000 ft. CFC 12 concentrations are about 10% higher in the north than in the south at ground level, and the difference is apparently greater for CFC 11.

Dr. R. A. RASMUSSEN -- Private -- 77-181. Measurement of the Concentration of Methyl Chloride in Air in Kenya (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Air samples were obtained at ground level and by aircraft in Kenya and over the Indian Ocean. Analyses showed CH_3Cl at 600-700 ppt over Kenya, rising to 900-2000 ppm in areas where slash burning was being conducted (cf. Lovelock, 77-144). Boundary layer analyses over the Indian Ocean were 750-880 ppm. N_2O levels were 324-378 ppb. Other analyses showed CFC 12, 235-246 ppt; CFC 11, 137-143 ppt; CH_3CCl_3, 74-96 ppt; and CCl_4, 120-135 ppt. Comparison with previous data showed interhemispheric differences for the above five species.

Dr. R. A. RASMUSSEN -- Oregon Graduate Center -- 78-260. Identification of FC-21 in the Atmosphere (completed).

Measurements of CFC 21 in Tasmania, at the South Pole, and in "clean" air from Cape Meares, OR, show concentrations of 0.05-0.6 ppt, compared with concentrations of 2 ppt at Harwell, U. K. GCMS identification confirms CFC 21, distinguishing CFC 21 from CH_3I. CFC 21 samples do not increase in CFC 21 content on storage, nor is CFC 21 produced from fluoroplastics examined, nor is CFC 21 observable in CFC 11 or CFC 12 standards. CFC 21 is highly variable, and more measurements are needed.

Dr. R. A. RASMUSSEN -- Private -- 80-308. F-22 Measurements in the Atmosphere (completed).

The concentration of CFC 22 has been measured in 99 air samples collected between April, 1978, and January, 1981, with supplemental samples from 1977. The average rate of increase in CFC 22 concentration over the last 3 years was found to be approximately 12%/yr. The atmosphere contains about 200 Mkg more than expected from the McCarthy, et. al., emission estimates. This discrepancy is small compared with the uncertainties in the absolute calibration, the accuracy of release estimates, and the limited global measurement coverage.

Dr. B. A. RIDLEY -- York University, Canada -- 76-102A, 76-102B. Measurement of Fluorocarbons and Related Chlorocarbons in the Stratosphere by Collection and Analysis (completed).

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Series of evacuated stainless steel spheres were used to obtain samples of stratospheric air at various altitudes up to 39 km from three balloon flights. Some problems were encountered in the absolute calibration of the electron capture gas chromatograph, but the results are consistent with a stratospheric photolysis sink for CFCs 11 and 12 and N_2O.

> Drs. P. M. SOLOMON and R. L. deZAFRA -- State University of New York, Stony Brook -- 76-130, 77-225, 79-278, 80-316, 81-362, 82-410, 83-467, 84-521. Millimeter Wave Observations of Chlorofluoromethane Byproducts in the Stratosphere.

This study is directed toward the development of a ground-based method for continuous determination of ClO. One of the millimeter wave observing systems is based on a 3-nm maser, a unique instrument that is the most sensitive detector in the world in the 83-94 GHz range.

A 256-channel radio frequency spectrometer has been built and tested for the analysis and identification of the weak pressure-broadened 93 GHz signal from stratospheric ClO. An upper limit of 1.5 ppb ClO was measured with the 130 GHz receiver. In a joint effort with Bell Laboratories ClO has been detected at 204 GHz at the FCRAO radio astronomy observatory near Amherst, Mass.

Measurements of ClO have been made at 278 GHz during January-March, 1981, at FCRAO observatory and from Mt. Hopkins, Arizona, during April-May, 1981. A cooled mixer was used with this equipment, which made this equipment the most sensitive produced so far at this frequency. For the first time ClO has been detected at night. ClO data from Mt. Hopkins are in good agreement with predictions using 2-D models in contrast to Anderson's in situ ClO measurements, which are higher than model predictions above 35 km.

ClO measurements at 204 GHz were made during the spring of 1982 at the University of Massachusetts observatory with a receiver that contained a cooled mixer. Results are consistent with the previous 204 and 278 GHz measurements.

Since September, 1982, five ground-based measurement campaigns have been made at Mauna Kea, Hawaii. The high altitude of

Table 3 (continued)

Tropospheric and Stratospheric Measurements

this site (approximately 4.3 km) minimizes interference from tropospheric water vapor. Diurnal measurements were obtained for ClO with a time resolution of two hours. Both HO_2 and HCN have also been detected at approximately 266 GHZ.

Drs. G. M. STOKES and D. W. JOHNSON -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 82-417. Review of Kitt Peak Data Archives for Methane and Other Species.

Spectral data obtained at Kitt Peak National Observatory from 1978 through 1983 are being analyzed by Stokes and by Zander (see Zander, 82-439). Data have been used to derive a trend for atmospheric methane during this period and to look for selected trace gas species.

For trace species most effort has been directed toward ClO (around 820 cm^{-1}) and $ClONO_2$. With the current signal to noise ratio, only an upper limit, which falls within the range of the in situ measurements, can be deduced for ClO. The $ClONO_2$ signal is merged with lines of CO_2 and O_3.

See Zander 82-439.

Drs. G. M. STOKES, D. W. JOHNSON, and E. W. PEARSON -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 84-493. Analysis of Data on Stratospheric Nitrogen Species.

The atmospheric burden of NO and NO_2 will be studied by measurements using high resolution Fourier transform spectroscopy at the Kitt Peak National Observatory. Major emphasis will be placed on the diurnal variation.

Drs. G. M. STOKES, D. W. JOHNSON, and G. J. SCHUSTER -- Battelle Memorial Institute, Pacific Northwest Laboratories -- 82-397. Balloon Intercomparison Campaign (completed).

See Ogawa and Iwagami -- 82-391 and 82-438.

Drs. F. W. TAYLOR and H. K. ROSCOE -- Oxford University, England -- 82-393, 82-434. Balloon Intercomparison Campaign.

See Ogawa and Iwagami -- 82-391 and 82-438.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Drs. F. W. TAYLOR and H. K. ROSCOE -- Oxford University, England -- 83-484, 84-532. Balloon Measurements, with Pressure Modulators and Selective Absorbers.

The Pressure Modulator Radiometer used to measure stratospheric NO and NO_2 was damaged in a 1983 balloon flight. It is being rebuilt to an improved design.

Dr. O. C. TAYLOR -- University of California at Riverside -- 73-3, 74-2. Monitoring and Atmospheric Reactions of Fluorocarbons (completed).

An electron capture gas chromatograph was used to measure the concentrations of CFCs 11 and 12 in the troposphere over southern California and in the lower stratosphere over New Mexico and Colorado. The tropospheric concentrations were found to vary from day to day as climatic conditions affected dispersion and dilution. Concentration decreased with increasing altitude in the lower stratosphere.

Drs. W. A. TRAUB and K. V. CHANCE -- Smithsonian Astrophysical Observatory at Harvard University -- 84-537. Construction of a Duplicate Single Axis Platform.

A single axis platform will be built for accurate control of the viewed elevation angle of far infrared spectrometers. The platform is for use by the U. of Florence/IROE team. The improved pointing accuracy will result in greater altitude resolution of retrieved stratospheric constituent profiles. See also Bonetti and Carli, 85-543.

Dr. P. T. WOODS -- National Physical Laboratory, England -- 82-403, 82-432. Balloon Intercomparison Program.

See Ogawa and Iwagami -- 82-391 and 82-438.

Drs. P. T. WOODS, S. POLLITT, M. J. BANGHAM, R. H. BRADSELL, D. G. MOSS, and N. R. SWANN -- National Physical Laboratory, England -- 82-394, 82-433. Balloon Intercomparison Campaign.

See Ogawa and Iwagami -- 82-391 and 82-438.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

Dr. R. A. YOUNG -- Xonics, Inc. -- 75-50, 75-86. Development of an Instrument to Measure O, ClO, O_3, and Total Cl in the Stratosphere (completed).

A preliminary evaluation of resonance fluorescence for the stratospheric measurement of ClO and total chlorine was made during the September, 1975, STRATCOM balloon flight. This work and subsequent laboratory work indicated that alternative methods for these measurements hold greater near-term promise.

Dr. R. ZANDER -- University of Liege, Belgium -- 76-141, 78-232. Ground-based Infrared Measurements (completed).

The 7.5-meter focal length double-pass infrared spectrometer at the Jungfraujoch International Scientific Station (altitude 3580 m) was used to monitor atmospheric column densities of HF and HCl. Resolution of the instrument is about 0.02 cm^{-1}. The HF concentration has increased about 10% per year over the Jungfraujoch between the years 1976 and 1983. Similar data from Kitt Peak indicate a 5% per year increase of HF between the years 1969 and 1979. The relative concentration of HF at both stations supports a meridional increase versus latitude. There is no sign of an increase in HCl during the same period although there is a meridional increase versus latitude. Frequently a high variability in the HCl column density, which may be due largely to the troposheric component of the HCl column, was observed.

$ClONO_2$ is qualitatively observable from the ground at 780.21 cm^{-1} in Kitt Peak solar spectra and with the new FTIR instrument at Jungfraujoch. CFC 11, CFC 12, and CFC 22 are also observable in the 8-12 micron region. Better definition of line strength and temperature dependence should also permit measurement of ClO with a ground-based spectrometer. The CH_4 trend above the Jungfraujoch station was determined in the spectral data since 1952.

Dr. R. ZANDER -- University of Liege, Belgium -- 82-395, 82-435. Balloon Intercomparison Campaign.

See Ogawa and Iwagami -- 82-391 and 82-438.

Dr. R. ZANDER -- University of Liege, Belgium -- 82-439, 84-517. Interpretation of Kitt Peak Spectra.

Table 3 (continued)

Tropospheric and Stratospheric Measurements

The Kitt Peak National Observatory data archives have been searched for atmospheric species of interest. These include HNO_3, N_2O, NO, NO_2, HCHOOH, HF, HCl, and CH_4. Revised laboratory data indicate that it should be possible to deduce an upper limit for HOCl.

Observations at the Jungfraujoch have been carried out to investigate the variability of atmospheric trace gases and to refine the trends for CH_4, HCl, and HF.

A Fourier Transform Spectrometer providing a spectral resolution of 0.005 cm^{-1} has been operating at the Jungfraujoch station since the end of 1984. This instrument, although primarily designed for the wave length range 1.5-5.5 μm, has been converted to the more interesting region of 8-13 μm. After optimal performance is achieved, measurements will be taken routinely with higher resolution than can be obtained with the grating instrument.

See Stokes 82-417.

E. Modeling

Dr. G. BRASSEUR -- Institut d'Aeronomie Spatiale, Belgium -- 80-320, 82-396, 83-468, 84-534. Modeling of the CFC Effect on the Ozone Layer.

A one dimensional model that can be used to study the diurnal variations of short lived trace species and to evaluate the variation of atmospheric temperature profiles due to changes in the concentration of the radiative active gases is available. Time-dependent, coupled-perturbation calculations have been performed with several emission scenarios for CFCs, CH_4, N_2O, CO_2, and aircraft NO_x. The calculated changes in total column ozone are less than ± 1% for scenarios simulating the past emission of these trace gases and extrapolating them into the next century. Measured stratospheric CH_3CN profiles were analyzed for use as a tracer for the active chlorine concentration in the upper stratosphere. The unexpectedly slow rate constant for the reaction of Cl with CH_3CN prevented such a use. The model will continue to be used for the evaluation of speculative chemistry, and an improved 2-D model will be developed.

Table 3 (continued)

Modeling

Dr. G. BRASSEUR -- Institut d'Aerononie Spatiale, Belgium -- 84-505. Incorporation of Chemistry into the Free University of Berlin 3-D Model

Cooperation between the two groups is being increased by support of a student from the Free University of Berlin at the Institut d'Aeronomie Spatiale.

Drs. D. M. CUNNOLD, F. N. ALYEA, and R. G. PRINN -- CAP Incorporated -- 75-24, 76-122, 77-199, 78-252, 79-281, 80-323, 81-361, 82-422. Meteorological and Multi-Dimensional Modeling Considerations Relating to Atmospheric Effects of Halocarbons (completed).

Studies to assess the accuracy and shortcomings of the 1-D model used to estimate ozone depletion indicated that a tropospheric lifetime for CFCs 11 and 12 as short as 10 years was not inconsistent with atmospheric measurements. Thus, ozone depletion estimates might be considerably less than present estimates. The great variability of stratospheric measurements indicates that simultaneous measurements for many important stratospheric species are needed and that seasonal dependence of species must be considered.

The neglect of dynamical feedback processes in the radiative models used to calculate warming (greenhouse effect) limits the value of calculated effects. Preliminary calculations have been made including feedback effects due to inclusion of the hydrological cycle and circulatory effects. Preliminary results indicate that inclusion of the hydrological cycle would strongly counteract the greenhouse effect, whereas circulatory changes would slightly increase it.

Because it has been shown that meteorological conditions can cause variations in both tropospheric and lower stratospheric fluorocarbon measurements in Alaska, temporal and latitudinal variability of fluorocarbon concentration has been estimated, and the results related to the sensitivity of trend detection in the Atmospheric Lifetime Experiment (cf. 82-422) and to previous interhemispheric observations.

A preliminary estimate was made for the lifetime of a tropospheric sink due to photodecomposition of CFCs on sand. The sink would imply a lifetime of 30 years if 40% of the CFCs were destroyed over the Sahara Desert.

Table 3 (continued)

Modeling

A methodology was developed for determining the lifetime of tropospheric sinks of CFCs by daily monitoring. This methodology is being implemented under 82-421, 81-376, 81-377, and 83-476.

The surface temperature increase resulting from atmospheric CFC mixing ratios increasing to 2 ppbv has been reestimated at 0.2 ± 0.5°C (95% confidence limits). The significance of its impact is thus extremely uncertain and is only one of a number of factors that could induce climatic change.

M. KINOSHITA -- Mitsubishi Research Institute, Japan -- 83-461. One Dimensional Radiative-Convective Model of the Atmosphere.

This project entails the upgrading and optimization of MRI's 1-D photochemical-eddy diffusion model through inclusion of tropospheric chemistry, development of diurnal capability, inclusion of coupled perturbations, and development of a radiative-convective model.

Development of the reactive-convective model has been completed. Improvements have been made to the 1-D photochemical eddy diffusion model. Efforts are being focused on the coupling of these two models.

Dr. N. D. SZE -- Environmental Research and Technology, Inc. -- 75-32, 76-115. Model Analysis of The Fluorocarbon Problem (completed).

A one-dimensional model has been used to evaluate the role of stratospheric water in the NO_x and ClX cycles, the relationship of eddy diffusion coefficient and CFC lifetime, the use of CFC measurements to calculate lifetime, and the effect of chlorine nitrate. The importance of OH concentration on calculated ozone depletion was shown, and key reactions were identified. Analyses showed 10-20 year tropospheric lifetimes were not inconsistent with measurements and helped to define quantitatively the uncertainties associated with ozone depletion calculations.

Inclusion of multiple scattering in the model had a negligible effect on the ozone depletion estimates. The modeled ozone profile above 40 km is a factor of 2-3 lower than recent measurements. Calculated ClO profiles are a factor of 2-4 too low at 28-35 km when compared with Anderson's ClO data.

Table 3 (continued)

Modeling

A diurnal model has been developed that permits calculation of stratospheric concentration profiles of any HO_x, ClO_x, or O_x species.

> Dr. N. D. SZE -- Atmospheric and Environmental Research, Inc. -- 77-173, 78-234, 79-273, 80-311, 81-366, 82-405, 83-465, 85-523. Theoretical Models of Stratospheric Chemistry, Perturbations, and Trace Gas Measurements (continuation of 76-115).

Iterative procedures, which lower the computer time by a factor of 3 for the diurnal model, have been developed.

The modeled HF/HCl ratios using 1978 rate data are at least a factor of 2 higher than the measured values. A possible explanation is that OH is less than model predictions, thus indicating a greater reservoir of inactive chlorine. If the rate of formation of OClCO is sufficiently rapid, it can constitute a "holding tank" for active chlorine.

Theoretical calculations indicate that the possibility of a 20-year tropospheric sink due to adsorption of CFCs 11 and 12 on desert sand with subsequent photodecomposition by sunlight cannot be ruled out.

A 2-D model with full diurnal capability has been developed with joint CMA FPP and Air Force funding. This represents a substantial upgrading of the 2-D model.

Analysis of the vertical gradient for CFCs 11 and 12 indicates a discrepancy between measured and modeled values. A possible explanation for this discrepancy is that the solar flux in the Herzberg continuum between 200 and 220 nm has been underestimated. A recent measurement of solar irradiance in the stratosphere confirms that the calculated solar flux may indeed be too low. As a result the atmospheric lifetimes of CFCs 11 and 12 would be lowered, which also would reduce the ozone depletion estimate.

The effect of anthropogenic and natural emissions of organic bromine compounds has been considered in the model and found to have a minimal effect on the ozone depletion estimate.

Measurement of C_2H_6 and C_2H_2 can be used to infer local concentrations of HO and Cl, a further check on observed and calculated profiles.

Table 3 (continued)

Modeling

Based on NASA/WMO 1981 recommended rate constants for reaction of OH with HO_2, HO_2NO_2, HNO_3 and on recent remeasurements of the UV absorption cross section of HO_2NO_2, the steady state ozone depletion forecast is now 6%. In addition, there is now better agreement between measured and modeled concentration profiles of key stratospheric species.

Latest model results based on the most recent NASA/JPL recommended values for the rate constants (1982) show a further reduction of the steady state ozone depletion estimate to 3.2%. Calculated ClO at 40 km is now in better agreement with the observations. Further improvement in the agreement between theory and observation is possible if the rate constant for the O + ClO reaction proves to be slower, but the agreement between the calculated and observed ozone in the upper stratosphere becomes much poorer.

A calculation was performed on the effect of coupling the perturbations to the atmosphere of CFCs together with increased emission rates of CH_4, CO_2, N_2O, and NO_x. Results show that at 2010 a slight increase of about 1% in total ozone is calculated, whereas with CFCs alone a 2% decrease is calculated.

There is difficulty in reproducing a pronounced spring ozone maximum at high latitudes. This may reflect overestimation of NO_2 by the model as evidenced from comparison with the observed low concentration of NO_2 in winter at high latitudes.

Detailed calculations of the diurnal variations of stratospheric trace species have been performed. The model-predicted diurnal variations of column densities of ClO above 30 and 40 km are in good agreement with the de Zafra, Solomon, et al., 1984 observations. It is argued that observation of the diurnal behavior of stratospheric ClO can place important constraints on the chemistries of HOCl and $ClONO_2$. This is significant because so far there has been no definitive detection of these last two species.

A new tracer transport scheme has been developed in isentropic coordinates with advective transport driven by diabatic circulation and with eddy transport parameterized by a single horizontal diffusion coefficient, K_{yy}. Calculations of the latitudinal and vertical distributions of N_2O and

Table 3 (continued)

Modeling

HNO_3 based on this new transport scheme are in good agreement with observation.

Having the validity of the new transport formulation established permitted the full chemical scheme (including the diurnal code) to be interfaced with the new 2-D model. The calculated distribution of ozone (both seasonal and latitudinal) is in significantly better agreement with observations than with the older version of the AER 2-D model.

The refined new 2-D model has been used for interpreting new field data (e.g., BIC data) and for assessing ozone perturbations due to future increases of CFCs and other gases.

The nonlinear response of ozone to stratospheric chlorine perturbations has been investigated using the AER 1- and 2-D models. Various factors contributing to the nonlinear chemistry/perturbations have been identified and assessed. The amount of stratospheric NO_x is among one of the most critical contributing factors. The onset of nonlinear chemistry occurs as the amount of stratospheric ClX approaches that of NO_x.

Slow reactions that might be of importance to stratospheric chemistry have been identified and assessed. They include reactions such as $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$; $N_2O_5 + H_2O \rightarrow 2HNO_3$; $HNO_4 + H_2O \rightarrow HNO_3 + H_2O_2$; $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$; and $H_2O + O_3 \rightarrow H_2O_2 + O_2$. These reactions could have considerable impact on stratospheric chemistry if their rate constants lie between 10^{-23} and 10^{-16} $cm^3 molec^{-1} s^{-1}$.

Preliminary 2-D model results show that the calculated amounts of column ozone reduction are in direct proportion to stratospheric chlorine abundances (from 0 to 15 ppb range). These results are in sharp contrast to 1-D model calculations, which exhibit significant nonlinear response of column ozone to stratospheric chlorine perturbations.

Dr. W. C. WANG -- Atmospheric and Environmental Research, Inc. -- 84-518. Possible Climatic Effect of Atmospheric Trace Gases.

The studies of Wang and Sze (see 83-448) were extended by the use of a 2-D (altitude-latitude) radiative-dynamical model developed by one of the investigators. Major findings are: the thermal radiation flux perturbations caused by increase of carbon dioxide that result in climate change are different in nature from those caused by other trace gases; use of the 2-D model yields more realistic temperatures and humidity distributions than does use of the 1-D model; in spite of its limitations, use of the 1-D model leads to surface warming effects when using the moist-adiabatic critical lapse rate, which are in close agreement with those obtained by the 2-D model.

Using the 2-D model and scenarios which they describe, the investigators calculate potential surface warming effects of the various trace gases.

> Drs. W. C. WANG and N. D. SZE -- Atmospheric and Environmental Research, Inc. -- 83-448. Modeling Climatic Effects of CFCs and O_3 (completed).

This work encompassed modeling studies of the effects of CFCs, O_3, and other atmospheric trace gases on the temperature at the surface of the earth and at various levels above the surface.

Using a one-dimensional radiative-convective-photochemical model developed by the investigators, they addressed direct surface warming effects of CFCs, potential combined effect of CFCs and O_3 on surface temperature, sensitivity of climatic effects of CFCs and O_3 to model physical parameterization, and potential combined climatic effects due to emissions of CFCs, CO_2, N_2O, CH_4, NO_x, and O_3. The investigators found that, for the scenario they used covering the period 1980 - 2010, CO_2 contributed a surface warming effect of 0.4 K, and an additional surface warming effect of 0.4 K can be attributed roughly equally to the direct radiative effect of NO_x, CFCs, CH_4, and N_2O and to the indirect radiative effect associated with O_3 redistribution.

F. Other

> Dr. M. J. BAILEY -- University of Maryland -- 80-317. Uncertainties and Benefit-Cost Analysis of CFC Control (completed).

A recently concluded, EPA-funded analysis of the potential costs and benefits of CFC control has been expanded and

Other

further refined. The new study takes into account recent revisions in atmospheric models and projected future changes in atmospheric composition. Although the range of possible outcomes is broad, indications for the most likely case are that the benefits of unregulated fluorocarbon use will outweigh any of their harmful effects.

Drs. D. BERGER and F. URBACH -- Temple University -- 75-62, 82-414. Ground-Level Monitoring of Ultraviolet Solar Radiation (completed).

The monitoring of solar ultraviolet radiation, which was initiated by the Climatic Impact Assessment Program (CIAP) and subsequently funded for one year by CMA FPP, was then supported by NOAA with EPA funds. It was again funded by CMA FPP for the period January 1 - June 30, 1983.

Dr. F. O. CLARK -- University of Kentucky at Lexington -- 84-530. Collection and Analysis of Stellar Photometry Data.

This project entails collection of world-wide stellar photometry data, which will be used to correct past and future Umkehr ozone data for aerosol effects. At present, solar transmission data taken at Mauna Loa, Hawaii, are assumed to be representative world-wide and are applied to the measurements taken from other stations in the network.

A feasibility study was carried out under a NOAA subcontract (see 83-466), to determine whether sufficient data sets were available. Data have been collected from over 14 astronomical observatories, which span a latitude range of 33°S to 60°N. Lengths of these data sets vary from 1-31 years. The data are being processed in a form suitable for use in correcting unknown data for aerosol effects.

Dr. J. J. DeLUISI -- National Oceanic and Atmospheric Administration, Boulder -- 83-466. Umkehr Aerosol Corrections.

This project entails collection of world-wide solar transmission and lidar measurements, which will be assimilated into a data set for the purpose of correcting past and future Umkehr ozone data for aerosol effects. At present, solar transmission data taken at Mauna Kea, Hawaii, are assumed to be

Table 3 (continued)

Other

representative of the global scale and are applied to the measurements taken from other stations in the world-wide network.

Dr. Frank Clark was given a subcontract to determine whether there were sufficient stellar photometry data sets available in order to derive the latitudinal and temporal variations of the solar transmission data. He has been able to locate many observatories that have made stellar photometry measurements continuously. Collection and analysis of these data sets are being carried out through a contract between Dr. Clark and CMA (see 84-530).

Because there were difficulties in obtaining personnel to perform any additional aspects of this work (over and above stellar photometry), the contract was terminated by mutual consent.

> Drs. E. PARZEN and M. PAGANO -- Frontier Science and Technology Research Foundation, Inc. -- 76-106. Total World Ozone Level: Statistical Analysis (completed).

Ozone column measurements from at least 20 stations have been evaluated statistically to detect trends in recorded ozone concentrations and to establish the limits of detection for such trends. Time series analysis has been shown to be substantially more sensitive in detecting non-random ozone changes than the estimates of such sensitivity made by the Federal Task Force on Inadvertent Modifications of the Stratosphere (IMOS) in 1975. Analysis of ozone data from 9 stations shows that no detectable abnormal trend in the ozone data has occurred over the period 1970-75. The absence of detectable trends provides an upper limit for actual depletion and a test of model predictions.

If sufficient sensitivity is achieved, this technique will enable an effective early warning system for ozone depletion to be established.

> Dr. J. A. PYLE -- Rutherford Appleton Laboratory, England -- 83-456, 84-511. Diurnal Variations by Comparisons of Field Data and Calculations.

The 2-D model developed at Oxford University has been updated and transferred to the Rutherford Appleton Laboratory. It is being used to study diurnal variations of stratospheric

Table 3 (continued)

Other

species by detailed comparison of field data (from balloon and satellite instruments) and numerical model calculations.

> Drs. G. C. TIAO and G. REINSEL -- University of Chicago (formerly University of Wisconsin); University of Wisconsin -- 78-250, 80-304, 81-374, 83-462. Statistical Analysis of World-wide Stratospheric Ozone Data for the Detection of Trend.

Ground-based and satellite total column ozone and profile ozone data have been analyzed using statistical time series analysis. For the fourteen-year period 1970-1983, the average change in total ozone based on 36 Dobson stations is (-0.17 ± 1.10)%/decade. The error limits are 95% confidence limits. The analysis takes into account instrumental shifts and solar variability. The change is not statistically significant.

In an analysis of Umkehr ozone profile data through 1981 from 13 Dobson stations, changes of -3.2 ± 3.30%/decade in layer 9 (43-48 km), -3.2 ± 1.7%/decade in layer 8 (38-43 km), -2.6 ± 1.7 %/decade in layer 7 (34-38 km), +0.3 ± 1.6%/decade in layer 6 (29-34 km), and -0.3 ± 1.6%/decade in layer 5 (24-29 km) are estimated. Corrections for aerosol volcanic effects using Mauna Loa, Hawaii, atmospheric transmission data, for instrument problems, and for solar activity are included in the trend models. The trends in layers 7 and 8 are statistically significant. Layers 1-5 have also been analyzed, with a statistically significant change of +8.7 ± 7.6%/decade seen in layer 1 (5-10 km). The estimated changes in the Umkehr profile are not inconsistent with chemical model calculations for coupled perturbation effects.

A preliminary analysis of balloon ozonesonde data has been made for trends in the region below 33 km during the period 1970-1982 at 13 stations. In the 15-20 km region, significant changes of -6.9 ± 3.0%/decade in layer 3A and -5.0 ± 3.4%/decade in layer 3B are not consistent with chemical model calculations, which show little or no change. A significant positive change of +8.3 ± 8.2%/decade was found for layer 1A and +6.7 ± 5.6%/ decade for layer 1B, as was the case with Umkehr data. The impact of instrumental problems on the trend estimates is being investigated.

The first four years of Nimbus 7 satellite ozone data (1978-82) have been analyzed. Results for this limited period of time show significant positive trends in layers 5

Table 3 (continued)

Other

and 6 and significant negative trends in layers 9 and 10. The satellite data also indicate that there is good global representation with the Umkehr network for this period. Earlier studies with Nimbus 4 satellite data (1970-1977) show good global representation over the period for both the 13 station Umkehr network and the 36 station Dobson total ozone network used in the trend studies.

Ozone changes associated with solar effects are observed to be a factor of two to four less than those calculated by the chemical models for the upper profile (layers 5-9) and the total column.

Dr. G. S. WATSON -- Princeton University -- 78-257, 81-360; Drs. G. S. WATSON and G. W. OEHLERT -- Princeton University -- 82-409, 83-477. Statistical Investigations of the CFM Problem.

Total column ozone data through 1982 from 36 Dobson stations are analyzed for trends. After correction is made for instrument shifts and solar variability, the trend is (-0.59 ± 1.16)%/decade. The estimate is not statistically significant. One possible interpretation for the change in sign upon inclusion of the solar flux variation is that ozone has increased during 1970-1981 but not as much as the solar curve would predict.

An alternative method has been developed for examining the Umkehr data for trends in the ozone profile. This scheme uses noninverted N values from the Umkehr observations and determines changes in the shape of these values as a function of solar zenith angle. The analysis has been carried out using the linear part of the N values curve. Use of a hockey stick CFC depletion curve and a proxy (atmospheric transmitance) for atmospheric aerosols indicates that the estimated change is -9.2% at 40 km for the period 1970-1980. The result is not statistically significant.

The data base of 1957-1979 atmospheric temperatures (radiosondes) covering the pressure range of 30 to 850 mb has been examined. The objective was to see if stratospheric cooling was occurring as predicted from the CO_2 build-up. The analysis shows that a relative change in the temperature profile of the atmosphere is occurring with approximately the shape predicted by the atmospheric models. The analysis

Table 3 (continued)

Other

shows a cooling pattern above and a warming pattern below 12 km.

Dr. S. ZEGER -- Johns Hopkins University -- 83-460.
Dose Response of Nonmelanoma Skin Cancer to UV Light.

The purpose of this study is to validate current estimates of dose-response relationship between ultra-violet light and non-melanoma skin cancer.

The available literature on the relationship between non-melanoma skin cancer (NMSC) and ultraviolet radiation (UV) has been summarized. The study provides an overview of the subject together with detailed listings of papers on epidemiologic studies and laboratory animal studies. Furthermore, it provides a statistical critique of the 1981 epidemiological study by Scotto, et al.

Among the major findings are:

1) Clear and conclusive evidence that the incidence rate for NMSC increases with increasing exposure to UV.

2) Several potentially important variables have not yet been included in estimates of the biological amplification factor, which relates NMSC incidence rate to increase in UV intensity. In particular, those estimates that are based on the assumption of reciprocity are not suitable for analyzing data from epidemiological studies.

3) Squamous cell NMSCs have a stronger UV dependence than the more prevalent basal cells.

The report also identifies major issues needing further scientific consideration.

G. Consultants

Dr. J. G. Anderson	Harvard University	Stratospheric Measurements
Dr. A. W. Castleman, Jr.	Pennsylvania State University	Heterogeneous Chemistry

Table 3 (continued)

Consultants

Dr. F. O. Clark	University of Kentucky	Millimeter Wavelength Spectroscopy
Dr. W. C. Gardiner, Jr.	University of Texas	Chemical Kinetics
Dr. W. L. Gates	Oregon State University	Effects: Climate
Dr. D. R. Herschbach	Harvard University	Homogeneous Chemistry, Kinetics, and Spectroscopy
Dr. W. Klemperer	Harvard University	Kinetics and Atmospheric Spectra
Dr. J. E. Lovelock	Private	Atmospheric Measurements
Dr. D. G. Murcray	University of Denver	Stratospheric Measurements
Dr. J. H. Shaw	Ohio State University	Atmospheric Spectra
Dr. L. E. Snyder	University of Illinois	Millimeter Wavelength Spectroscopy
Dr. P. H. Stone	Massachusetts Institute of Technology	Effects: Climate
Dr. F. Urbach	Temple University	Effects: Human
Dr. R. T. Watson	NASA	Chemical Kinetics and Photochemistry

June 1, 1985

Table 4A

Research Funded by the Chlorofluorocarbon Industry

and

Administered by the Chemical Manufacturers Association

WORK COMPLETED*

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Investigation of spectroscopy of and photochemical changes in fluorocarbons	Sandorfy	U. of Montreal	73-2	10/11/74
Monitoring of fluorocarbons in the atmosphere and simulation of atmospheric reactions of fluorocarbons[b]	Taylor	U. of California, Riverside	73-3	10/16/74
Measurement of fluorocarbons in the atmosphere[b]	Lovelock	U. of Reading	73-1	10/27/74
Laboratory investigation of the feasibility of measuring ClO in the atmosphere by the chemical conversion-resonance fluorescence detection method	Stedman	U. of Michigan	74-7	2/28/75
Laboratory determination of sensitivity of laser-induced fluorescence for the detection of ClO under atmospheric conditions	Davis	U. of Maryland	74-10	5/31/75
Continuation of 73-3[b]	Pitts	U. of California, Riverside	74-2	12/31/75
ntinuation of 73-1[b]	Lovelock	U. of Reading	74-3	12/31/75
Investigation of ion-molecule reactions involving chlorofluorocarbons	Mohnen	SUNY-Albany	75-64	4/1/76
Development of an instrument to measure O, ClO, O_3, and total Cl in the stratosphere[b]	Young	Xonics, Inc.	75-50	4/7/76

(continued)

---

*Copies of final reports are available upon request to Fluorocarbon Program Manager, Chemical Manufacturers Association, 2501 M Street, NW, Washington, DC 20037.

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Measurement of fluorocarbons and related chlorocarbons in the stratosphere and upper troposphere[b]	Rasmussen	Washington State U.	75-2	4/15/76
Continuation of 74-2	Pitts	U. of California, Riverside	75-12	4/15/76
Investigation of the destruction of chlorofluoromethanes by naturally occurring ions	Campbell	Washington State U.	75-53	4/23/76
Ground-based millimeter wavelength observations of stratospheric ClO	Ekstrom	Battelle Northwest	75-27	5/24/76
Laboratory and theoretical studies of the ultraviolet and visible electronic spectra of ClO[b]	Nicholls	York U.	75-11	6/14/76
Modeling of the fluorocarbon-ozone system[b]	Sze	ERT, Inc.	75-32	8/18/76
Critique of models used to estimate chlorofluorocarbon effects on ozone[b]	Cunnold, Alyea, Prinn	CAP Associates	75-24	9/10/76
Studies of reactions of HO_2 by laser magnetic resonance	Thrush	U. of Cambridge	75-58	11/8/76
Continuation of 75-50	Young	Xonics, Inc.	75-86	11/15/76
Measurement of stratospheric distribution of fluorocarbons and related species by infrared absorption spectroscopy[b]	Murcray	U. of Denver	75-13	1/24/77
Measurement of reaction rates relevant to the fluorocarbon-ozone problem[b]	Birks	U. of Illinois	75-1	2/4/77
Measurement of OH in the stratosphere by laser induced fluorescence	Davis	U. of Maryland	75-87	2/23/77

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Exploration for unidentified factors in the fluorocarbon-ozone problem[b]	Lovelock	Private	75-67	3/10/77
Laboratory studies of the infrared vibration-rotation spectrum of ClO	Nicholls	York U.	75-30b	3/25/77
Absolute calibration of fluorocarbon measurements	Stedman	U. of Michigan	76-132	4/1/77
Collection and analysis of Antarctic ice cores	Rasmussen	Rasmussen Assoc.	75-84	4/19/77
The electron capture detector s a reference standard in the analysis of atmospheric halocarbons	Lovelock	Private	76-120	5/3/77
Laboratory measurement of spectroscopic absorption cross sections of ClO	Davis	U. of Maryland	75-73	5/12/77
Measurement of fluorocarbon content of "antique" air samples	Rasmussen	Washington State U.	75-71	9/2/77
Measurement of HCl and HF in the stratosphere by Fourier transform spectroscopy[b]	Buijs	Bomem, Inc.	75-98	9/26/77
Continuation of program for ground level monitoring of ultraviolet solar radiation[b]	Berger	Temple U.	75-62	10/20/77
Continuation of 75-1[b]	Birks	U. of Illinois	76-117A	12/12/77
tudies of heterogeneous reactions[b]	Birks	U. of Illinois	76-117B	12/12/77
eteorological and multi-dimensional modeling considerations relating to atmospheric effects of halocarbons[b]	Cunnold, Alyea, Prinn	CAP Associates	76-122	12/12/77
Climatic effects of fluorocarbons[b]	Cunnold, Alyea, Prinn	CAP Associates	76-122S	12/12/77

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Electron spin resonance detection of stratospheric radicals	Ehhalt	Nuclear Research Establishment - Juelich	76-145	12/12/77
Measurement of the concentration of methyl chloride in air in Kenya	Rasmussen	Private	77-181	12/12/77
Continuation of 75-67[b]	Lovelock	Private	77-144	12/23/77
Kilauea volcanic emissions--halocarbon measurement	Rasmussen	Oregon Graduate Center	77-215	12/27/77
Laboratory determination of the feasibility of laser magnetic resonance for ClO detection and reaction studies	Howard	NOAA-Boulder	75-47	1/10/78
Photochemical and chemical kinetic measurements of stratospheric importance with respect to the fluorocarbon issue[b]	Timmons	Catholic U.	76-129	1/16/78
Laboratory measurement of high resolution infrared spectra of chlorine-containing molecules of stratospheric interest[b]	Murcray	U. of Denver	75-92	2/10/78
Reactions of the HO_2 radical studied by laser magnetic resonance	Thrush	U. Of Cambridge	75-58 II	3/2/78
Construction of Fourier transform spectrometer	Buijs	Bomem, Inc.	75-90	3/8/78
Interlaboratory comparisons of fluorocarbon measurements[b]	Rasmussen	Private	76-142	3/8/78
Generation and exchange of calibrated samples of fluorocarbons	Stedman	U. of Michigan	77-151	3/10/78
Laboratory investigation of the heterogeneous interaction of Cl and ClO with H_2SO_4[b]	Martin	Aerospace Corp.	75-81	3/27/78

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Continuation of 75-32[b]	Sze	ERT, Inc.	76-115	3/28/78
udies of compounds of sulfur, oxygen, and chlorine[b]	Kaufman	Emory U.	76-126	5/24/78
Total world ozone level: statistical analysis	Parzen, Pagano	Frontier Science and Technology Research Foundation, Inc.	76-106	5/25/78
Stratospheric measurement of ClO and OH	Murcray	U. of Denver	76-135	5/30/78
Laboratory study of the UV and IR spectra of HOCl, $HOONO_2$, and $HClO_4$ in the temperature range of the stratosphere	Knauth	U. of Kiel	77-171	6/14/78
Photochemistry of small chlorinated molecules[b]	Wiesenfeld	Cornell U.	76-128	7/5/78
Continuation of 75-2	Rasmussen	Washington State U.	75-59	8/10/78
Atmospheric chemistry of peroxynitric acid	Pitts	U. of California, Riverside	77-190	11/13/78
Continuation of 75-81	Martin	Aerospace Corp.	75-81 II	12/6/78
Ground-based infrared measurements[b]	Zander	U. of Liege	76-141	12/11/78
Measurements of HCl, HF, ClO, etc., in the stratosphere by high resolution infrared spectroscopy	Girard	ONERA-France	75-88	1/2/79
Coordination and analysis of data for atmospheric lifetime experiment[b]	Cunnold, Alyea, Prinn	CAP Associates	77-213	2/13/79
urement of fluorocarbons d related chlorocarbons the stratosphere by llection and analysis	Ridley	York U.	76-102	2/26/79
inuation of 76-122[b]	Cunnold, Alyea, Prinn	CAP Associates	77-199	2/26/79

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Operation of stations at Adrigole and Barbados for atmospheric lifetime experiment[b]	Lovelock, Simmonds	Private	77-193	2/28/79
Operation of stations in American Samoa and Tasmania for atmospheric lifetime experiment[b]	Rasmussen	Oregon Graduate Center	77-201	3/29/79
Development of primary fluorocarbon standards	Lovelock	Private	78-226	4/2/79
Experimental investigation of the branching ratio in the $O(^1D) + H_2O$ reaction	Zellner	U. of Goettingen	77-195	4/12/79
Acquisition of on-board digital recording system	Murcray	U. of Denver	77-211	4/12/79
Theoretical models of stratospheric chemistry, perturbations, and trace gas measurements[b]	Sze	AER, Inc.	77-173	4/17/79
Determination of the photodissociation process and absorption cross section of FC-11 and 12 in the near UV	Stuhl	U. of Bochum	77-170	5/3/79
Continuation of 76-129[b]	Timmons	U. of Texas, Arlington	77-214	6/15/79
Total chlorine measurements in the troposphere and stratosphere	Eggleton	AERE Harwell	76-116	7/6/79
Millimeter wave observations of chlorofluoromethane byproducts in the stratosphere[b]	Solomon, deZafra	SUNY Stony Brook	76-130	7/6/79
Continuation of 76-126	Kaufman	Emory U.	77-197	7/6/79
Photoabsorption cross sections for compounds of atmospheric interest	Takacs	Rochester Inst. Technol.	77-196	7/24/79

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Lower stratospheric measurement of non-methane hydrocarbons	Rasmussen	Private	76-140	7/30/79
Laboratory study for determination of the equilibrium constant of the reaction $Cl_2O + H_2O = 2\ HOCl$ and the UV spectrum of HOCl	Knauth	U. of Kiel	77-224	8/9/79
Effect of aerosol scattering on ozone measurements with the Dobson spectrophotometer	Moe	Private	78-235	9/12/79
Continuation of 75-92[b]	Murcray	U. of Denver	77-152	10/17/79
Studies of reactions of importance in the stratosphere[b]	Birks	U. of Colorado	77-192	11/8/79
Photodegradation of chlorofluoromethanes in the troposphere	Korte	U. of Munich	77-194	11/16/79
Follow-up for photodecomposition of chloromethanes absorbed on silica surfaces[b]	Ausloos	NBS	77-186	11/28/79
Continuation of 77-213[b]	Cunnold, Alyea, Prinn	CAP Associates	78-251	12/17/79
Continuation of 77-199[b]	Cunnold, Alyea, Prinn	CAP Associates	78-252	1/18/80
Continuation of 76-128	Wiesenfeld	Cornell	77-220	2/1/80
Measurement of halogen compounds for determination of total chlorine and total fluorine in the stratosphere using long-path interferometric spectroscopy	Buijs	Bomem, Inc.	77-168	2/4/80

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Determination of a measurement system for the determination of total chlorine in air	Skogerboe	Colorado State U.	77-206	2/4/80
Identification of FC 21 in the atmosphere	Rasmussen	Oregon Graduate Center	78-260	2/5/80
Continuation of 76-130[b]	Solomon, deZafra	SUNY Stony Brook	77-225	2/13/80
Continuation of 77-193[b]	Lovelock, Simmonds	Private	78-243	2/18/80
Continuation of 77-192[b]	Birks	U. of Colorado	78-244	2/20/80
Laser magnetic resonance study of HO_2 chemistry	Howard	NOAA-Boulder	76-100	3/12/80
Study of ClO chemistry by laser magnetic resonance	Howard	NOAA-Boulder	77-223	3/12/80
Continuation of 77-201[b]	Rasmussen	Oregon Graduate Center	78-248	4/24/80
Development and implementation of a simplified multidimension model for stratospheric chemistry perturbations, radiation feedback and trace gas measurement[b]	Sze	AER, Inc.	78-234	5/14/80
Continuation of 77-142	Rasmussen	Oregon Graduate Center	78-247	5/28/80
Detection of selected molecules by ground-based solar spectroscopy	Murcray	U. of Denver	78-228	5/29/80
Analysis of Release of FC-11 from Rigid Plastic Foam Products in the U.S.	Shamel	A. D. Little, Inc.	79-275	5/29/80
Effectiveness of various untreated sand surfaces bringing about the oxidation of CCl_4, $CFCl_3$, and CF_2Cl_2	Ausloos	NBS	78-254	6/6/80

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
The exponential dilution chamber for the calibration of instruments and the preparation of standards[b]	Lovelock	Private	78-264	7/9/80
Rates of reaction of Cl atoms with the primary products of alkane photooxidation	Kurylo	NBS	78-233	9/4/80
Determination of FC-21 and other halocarbons in the troposphere	Bruner	Urbino U.	78-256	9/23/80
Determination of atomic oxygen yields in the photolysis of HOCl and ClOO	Phillips	U. of Canterbury (N.Z.)	78-241	9/30/80
Submillimeter-infrared balloon experiment[b]	Bonetti, Carli, Harries	CNR-IROE, U. of Florence, National Physical Laboratory	76-137	11/6/80
Continuation of 78-243[b]	Simmonds	Private	79-280	12/22/80
Continuation of 78-248[b]	Rasmussen	Oregon Graduate Center	79-279	12/29/80
Operation of Fifth ALE Station, Cape Meares, OR[b]	Rasmussen	Oregon Graduate Center	78-263	1/5/81
Combination and continuation of 78-251 and 78-252[b]	Cunnold, Alyea, Prinn	CAP Associates	79-281	1/5/81
The $A^2 \pi_i \leftarrow X^2 \pi_i$ Band System of ClO[b]	Coxon	Dalhousie U.	78-255	1/22/81
Statistical analysis of worldwide stratospheric ozone data for the detection of trends[b]	Tiao, Reinsel	U. of Wisconsin	78-250	1/26/81
Continuation of 78-244[b]	Birks	U. of Colorado	79-276	1/27/81

(Continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Determination of tropospheric halocarbons and their relative importance	Simmonds, Lovelock	Private	79-269	3/10/81
Laboratory measurement of infrared spectra of selected stable molecules	Buijs	Bomem, Inc.	77-221	3/11/81
Continuation of 77-225[b]	Solomon, deZafra	SUNY Stony Brook	79-278	4/6/81
Continuation of 75-11	Nicholls	York U.	75-11 II	4/27/81
Continuation of 78-234[b]	Sze	AER, Inc.	79-273	5/28/81
Continuation of 78-264	Lovelock	Private	80-293	5/29/81
Simultaneous balloon flight with J. G. Anderson	Murcray	U. of Denver	77-166	6/8/81
F-22 measurements in the atmosphere	Rasmussen	Private	80-308	6/8/81
Uncertainties and benefit cost analysis of CFC control	Bailey	U. of Maryland	80-317	10/20/81
Statistical investigations of the CFM problem[b]	Watson	Princeton U.	78-257	10/21/81
Continuation of 77-152[b]	Murcray	U. of Denver	78-265	10/30/81
Continuation of 79-281[b]	Cunnold, Alyea, Prinn	CAP Associates	80-323	11/23/81
Continuation of 79-280[b]	Simmonds	Private	80-324	1/27/82
Operational costs for flights planned in 1977	Buijs	Bomen, Inc.	77-156	3/22/82
Continuation of 79-273[b]	Sze	AER, Inc.	80-311	4/20/82
Continuation of 80-325	Rasmussen	Oregon Graduate Center	81-376	4/20/82

(Continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Continuation of Part of 80-323	Rosen	ERT, Inc.	81-377	4/26/82
An intercomparison of measurements of stratospheric HCl	Murcray, Roscoe	U. of Denver, Oxford U.	80-328	6/1/82
Continuation of 79-278[b]	Solomon, deZafra	SUNY Stony Brook	80-316	6/2/82
Continuation of 78-263 and 79-279	Rasmussen	Oregon Graduate Center	80-325	6/2/82
Joint Calibration Study of F-21	Bruner	Urbino U.	81-365	6/2/82
eling of the CFC effect on the ozone layer[b]	Brasseur	Institut d'Aeronomie Spatiale	80-320	6/3/82
Development of technique for measuring total chlorine content of air	Howard, Birks, Fehsenfeld	NOAA-Boulder/ U. of Colorado	77-222	6/15/82
Absorption measurements of HOCl and related molecules	Timmons	U. of Texas, Arlington	78-258	6/15/82
Continuation of 79-276[b]	Birks	U. of Colorado	80-321	6/28/82
Continuation of 79-276[b]	Birks	U. of Colorado	80-329	6/28/82
Measurement of the Vertical Distribution of HCl, O_3, and HCHO and the ratio HF/HCl	Jouve	U. of Reims	79-290	7/30/82
-infrared laboratory spectroscopy of halogen-containing molecules[b]	Traub, Chance	Smithsonian Astrophysical Observatory at Harvard	80-318	8/20/82
Continuation of 78-250[b]	Reinsel, Tiao	U. of Wisconsin	80-304	10/26/82
Millimeter Measurements and Spectral Predictions	Lovas, Suenram	NBS	81-350	11/18/82

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Continuation of 80-323[b]	Cunnold, Alyea, Prinn	CAP Inc.	81-361	12/03/82
Continuation of 80-324[b]	Simmonds	Private	81-370	12/21/82
Yield of Atomic Oxygen from HOCl Photolysis	Phillips	U. of Canterbury (N.Z.)	81-342	12/29/82
Continuation of 76-137	Bonetti Carli	U. of Florence, CNR-IROE	80-297	2/7/83
Reactions within the HO_x cycle	Kurylo	NBS	80-307	2/14/83
Joint Calibration Study of F-21	Rasmussen	Oregon Graduate Center	81-356	2/22/83
Near- and Far-Infrared Spectroscopy	Saykally	U. of California, Berkeley	80-300	5/12/83
Comparison of Umkehr and Microwave Ozone Profiles	Duetsch Kuenzi	ETH, U. of Bern	81-371	5/13/83
Atmospheric Monitoring of F-21	Bruner	Urbino U.	80-330	5/24/83
IR Laser Investigation of Halogen Species	Burrows, Cox	AERE, Harwell	80-334	5/24/83
Laboratory Studies of Stratospheric Reactions[b]	Ravishankara	Georgia Tech.	81-368	5/24/83
Continuation of 80-316[b]	Solomon, deZafra	SUNY Stony Brook	81-362	6/22/83
Continuation of 75-13	Murcray	U. of Denver	76-101	6/24/83
Continuation of 78-255	Coxon	Dalhousie U.	80-315	7/18/83
Continuation of 78-257[b]	Watson	Princeton U.	81-360	7/26/83
Continuation of 80-311[b]	Sze	AER, Inc.	81-366	8/16/83

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Continuation of 81-366[b]	Sze	AER, Inc.	82-405	8/16/83
Collaborative studies on atmospheric spectroscopy[b]	Goldman, Barbe	U. of Denver, U. of Reims	80-322	8/23/83
Continuation of 75-62	Urbach	Temple U.	82-414	8/23/83
Reaction of ClO with OH	Donovan	U. of Edinburgh	79-286	9/9/83
Reaction of OH with ClO	Ravishankara	Georgia Tech.	80-295	9/12/83
Quantitative Infrared Line Strengths for O_2[b]	Zahniser, Kolb	Aerodyne Research, Inc.	81-355	9/13/83
Equilibrium Constant for OClOO Formation	Zellner	U. of Goettingen	80-331	10/28/83
Continuation of 80-318[b]	Traub, Chance	Smithsonian Astrophysical Laboratory at Harvard	81-375	10/28/83
Continuation of 76-141[b]	Zander	U. of Liege	78-232	11/7/83
Continuation of 78-265[b]	Murcray	U. of Denver	81-364	11/7/83
Continuation of 80-321, 80-329[b]	Birks, Sievers	U. of Colorado	81-358	1/20/84
Continuation of 81-361[b]	Cunnold, Alyea, Prinn	CAP, Inc.	82-422	1/20/84
Airborne Millimeter Wave Determination of ClO	Beckman	Queen Mary College, London	79-282	3/15/84
Reactions of HO_2 Radicals	Thrush	U. of Cambridge	81-378	4/13/84
tinuation of 80-320[b]	Brasseur	Institut d'Aeronomie Spatiale	82-396	4/13/84

(continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Kitt Peak Observations with Balloon Intercomparison Campaign	Stokes	Battelle Northwest	82-397	4/30/84
Chemistry of Halogen Species Using IR Diode Laser Spectroscopy	Cox	AERE Harwell	82-400	5/29/84
Continuation of 81-360[b]	Watson, Oehlert	Princeton U.	82-409	5/29/84
ALE Participation	Fraser	CSIRO	82-415	5/29/84
Continuation of 81-370	Simmonds	Private	82-421	5/29/84
Continuation of 80-304[c]	Reinsel, Tiao	U. of Wisconsin	81-374	7/3/84
Kinetic Studies of Stratospheric Chlorine Chemistry	Howard	NOAA-Boulder	79-289	7/17/84
Gas Phase Reaction of NaOH with HCl[b]	Silver, Zahniser, Kolb	Aerodyne Research, Inc.	82-401	8/15/84
Continuation of 81-362[c]	Solomon, deZafra	SUNY Stony Brook	82-410	9/22/84
Continuation of 81-375[c]	Traub, Chance	Smithsonian Astrophysical Laboratory at Harvard	82-445	9/26/84
Publication of High Resolution Laboratory Spectra	Murcray	U. of Denver	82-413	10/23/84
Laboratory Spectroscopic Studies of Stratospheric Gases	Ballard	RAL	82-444	12/10/84
Continuation of 81-364	Murcray	U. of Denver	82-423	12/27/84
Identification of Photodissociation Products by REMPI	Steimle	U. of Oregon	82-418	3/4/85

(Continued)

Table 4A (continued)

Program	Investigator	Organization[a]	Proposal Number	Completion Date
Modeling Climatic Effects of CFCs and O_3	Wang, Sze	AER, Inc.	83-448	4/4/85
Balloon Intercomparison Campaign	Ogawa, Iwagami	U. of Tokyo	82-391	4/5/85
Pressure and Temperature Dependence of $HO + HO_2NO_2$	Becker	U. of Wuppertal	83-455	4/5/85
Automation of Dobson Spectrophotometer for Umkehr Measurements	Komhyr, Grass, Evans, Chopra	NOAA-Boulder, U. of Colorado	81-363	4/30/85
Photoabsorption Cross Section of O_2 in the 192-204 nm region[c]	Freeeman, Yoshino, Parkinson	Harvard U.	82-412	4/30/85
Continuation of 81-358[c]	Birks	U. of Colorado	82-425	4/30/85
Latitudinal Variations of Several Compounds[b]	Murcray	U. of Denver	81-380	c
Balloon Intercomparison Campaign	Zander	U. of Liege	82-395	c
Continuation of 81-368[c]	Ravishankara	Georgia Tech.	83-449	c

---

a. Abbreviated affiliations are expanded under study descriptions in Table 3.

b. Work continued in a follow-on contract.

Final report accepted by the Panel.

June 1, 1985

Table 4B

Research Funded by the Chlorofluorocarbon Industry

and

Administered by the Chemical Manufacturers Association

WORK IN PROGRESS

Program	Investigator	Organization[a]	Proposal Number	Contract Date	Contract Period
Consulting for Atmospheric Lifetime Experiment	Lovelock	Private	81-348	6/17/81	Open
Infrared spectroscopy of atmospheric species	Howard	NOAA-Boulder	80-299	6/4/82	12 mo.[b]
Balloon Intercomparison Campaign[d]	Bonetti, Carli	U. of Florence, CNR-IROE	82-389	6/24/82	20 mo.[b]
Balloon Intercomparison Campaign[d]	Pommereau	Service d'Aeronomie	82-392	6/24/82	20 mo.[b]
Balloon Intercomparison Campaign[d]	Taylor, Roscoe	Oxford U.	82-393	6/24/82	20 mo.[b]
Balloon Intercomparison Campaign[d]	Woods, Pollitt, Bangham, Bradsell, Moss, Swann	NPL	82-394	6/24/82	20 mo.[b]
Balloon Intercomparison Campaign: Master Contract	Woods	NPL	82-403	6/24/82	20 mo.[b]
CFC 11 Release Rate from Rigid Polyurethane Foams	Rasmussen	Oregon Graduate Center	82-416	10/22/82	12 mo.[b]
Kinetic Measurements of Atmospheric Constituents	Kurylo, Laufer	NBS	82-402	10/22/82	12 mo.[b]
Resonance Fluorescence Measurement of ClO and Related Species Using Reel-Down Technique	Anderson	Harvard U.	82-429	1/27/83	7 mo.[b]

(continued)

Table 4B (continued)

Program	Investigator	Organization[a]	Proposal Number	Contract Date	Contract Period
Continuation of 79-289	Howard	NOAA-Boulder	82-424	2/19/83	12 mo.[b]
Detection of Stratospheric OH, HO_2, and H_2O by Copper Vapor Laser	Anderson	Harvard	82-428	2/23/83	7 mo.[b]
Continuation of 82-391	Ogawa, Iwagami	U. of Tokyo	82-438	3/1/83	15 mo.[b]
Interpretation of Kitt Peak Spectra[c]	Zander	U. of Liege	82-439	4/5/83	14 mo.[b]
Review of Kitt Peak Data Archives for H_4 and Other pecies	Stokes	Battelle Northwest	82-417	4/12/83	15 mo.[b]
Continuation of 82-403	Woods	NPL	82-432	5/9/83	15 mo.[b]
Continuation of 82-394[e]	Woods	NPL	82-433	5/9/83	15 mo.[b]
Continuation of 82-393[e]	Taylor, Roscoe	Oxford U.	82-434	5/9/83	15 mo.[b]
Continuation of 82-395[e]	Zander	U. of Liege	82-435	5/9/83	15 mo.[b]
Continuation of 82-392[e]	Pommereau	Service d'Aeronomie	82-436	5/9/83	15 mo.[b]
Continuation of 82-389[e]	Bonetti, Carli	U. of Florence, CNR-IROE	82-437	5/9/83	15 mo.[b]
Diurnal Variations by omparisons of Field Data and Calculations[c]	Pyle	RAL	83-456	8/9/83	15 mo.[b]
Continuation of 81-374	Reinsel, Tiao	U. of Wisconsin, U. of Chicago	83-462	8/22/83	18 mo.[b]
ntinuation of 82-405[c]	Sze	AER, Inc.	83-465	9/29/83	12 mo.[b]
-Dimensional Radiative nvective Model of the tmosphere	Kinoshita	Mitsubishi Res. Inst.	83-461	12/23/83	12 mo.[b]

(continued)

Table 4B (continued)

Program	Investigator	Organization[a]	Proposal Number	Contract Date	Contract Period
Continuation of 80-322	Goldman, Barbe	U. of Denver, U. of Reims	83-457	2/29/84	12 mo.[b]
Continuation of 81-355	Zahniser	Aerodyne Research, Inc.	83-469	3/8/84	12 mo.[b]
Product Determination of Atmospheric Reactions	Lee	Tsing-Hua U.	83-480	3/14/84	24 mo.[b]
Continuation of 82-409	Watson, Oehlert	Princeton U.	83-477	3/15/84	12 mo.[b]
Continuation of 82-422	Cunnold, Alyea, Prinn	CAP, Inc.	83-476	3/26/84	12 mo.[b]
Balloon Measurements with Pressure Modulators and Selective Absorbers[c]	Taylor, Roscoe	Oxford U.	83-484	4/4/84	12 mo.[b]
Continuation of 81-380	Murcray	U. of Denver	84-497	4/5/84	6 mo.[b]
Continuation of 82-425	Birks	U. of Colorado	83-490	4/9/84	8 mo.[b]
Continuation of 82-396[c]	Brasseur	Institute d'Aeronomie Spatiale	83-468	4/11/84	12 mo.[b]
Laboratory Study of ClO + O	Zellner	U. of Goettingen	83-478	4/16/84	17 mo.
Temperature Dependence of the IR Bond Strengths for F-11 and F-12	Elkins	NBS	83-473	5/10/84	12 mo.[b]
Laboratory Measurements of Rotational and Vibrational Spectra	Trombetti, et al.	U. of Bologna and other Italian Institutions	83-472	5/29/84	12 mo.[b]
Dose response of Non-Melanoma Skin Cancer to UV light	Zeger	Johns Hopkins U.	83-460	5/30/84	12 mo.[b]
Halogen Species Chemistry by IR and UV Spectrocopy	Cox	AERE, Harwell	83-483	6/6/84	12 mo.
Umkehr Aerosol Corrections	DeLuisi	NOAA-Boulder	83-466	6/8/84	12 mo.

(continued)

Table 4B (continued)

Program	Investigator	Organization^a	Proposal Number	Contract Date	Contract Period
tudy of OH + ClO	Le Bras	CNRS Orleans	83-488	6/20/84	6 mo.
ntinuation of 82-412	Parkinson, Freeman, Yoshino	Harvard U.	83-486	6/28/84	12 mo.
Continuation of 83-449	Ravishankara, Wine	Georgia Tech.	84-499	6/29/84	12 mo.
Continuation of 82-445^c	Traub, Chance	Smithsonian Astrophysical Laboratory at Harvard	83-489	7/2/84	12 mo.
tinuation of 82-410^c	Solomon, deZafra	SUNY Stony Brook	83-467	7/3/84	12 mo.
Continuation of 82-401	Silver, Kolb	Aerodyne Research, Inc.	84-494	7/9/84	12 mo.
Possible Climatic Effect of Atmospheric Trace Gases	Wang	AER, Inc.	84-518	10/3/84	12 mo.
Continuation of 83-465	Sze	AER, Inc.	84-523	10/3/84	12 mo.
Absorption Cross Section of HO_2NO_2	Steimle	U. of Oregon	84-509	10/10/84	12 mo.
High Resolution IR Spectroscopy of HOCl	Lafferty	NBS	84-501	10/18/84	12 mo.
Incorporation of Chemistry into U. of Berlin 3D Model	Brasseur	Institute d'Aeronomie Spatiale	84-505	10/24/84	12 mo.
Continuation of 83-456	Pyle	RAL	84-511	11/14/84	12 mo.
GAGE, Barbados Station	Simmonds	Private	84-515	11/24/84	12 mo.
Stratospheric Trace Gas Measurements Using Matrix Isolation FTIR Analysis	Griffith	Max Planck, Mainz	84-526	1/2/85	12 mo.
Atmospheric Aerosol from Astronomical Data	Clark	U. of Kentucky	84-530	1/21/85	12 mo.
Continuation of 82-439	Zander	U. of Liege	84-517	1/22/85	24 mo.

(continued)

Table 4B (continued)

Program	Investigator	Organization[a]	Proposal Number	Contract Date	Contract Period
Continuation of 83-467	Solomon, deZafra	SUNY Stony Brook	84-521	1/29/85	8 mo.
Analysis of Data on Stratospheric Nitrogen Species	Stokes, Johnson, Pearson	Battelle Northwest	84-493	2/22/85	12 mo.
Continuation of 83-468	Brasseur	Institute d'Aeronomie Spatiale	84-534	3/13/85	12 mo.
Participation in GAGE Meetings	Fraser	CSIRO	85-540	3/18/85	9 mo.
A Duplicate Single-Axis Platform	Traub, Chance	Smithsonian Astrophysical Laboratory at Harvard	84-537	3/22/85	12 mo.
Gas Phase Reactions of $ClONO_2$	Atkinson	U. of Calif., Riverside	84-531	4/19/85	12 mo.
Monitoring of Ozone Profile by Ground-Based Lidar	Megie	Service d'Aeronomie	84-510	5/10/85	5 mo.
Balloon Lidar Measurements of OH and O_3	Heaps	NASA - Goddard	84-508	pending	-
Continuation of 83-484	Taylor, Roscoe	Oxford U.	84-532	pending	-
Line Studies Using TuFIR Spectrometer	Evenson	NBS-Boulder	84-533	pending	-
High Resolution Submillimeter Balloon Spectroscopy	Bonetti, Carli	U. Florence, CNR-IROE	85-543	pending	-
Continuation of 83-489	Traub, Chance	Smithsonian Astrophysical Laboratory at Harvard	85-444	pending	-
Kinetic Study of the Reactions of N_2O_5	Le Bras	CNRS, Orleans	85-545	pending	-

(continued)

Table 4B (continued)

Program	Investigator	Organization[a]	Proposal Number	Contract Date	Contract Period
Feasibility Study of ClO Column Measurement	Burnett	Florida Atlantic U.	85-547	pending	-
MAP GLOBUS Support	Pommereau	Service d'Aeronomie	85-550	pending	-

---

a. Abbreviated affiliations are expanded under study descriptions in Table 3.
b. Contract extended.
c. Work continued in a follow-on contract.
d. Subcontract, see Woods 82-403.
e. Subcontract, see Woods 82-432.

Table 5

PUBLICATIONS FROM WORK SUPPORTED BY CHLOROFLUOROCARBON MANUFACTURERS[a]

Alexander Grant & Company

1. Environmental Analysis of Fluorocarbons FC-11, FC-12, and FC-22, February 5, 1976.
2. Environmental Analysis of Fluorocarbons FC-11, FC-12, and FC-22--Manufacturing Chemists Association, July 8, 1977.
3. 1977 World Production and Sales of Fluorocarbons FC-11 and FC-12, June 26, 1978.
4. 1978 World Production and Sales of Fluorocarbons FC-11 and FC-12, July 24, 1979.
5. 1979 World Production and Sales of Fluorocarbons FC-11 and FC-12, May 12, 1980.
6. 1980 World Production and Sales of Fluorocarbons FC-11 and FC-12, May 1, 1981.
7. United States Production and Sales of Chlorofluorocarbons FC-11 and FC-12 from 1976 through 1980, Chemical Manufacturers Association, Inc., September 22, 1981.
8. Carbon Tetrachloride Consumption in Production of Chlorofluorocarbons FC-11 and FC-12, Chemical Manufacturers Association, Inc., July 23, 1982.
9. 1981 World Production and Sales of Fluorocarbons FC-11 and FC-12, Chemical Manufacturers Association, August 25, 1982.
10. 1982 World Production and Sales of Fluorocarbons FC-11 and FC-12, Chemical Manufacturers Association, May 12, 1983.
11. 1983 Production and Sales of Chlorofluorocarbons CFC-11 and CFC-12, Chemical Manufacturers Association Fluorocarbon Program Panel, October 22, 1984.

Allied Corporation

1. Statistical Modeling of Total Ozone Measurements with an Example Using Data from Arosa, Switzerland, W. J. Hill and P. N. Sheldon, *Geophys. Res. Lett.*, 21 (12), 541-4 (1975).
2. Analyzing Worldwide Total Ozone for Trends, W. J. Hill, P. N. Sheldon, and J. J. Tiede, *Geophys. Res. Lett.*, 4 (1), 21-4 (1977).
3. Quantifying the Threshold of Stratospheric Ozone Trend Detection Using Time Series Analysis, P. N. Sheldon, J. J. Tiede, and W. J. Hill, *Proc. Fifth Conf. Probability Statistics* (Am. Meterol. Soc.), 234-9 (1977).

---

[a] Refereed publications plus selected reports issued by CMA.

Table 5 (continued)

Allied Corporation (continued)

4. Ozone Trend Detectability: Update and Discussion, J. J. Tiede, P. N. Sheldon, and W. J. Hill, *Atmos. Environ.*, 13 (7), 999-1003 (1979).

5. Analyzing Total Ozone for Natural and Man-Made Trend Variability, L. Bishop and W. J. Hill, *Geophys. Res. Lett.*, 9 (4), 485-8 (1982).

6. Bayesian Probability Calculations for Stratospheric Ozone Modifications, L. Bishop and W. J. Hill, *J. Geophys. Res.*, 89 (D2), 2589-94 (1984).

P. Ausloos, National Bureau of Standards

1. Decomposition of N_2O Over Particulate Matter, R. E. Rebbert and P. A., *Geophys. Res. Lett.*, 5 (9), 761-4 (1978).

M. J. Bailey, University of Maryland

1. Benefits, Costs, and Risks of CFC Controls, M. J. B., ms. of paper presented at Air Pollution Control Association national meeting, Philadelphia, Pa., June 21-6, 1981.

2. Risks, Costs, and Benefits of Fluorocarbon Regulation, M. J. B., *Am. Econ. Rev.*, 77 (2), 247-50 (1982).

J. Ballard, Rutherford Appleton Laboratory

1. Experimental Determination of the Temperature Dependence of Nitrogen Broadened Line Widths in the $1 \leftarrow 0$ Band of HCl, J. B., W. B. Johnston, P. H. Moffat, and D. T. Llewellyn-Jones, draft ms.

D. S. Berger and F. Urbach, Temple University

1. A Climatology of Sunburning Ultraviolet Radiation, D. S. B. and F. U., *Photobiol. Photochem.*, 35 (2), 187-92 (1982).

J. W. Birks, University of Colorado (Formerly University of Illinois)

1. Studies of Reactions of Importance in the Stratosphere. I. Reaction of Nitric Oxide With Ozone, J. W. B., B. Shoemaker, T. J. Leck, and D. M. Hinton, *J. Chem. Phys.*, 65 (12), 5181-5 (1976).

2. Studies of Reactions of Importance in the Stratosphere. II. Reactions Involving Chlorine Nitrate and Chlorine Dioxide, J. W. B., B. Shoemaker, T. J. Leck, R. M. Borders, and L. J. Hart, *J. Chem. Phys.*, 66 (10), 4591-9 (1977).

3. Studies of Reactions of Importance in the Stratosphere. III. Rate Constant and Products of the Reaction Between ClO and HO_2 Radicals at 298 K, T. J. Leck, J-E. L. Cook, and J. W. B., *J. Chem. Phys.*, 72 (4), 2364-73 (1980).

Table 5 (continued)

J. W. Birks, University of Colorado (continued)

4. Studies of Reactions of Importance in the Stratosphere. IV. Rate Constant for the Reaction of Cl + HOCl → HCl + ClO over the Temperature Range 243-365 K, J-E. L. Cook, C. A. Ennis, T. J. Leck, and J. W. B., J. Chem. Phys., 74 (1), 545-9 (1981).

5. Products of the Reaction Between Cl and HOCl, J-E. L. Cook, C. A. Ennis, T. J. Leck, and J. W. B., J. Chem. Phys., 75 (1), 497-8 (1981).

6. Formation of Oxygen Atoms in the Reaction of Chlorine Atoms with Ozone, J. W. Vanderzanden and J. W. B., Chem. Phys. Lett., 88 (1), 109-14 (1982).

7. High Precision Measurements of Activation Energies Over Small Temperature Intervals: Curvature in the Arrhenius Plot for the Reaction $NO + O_3 \rightarrow NO_2 + O_2$, R. A. Borders and J. W. B., J. Phys. Chem., 86 (17), 3295-302 (1982).

8. Kinetics of $Cl_2(B^3\pi(0_u^+) \rightarrow X^1\Sigma_g^+)$ Chemiluminescence in the Reactions of Cl with Cl_2O, ClO_2, and O_3, J. W. Vanderzanden and J. W. B., draft ms.

9. Studies of Reactions of Importance in the Stratosphere. V. Rate Constants for the Reactions $O + NO_2 \rightarrow NO + O_2$ and $O + ClO \rightarrow Cl + O_2$ at 298 K, A. P. Ongstad and J. W. B., J. Chem. Phys., 81 (9), 3922-30 (1984).

10. Applications of a New Laboratory Source of Gaseous HOCl. I. Product of Distribution in the Cl + HOCl Reaction and Equilibrium Constant for the Reaction $Cl_2O + H_2O = 2\ HOCl$, C. A. Ennis and J. W. B., J. Phys. Chem., 89 (1), 186-91 (1985).

A. Bonetti, University of Florence, and B. Carli, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy

1. New Measurements of Stratospheric Composition Using Submillimetre and Infrared Emission Spectroscopy, M. J. Bangham, A. B., R. H. Bradsell, B. C., J. E. Harries, F. Mencaraglia, D. G. Moss, S. Pollitt, E. Rossi, and N. R. Swann, draft ms.

2. Fourier Spectroscopy of the Stratospheric Emission, B. C., F. Mencaraglia, and A. B., Int. J. Infrared Millimeter Waves, 1 (2), 263-76 (1980).

3. New Assignments in the Submillimeter Emission Spectrum of the Stratosphere, B. C., F. Mencaraglia, and A. B., Int. J. Infrared Millimeter Waves, 3 (3), 385-94 (1982).

4. Phase Error Correction in F. T. Spectroscopy of Spectra with Positive and Negative Intensities, B. C., F. Forni, and F. Mencaraglia, Int. J. Infrared Millimeter Waves, 3 (4), 529-40 (1982).

5. Submillimeter Detection of Stratospheric OH and Further Line Assignments in the Stratospheric Emission Spectrum, B. C., F. Mencaraglia, A. B., B. M. Dinelli, and F. Forni, Int. J. Infrared Millimeter Waves, 4 (3), 475-88 (1983).

Table 5 (continued)

A. Bonetti, University of Florence, and B. Carli, Istituto di Ricerca sulle Onde Elettromagnetiche, Italy (continued)

6. Atlas of Stratospheric Submillimeter Lines. I. The 7-20 cm^{-1} Interval, M. G. Baldecchi, B. C., F. Mencaraglia, A. B., and M. Carlotti, J. Geophys. Res., 89 (D7), 11689-704 (1984).

7. The High Resolution Spectrum of Ozone Between 8 cm^{-1} and 150 cm^{-1}, M. Carlotti, G. Di Lonardo, L. Fusina, A. Trombetti, A. B., B. C., and F. Mencaraglia, J. Mol. Spectrosc., 107 (1), 84-93 (1984).

8. The Pure Rotation Spectrum of Nitrogen Dioxide between 10 and 80 cm^{-1}, B. C., M. Carlotti, F. Mencaraglia, A. Mahmoudi, C. Camy-Peyret, and J. M. Flaud, Mol. Phys., 51 (6), 1505-9 (1984).

9. Submillimeter High-Resolution FT Spectrometer for Atmospheric Studies, B. C., F. Mencaraglia, and A. B., Appl. Opt., 23 (15), 2594-603 (1984).

10. Detection of Atomic Oxygen and Further Line Assignments in the Far Infrared Stratospheric Spectrum, B. C., F. Mencaraglia, A. B., M. Carlotti, and I. G. Nolt, draft ms.

G. Brasseur, Institut d'Aeronomie Spatiale, Belgium

1. Implication for Stratospheric Composition of a Reduced Absorption Cross Section in the Herzberg Continuum of Molecular Oxygen, G. B., A. de Rudder, and P. C. Simon, Geophys. Res. Lett., 10 (1), 20-3 (1983).

2. Acetonitrile in the Atmosphere, G. B., E. Arijs, A. de Rudder, D. Nevejans, and J. Ingels, Geophys. Res. Lett., 10 (8), 725-8 (1983).

3. Ozone and Temperature Trends Due to the Injection of Trace Species in the Atmosphere, G. B., Aeron. Acta A, No. 288 (1984).

4. Ozone in the 21st Century: Increase or Decrease? A. De Rudder and G. B., Aeron. Acta A, No. 291 (1984).

5. Is Hydrogen Cyanide (HCN) a Progenitor of Acetonitrile (CH_3CN) in the Atmosphere? G. B., R. Zellner, A. De Rudder, and E. Arijs, Geophys. Res. Lett. 12 (3), 117-20 (1985).

6. Detection of the Response of Ozone in the Middle Atmosphere to Short-Term Solar-Ultraviolet Variations, G. M. Keating, G. B., J. Y. Nicholson, III, and A. De Rudder, draft ms.

7. Stratospheric Response to Chemical Perturbations, G. B., A. De Rudder, and C. Tricot, draft ms.

Table 5 (continued)

F. Bruner, Urbino University

1. Calibration Method for the GC Analysis of Halocarbons in Atmospheric Samples Using Permeation Tubes and an Electron-Capture Detector, G. Crescentini, F. Mangani, A. R. Mastrogiacomo, and F. B., *J. Chromatogr.*, 204, 445-51 (1981).

2. Occurrence of F-21 ($CHCl_2F$) in the Troposphere, G. Crescentini and F. B., *Ann. Chim.* (Rome), 70 (11-12), 631-6 (1980).

3. Determination of $CHFCl_2$ (CFC 21) in the Troposphere, G. Crescentini and F. B., *J. Fluorine Chem.*, 16 (6), 621-2 (1980).

4. Determination of Halocarbons in Air by Gas Chromatography-High Resolution Mass Spectrometry, F. B., G. Crescentini, and F. Mangani, *Anal. Chem.*, 53 (6), 798-801 (1981).

5. Fast Determination of Some Halocarbons in the Atmosphere by Gas Chromatography - High Resolution Mass Spectrometry, G. Crescentini, F. Mangani, A. R. Mastrogiacomo, A. Cappiello, and F. B., *J. Chromatogr.*, 280, 146-51 (1983).

6. See 39 under Rasmussen.

7. Conclusive Quantitative Data About the Presence of FC-21 in the Atmosphere, G. Crescentini, F. Mangani, A. R. Mastrogiacomo, A. Cappiello, and F. B., draft ms.

H. L. Buijs, Bomem, Inc.

1. Simultaneous Measurement of the Volume Mixing Ratios of HCl and HF in the Stratosphere, H. L. B., G. L. Vail, G. Tremblay, and D. J. W. Kendall, *Geophys. Res. Lett.*, 7 (3), 205-8 (1980).

2. Stratospheric NO_2 and Upper Limits of CH_3Cl and C_2H_6 from Measurements at 3.4 m, D. J. W. Kendall and H. L. B., *Nature*, 303, 221-2 (1983).

3. Stratospheric HF Mixing Ratio Profiles in the Northern and Southern Hemispheres, J. H. Park, D. J. W. Kendall, and H. L. B., *J. Geophys. Res.*, 89 (D7), 11645-53 (1984).

M. J. Campbell, Washington State University

1. Halocarbon Decomposition by Natural Ionization, M. J. C., *Geophys. Res. Lett.*, 3 (11), 661-4 (1976).

2. Reply to comments by F. C. Fehsenfeld and D. L. Albritton on preceding paper [*Geophys. Res. Lett.*, 4 (1), 61-3 (1979)], M. J. C., *Geophys. Res. Lett.*, 4 (1), 64 (1977).

Table 5 (continued)

Chemical Manufacturers Association Fluorocarbon Program Panel

1. World Production and Release of Chlorofluorocarbons 11 and 12 Through 1978, August 6, 1979.
2. World Production and Release of Chlorofluorocarbons 11 and 12 Through 1979, May 23, 1980.
3. World Production and Release of Chlorofluorocarbons 11 and 12 Through 1980, Chemical Manufacturers Association Fluorocarbon Program Panel, July 29, 1981.
4. World Production and Release of Chlorofluorocarbons 11 and 12 through 1981, Chemical Manufacturers Association Fluorocarbon Program Panel, September 15, 1982.
5. CMA CFC-11 and CFC-12 Production and Release Data [World through 1982], Chemical Manufacturers Association Fluorocarbon Program Panel, June, 1983.
6. Production and Release of Chlorofluorocarbons 11 and 12 Based on Reported Data Through 1983, Chemical Manufacturers Association Fluorocarbon Program Panel, October, 1984.

M. A. A. Clyne, Queen Mary College, England

1. Reaction Kinetics Involving Ground $X^2\pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 1. Quenching Kinetics of OH $A^2\Sigma^+$ and Rate Constants for Reactions of OH $X^2\pi$ with CH_3CCl_3 and CO, M. A. A. C. and P. M. Holt, *J. Chem. Soc. Faraday Trans. 2*, 75 (3) 569-81 (1979).
2. Reaction Kinetics Involving Ground $X^2\pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 2. Rate Constants for Reactions of OH $X^2\pi$ with Halogenomethanes and Halogenoethanes, M. A. A. C. and P. M. Holt, *J. Chem. Soc. Faraday Trans. 2*, 75 (3), 582-91 (1979).
3. Kinetic Studies of Free Radical Reactions by Mass Spectrometry. I. The Reactions SO + NO_2 and ClO + NO, M. A. A. C. and A. J. MacRobert, *Int. J. Chem. Kinet.*, 12 (2), 79-96 (1980).

R. A. Cox, AERE Harwell, England

1. Kinetics of Chlorine Oxide Radicals Using Modulated Photolysis. Part 2. ClO and ClOO Radical Kinetics in the Photolysis of $Cl_2 + O_2 + N_2$ Mixtures, R. A. C., R. G. Derwent, A. E. J. Eggleton, and H. J. Reid, *J. Chem Soc. Faraday Trans. 1*, 75 (7), 1648-66 (1979).
2. Product Formation in the Association Reaction of ClO with NO_2, Investigated by Diode Laser Kinetic Spectroscopy, R. A. C., J. P. Burrows, and G. B. Coker, *Int. J. Chem. Kinet.*, 16 (4), 445-67 (1984).

Table 5 (continued)

R. A. Cox, AERE Harwell, England (continued)

3. Novel UV Product Spectra in the Photolysis of Chlorine Dioxide, R. A. Barton, R. A. C., and T. J. Wallington, J. Chem. Soc. Faraday Trans. 1, 80 (10), 2737-43 (1984).

J. A. Coxon, Dalhousie University, Canada

1. Absolute Absorption Cross Sections at High Resolution in the $A^2\pi_i - X^2\pi_i$ Band System of ClO, S. A. Barton, J. A. C., and U. K. Roychowdhury, Can. J. Phys., 62 (5), 473-86 (1984).

D. M. Cunnold, F. N. Alyea, R. G. Prinn, Massachusetts Institute of Technology and Georgia Institute of Technology

1. The Impact of Stratospheric Variability on Measurement Programs for Minor Constituents, R. G. P., F. N. A., and D. M. C., Bull. Am. Meteorol. Soc., 57 (6), 686-94 (1976).
2. Meteorological Control of Lower Stratospheric Minor Species Variations: An Observational Example, F. N. A. and D. M. C., Atmos. Environ., 12 (6-7), 1075-80 (1978).
3. Meterorological Constraints on Tropospheric Halocarbon and Nitrous Oxide Destructions by Siliceous Land Surfaces, F. N. A., D. M. C., and R. G. P., Atmos. Environ, 12 (6-7), 1009-11 (1978).
4. A Methodology for Determining the Atmospheric Lifetime of Fluorocarbons, D. M. C., F. N. A., and R. G. P., J. Geophys. Res., 83 (C11), 5493-500 (1978).
5. Uncertainties in Feedbacks in Simple Climate Models and Their Influence on Prediction of the Climatic Impact of Fluorocarbons, R. G. P., F. N. A., C. A. Cardelino, and D. M. C., draft ms.
6. Comment on "Measurement of CCl_3F and CCl_4 at Harwell over the Period January 1975-November 1977," D. M. C., F. N. A., and R. G. P., Atmos. Environ., 14 (5), 617-18 (1980).
7. The Atmospheric Lifetime Experiment. 1. Introduction, Instrumentation, and Overview, R. G. P., R. A. Rasmussen, R. D. Rosen, P. G. Simmonds, F. N. A., C. A. Cardelino, A. J. Crawford, D. M. C., P. J. Fraser, and J. E. Lovelock, J. Geophys. Res., 88 (C13), 8353-67 (1983).
8. The Atmospheric Lifetime Experiment. 3. Lifetime Methodology and Application to Three Years of $CFCl_3$ Data, D. M. C., R. G. P., R. A. Rasmussen, P. G. Simmonds, F. N. A., and C. A. Cardelino, J. Geophys. Res., 88 (C13), 8379-400 (1983).

Table 5 (continued)

D. M. Cunnold, F. N. Alyea, R. G. Prinn, Massachusetts Institute of Technology and Georgia Institute of Technology (continued)

9. The Atmospheric Lifetime Experiment. 4. Results for CF_2Cl_2 Based on Three Years of Data, D. M. C., R. G. P., R. A. Rasmussen, P. G. Simmonds, F. N. A., and C. A. Cardelino, J. Geophys. Res., 88 (C13), 8401-14 (1983).

10. The Atmospheric Lifetime Experiment. 5. Results for CH_3CCl_3 Based on Three Years of Data, R. G. P., R. A. Rasmussen, P. G. Simmonds, F. N. A., D. M. C., and B. C. Lane, J. Geophys. Res., 88 (C13), 8415-26 (1983).

11. See 5 under P. G. Simmonds.

D. D. Davis, Georgia Institute of Technology (Formerly University of Maryland)

1. A Temperature Dependent Kinetics Study of the Reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br, D. D. D., G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys., 65 (4), 1268-74 (1976).

2. A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3, CH_3CF_2Cl, and $CF_2ClCFCl_2$, R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. D., J. Phys. Chem., 81 (3), 256-62 (1977).

3. High Resolution Absorption Cross Sections for the $A^2\pi - X^2\pi$ System of ClO, P. H. Wine, A. R. Ravishankara, D. L. Philen, D. D. D., and R. T. Watson, Chem. Phys. Lett., 50 (1), 101-6 (1977) (8/15/77).

E. I. du Pont de Nemours & Company, Inc.

1. Atmospheric Stability of Fluoroalkanes - Implications for Ozone Depletion, R. L. McCarthy and J. P. Jesson, Symposium on Fluorine Chemistry, Kyoto, Japan, August 26, 1976.

2. Measurement of the Reaction Rate of $CFCl_3$ with Atmosphere-Like Ions, R. G. Hirsch, Atmos. Environ., 10 (9), 703-5 (1976). Comment, F. C. Fehsenfeld, D. L. Albritton, et al., Ibid., 11 (3), 283-4 (1977). Reply, R. G. H., 284-5.

3. Laboratory Microwave Spectrum of $ClONO_2$ and Evidence for the Existence of ClONO, R. D. Suenram, D. R. Johnson, L. C. Glasgow, and P. Z. Meakin, Geophys. Res. Lett., 3 (10), 611-14 (1976); 3 (12), 758 (1976).

4. The Fluorocarbon-Ozone Theory. I. Production and Release, World Production and Release of CCl_3F and CCl_2F_2 (Fluorocarbons 11 and 12) through 1975, R. L. McCarthy, F. A. Bower, and J. P. Jesson, Atmos. Environ., 11 (6), 491-7 (1977).

5. The Fluorocarbon-Ozone Theory. II. Tropospheric Lifetime, An Experimental Estimate of the Tropospheric Lifetime of CCl_3F, J. P. Jesson, P. Meakin, and L. C. Glasgow, Atmos. Environ., 11 (6), 499-508 (1977).

Table 5 (continued)

E. I. du Pont de Nemours & Company, Inc. (continued)

6. Photodecomposition of Chloromethanes Adsorbed on Silica Surfaces, P. Ausloos, R. E. Rebbert, and L. C. Glasgow, J. Res. Nat. Bur. Stand., A, 82 (1), 1-8.

7. A One-Dimensional Model of Atmospheric Transport and Photochemistry, P. Meakin, C. Miller, R. G. E. Franks, and J. P. Jesson, draft ms.

8. World Production and Release of Chlorofluorocarbons 11 and 12 Through 1976, July 15, 1977.

9. The Stratospheric Abundance of Peroxynitric Acid, J. P. Jesson, L. C. Glasgow, D. L. Filkin, and C. Miller, Geophys. Res. Lett., 4 (11), 513-16 (1977).

10. World Production and Release of Chlorofluorocarbons 11 and 12 Through 1977, July 17, 1978.

11. The Fluorocarbon-Ozone Theory. III. Fluorocarbon Mixing and Photolysis. The Effects of Eddy Diffusion and Tropospheric Lifetime on CCl_3F and CCl_2F_2 Tropospheric Mixing Ratios, P. Meakin, P. S. Gumerman, L. C. Glasgow, and J. P. Jesson, Atmos. Environ., 12 (6-7), 1271-85 (1978).

12. The Fluorocarbon-Ozone Theory. IV. Fluorocarbon Mixing and Photolysis. The Effects of Eddy Diffusion and Tropospheric Lifetime on Stratospheric Odd Chlorine Mixing Ratios, L. C. Glasgow, P. S. Gumerman, P. Meakin, and J. P. Jesson, Atmos. Environ., 12 (11), 2159-72 (1978).

13. The Fluorocarbon-Ozone Theory. V. One-dimensional Modeling of the Atmosphere, C. Miller, P. Meakin, R. G. E. Franks, and J. P. Jesson, Atmos. Environ., 12 (12) 2481-2500 (1978).

14. The Fluorocarbon-Ozone Theory. VI. Atmospheric Modeling--Calculation of the Diurnal Steady State, C. Miller, D. L. Filkin, and J. P. Jesson, Atmos. Environ., 13 (3), 381-94 (1979).

15. Extended Theory of Tandem Electron Capture Detectors, J. D. Lee and R. G. Hirsch, Atmos. Environ., 13 (9), 1305-9 (1979).

16. The Stratospheric Abundance of Hypochlorous Acid (HOCl), L. C. Glasgow, J. P. Jesson, D. L. Filkin, and C. Miller, Planet. Space Sci., 27 (8), 1047-54 (1979).

17. Temperature Dependent Absorption Cross-Sections for Formaldehyde (CH_2O): The Effect of Formaldehyde on Stratospheric Chlorine Chemistry, A. M. Bass, L. C. Glasgow, C. Miller, J. P. Jesson, and D. L. Filkin, Planet. Space Sci., 28 (7), 675-9 (1980).

18. The Fluorocarbon-Ozone Theory. VII. One-Dimensional Modeling. An Assessment of Anthropogenic Perturbations, C. Miller, J. M. Steed, D. L. Filkin, and J. P. Jesson, Atmos. Environ., 15 (5), 729-42 (1981).

Table 5 (continued)

E. I. du Pont de Nemours & Company, Inc. (continued)

19. Two-Dimensional Model Calculations of Stratospheric HCl and ClO, J. M. Steed, C. Miller, D. L. Filkin, and J. P. Jesson, Nature, 288, 461-4 (1980).

20. Time Series Search for Trend in Total Ozone Measurements, D. S. St. John, S. P. Bailey, W. H. Fellner, J. M. Minor, and R. D. Snee, J. Geophys. Res., 86 (C8), 7299-311 (1981).

21. Studies on the Ozone Depletion Hypothesis by Chlorofluorocarbons: Two-Dimensional Stratospheric Modelling and Implications for Stratospheric Chemistry, C. Miller, J. M. Steed, D. Filkin, and J. P. Jesson, J. Fluorine Chem., 16 (6), 623 (1980).

22. Time Series Analysis of Stratospheric Ozone, D. S. St. John, S. P. Bailey, W. H. Fellner, J. M. Minor, and R. D. Snee, Commun. Stat. Theor. Methods, A11 (12), 1293-333 (1982).

23. A Two-Dimensional Model of Stratospheric Chemistry and Transport, C. Miller, D. L. Filkin, A. J. Owens, J. M. Steed, and J. P. Jesson, J. Geophys. Res., 86 (C12), 12039-65 (1981).

24. Two-Dimensional Model Calculations of Potential Ozone Perturbation by Chlorofluorocarbons, J. M. Steed, A. J. Owens, C. Miller, D. L. Filkin, and J. P. Jesson, Nature, 295, 308-11 (1982).

25. The Atmospheric Lifetimes of CFC 11 and CFC 12, A. J. Owens, J. M. Steed, C. Miller, D. L. Filkin, and J. P. Jesson, Geophys. Res. Lett., 9 (6), 700-3 (1982).

26. The Potential Effects of Increased Methane on Atmospheric Ozone, A. J. Owens, J. M. Steed, D. L. Filkin, C. Miller, and J. P. Jesson, Geophys. Res. Lett., 9 (9), 1105-8 (1982).

27. Potential Man-made Changes to the Ozone Content and Thermal Structure of the Atmosphere, A. J. Owens, C. H. Hales, D. L. Filkin, C. Miller, A. Yokozeki, J. M. Steed, and J. P. Jesson, draft ms.

28. A Coupled One-Dimensional Radiative-Convective Chemistry-Transport Model of the Atmosphere. I. Model Structure and Steady-State Perturbation Calculations, A. J. Owens, C. H. Hales, D. L. Filkin, C. Miller, J. M. Steed, and J. P. Jesson, J. Geophys. Res., 90 (D1), 2283-311 (1985).

29. Stratospheric Ozone Modification by Man's Influence. A. J. Owens, A. Yokozeki, and J. M. Steed, in Hazard Assessment of Chemicals: Current Developments, J. Saxena, ed., Academic Press, San Diego, 3, 251-336 (1984).

30. Trace Gas Influences on Climate from 1850 to 1980, D. J. Wuebbles, A. J. Owens, and C. H. Hales, J. Am. Meteorol. Soc., in press.

31. Trace Gas Influence on Climate from 1980 to 2050, A. J. Owens, C. H. Hales, and D. J. Wuebbles, J. Am. Meteorol. Soc., in press.

Table 5 (continued)

E. I. du Pont de Nemours & Company, Inc. (continued)

32. Natural and Manmade Chlorocarbons and Chlorofluorocarbons in the Stratosphere: Sources, Sinks, and Calculated Impact on Ozone, A. J. Owens, D. L. Filkin, C. H. Hales, and C. Miller, J. Air Pollut. Control Assoc., in press.

33. Multiple Component Ozone Perturbation Calculations: The Base Case and High Chlorine Scenarios, A. J. Owens, D. A. Fisher, C. H. Hales, and M. McFarland, draft ms.

34. See 1 under ICI Americas Inc.

D. E. Harsch, Washington State University

1. Evaluation of a Versatile Gas Sampling Container Design, D. E. H., Atmos. Environ., 14 (9), 1105-7 (1980).

J. E. Harries, National Physical Laboratory, England

1. See 1 under Bonetti.

2. Stratospheric H_2O, H. W. Ellsaesser, J. E. H., D. Kley, and R. Penndorf, Planet. Space Sci., 28 (8), 827-35 (1980).

3. See 1 under Pyle.

Hoechst AG

1. Global Distribution of Fluorocarbons, O. Klais and H. J. Fink, Ber. Bunsenges. Phys. Chem., 82 (11), 1147-50 (1978).

2. Heterogeneous Photolysis of Fluorocarbons Adsorbed on Artificial and Natural Dusts and Sand Samples, O. Klais and M. F. Feser, Hoechst Internal Report, 1978.

C. J. Howard, NOAA Boulder

1. Kinetics of the Reaction of HO_2 with NO_2, C. J. H., J. Chem. Phys., 67 (11), 5258-63 (1977).

2. Kinetics of the Reaction of HO_2 with NO, C. J. H. and K. M. Evenson, Geophys. Res. Lett., 4 (10), 437-40 (1977).

3. Temperature Dependence of the Reaction of $HO_2 + NO \rightarrow OH + NO_2$, C. J. H., J. Chem. Phys., 71 (6), 2352-9 (1979).

4. Temperature Dependence of the Reaction of ClO and HO_2 Radicals, R. M. Stimpfle, R. A. Perry, and C. J. H., J. Chem. Phys., 71 (12), 5183-90 (1979).

Table 5 (continued)

C. J. Howard, NOAA Boulder (continued)

5. Kinetics of the Reaction of HO_2 with Ozone, M. S. Zahniser and C. J. H., *J. Chem. Phys.*, 73 (4), 1620-6 (1980).

6. Yields of HO_2 in the Reaction of Hydrogen Atoms with Ozone, C. J. H. and B. J. Finlayson-Pitts, *J. Chem. Phys.*, 72 (6), 3842-3 (1980).

7. Kinetic Study of the Equilibrium $HO_2 + NO = HO + NO_2$ and the Thermochemistry of HO_2, C. J. H., *J. Am. Chem. Soc.*, 102 (23), 6937-41 (1980).

8. Tunable Diode Laser Measurement of Nitrous Oxide in Air, P. S. Connell, R. A. Perry, and C. J. H., *Geophys. Res. Lett.*, 7 (12), 1093-6 (1980).

9. Laser Magnetic Spectroscopy of ClO and Kinetic Studies of the Reactions of ClO with NO and NO_2, Y. P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. H., *Int. J. Chem. Kinet.*, 14 (6), 711-32 (1982).

10. Temperature Dependence of the Rate Constant and the Branching Ratio for the Reaction $Cl + HO_2$, Y. P. Lee and C. J. H., *J. Chem. Phys.*, 77 (2), 756-63 (1982).

11. Room Temperature Rate Constant for the $HO_2 + HO_2$ Reaction at Low Pressures, G. A. Takacs and C. J. H., *J. Phys. Chem.*, 88 (10), 2110-16 (1984).

12. Rate Coefficient Temperature Dependence and Branching Ratio for the $OH + ClO$ Reaction, A. J. Hills and C. J. H., *J. Chem. Phys.*, 81 (10), 4458-65 (1984).

13. Kinetic Study of the Reaction $HO + HNO_3$, P. S. Connell and C. J. H., *Int. J. Chem. Kinet.*, 17 (1), 17-31 (1985).

ICI Americas Inc.

1. The Production and Release to Atmosphere of CCl_3F and CCl_2F_2 (Chlorofluorocarbons CFC 11 and CFC 12), P. H. Gamlen, B. C. Lane, P. M. Midgley, and J. M. Steed, draft ms.

Istituto G. Donegani, Italy (Funded by Montefluos)

1. SCF-HF Ab Initio Study of the Reactivity of Chlorofluorocarbons: From $CFCl_3$ to $CHFCl_2$, G. Ranghino, *J. Mol. Struct.*, 105 (1/2), 183-9 (1983).

2. Reactivity of Fluorochloromethanes with Desert Sands, L. Benzoni and F. Garbassi, *Ber. Bunsenges. Phys. Chem.*, 88 (4), 379-82 (1984).

M. Kaufman, Emory University

1. Rate Constant of the Reaction between Chlorine Atoms and Sulfur Dioxide and Its Significance for Stratospheric Chlorine Chemistry, L. W. Strattan, R. E. Eibling, and M. K., *Atmos. Environ.*, 13 (1), 175-7 (1979).

Table 5 (continued)

M. Kaufman, Emory University (continued)

2. Kinetic Studies Relevant to Possible Coupling Between the Stratospheric Chlorine and Sulfur Cycles, R. E. Eibling and M. K., Atmos. Environ., 17 (2), 429-31 (1983).

H. D. Knauth, University of Kiel, F. R. G.

1. Equilibrium Constant of the Gas Reaction $Cl_2O + H_2O = 2HOCl$ and the Ultraviolet Spectrum of HOCl, H. D. K., H. Alberti, and H. Clausen, J. Phys. Chem., 83 (12), 1604-12 (1979).

C. E. Kolb, J. A. Silver, and M. S. Zahniser, Aerodyne Research, Inc.

1. A Measurement of the Vibrational Strength for the ν_3 Band of the HO_2 Radical, M. S. Z. and A. C. Stanton, J. Chem. Phys., 80 (10), 4951-60 (1984).
2. The Gas Phase Reaction Rate of Sodium Hydroxide with Hydrochloric Acid, J. A. S., A. C. Stanton, M. S. Z., and C. E. K., J. Phys. Chem., 88 (14), 3123-9 (1984).
3. Measurement of Atomic Sodium and Potassium Diffusion Coefficients, J. A. S., J. Chem. Phys., 81 (11), 5125-30 (1984).

F. Korte, Technical University of Munich, F. R. G.

1. Mineralization of Chlorofluorocarbons in the Sunlight of the Troposphere, S. Gaeb, J. Schmitzer, H. W. Thamm, and F. K., Angew. Chem. Int. Ed. Engl., 17 (5), 366 (1978).
2. Heterogeneous Photodecomposition of Fluorochlorocarbons under Simulated Tropospheric Conditions, S. Gaeb and F. K., Ber. Bunsenges. Phys. Chem., 82 (11), 1151-3 (1978).
3. Degradation of CCl_2F_2: Formation of CO_2 upon Adsorption on Mecca Sand, M. Bahadir, S. Gaeb, J. Schmitzer, and F. K., Chemosphere, 7 (12), 941-2 (1978).
4. Mineralization of $^{14}CCl_2F_2$ Catalyzed by Active Surfaces, M. Bahadir, S. Gaeb, J. Schmitzer, and F. K., Z. Naturforsch. B, 34 (6), 822-6 (1979).
5. Mineralization of CCl_4 and CCl_2F_2 on Solid Surfaces, S. Gaeb, J. Schmitzer, W. V. Turner, and F. K., Z. Naturforsch. B, 35 (8), 946-52 (1980).

K. F. Kuenzi, University of Bern, and H. U. Duetsch, Federal Institute of Technology, Zurich, Switzerland

1. Comparison of Stratospheric Ozone Profiles Retrieved from Microwave-Radiometer and Dobson-Spectrometer Data, E. Lobsiger, K. F. K., and H. U. D., J. Atmos. Terr. Phys., 46 (9), 799-806 (1984).

Table 5 (continued)

M. J. Kurylo, National Bureau of Standards

1. Rate Constant Measurements for the Reaction Cl + $CH_2O \rightarrow HCl + CHO$. Implications Regarding the Removal of Stratospheric Chlorine, P. C. Anderson and M. J. K., J. Phys. Chem., 83 (16), 2055-7 (1979).

2. A Flash Photolysis Resonance Fluorescence Investigation of the Reaction OH + $CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$, M. J. K., P. C. Anderson, and O. Klais, Geophys. Res. Lett., 6 (10), 760-2 (1979).

3. An Upper Limit for the Rate Constant of the Bimolecular Reaction $CH_3 + O_2 \rightarrow HO + H_2CO$ at 368 K, O. Klais, P. C. Anderson, A. H. Laufer, and M. J. K., Chem. Phys. Lett., 66 (3), 598-601 (1979).

4. A Reinvestigation of the Temperature Dependence of the Rate Constant for the Reaction $O + O_2 + M \rightarrow O_3 + M$ (for $M = O_2$, N_2, and Ar) by the Flash Photolysis Resonance Fluorescence Technique, O. Klais, P. C. Anderson, and M. J. K., Int. J. Chem. Kinet., 12 (7), 469-90 (1980).

5. Atmospheric Quenching of Vibrationally Excited $O_2(^1\Delta)$, O. Klais, A. H. Laufer, and M. J. K., J. Chem. Phys., 73 (6), 2696-9 (1980).

6. Mechanistic Investigation of the HO + HO_2 Reaction, M. J. K., O. Klais, and A. H. Laufer, J. Phys. Chem., 85 (24), 3674-8 (1981).

7. A Flash Photolysis Resonance Fluorescence Investigation of the Reaction OH + $H_2O_2 \rightarrow HO_2 + H_2O$, M. J. K., J. L. Murphy, G. S. Haller, and K. D. Cornett, Int. J. Chem. Kinet., 14 (10), 1149-61 (1982).

8. Rate Constant Measurements of the Reaction of Cl Atoms with Nitric Acid over the Temperature Range 240-300 K, M. J. K., J. L. Murphy, and G. L. Knable, Chem. Phys. Lett., 94 (3), 281-4 (1983).

9. A Reinvestigation of the Cl + $ClONO_2$ Reaction by Flash Photolysis Resonance Fluorescence, M. J. K., G. L. Knable, and J. L. Murphy, Chem. Phys. Lett., 95 (1), 9-12 (1983).

10. A Kinetics Investigation of the Gas Phase Reactions of $Cl(^2P)$ and OH (X^2) with CH_3CN: Atmospheric Significance and Evidence for Decreased Reactivity Between Strong Electrophiles, M. J. K. and G. L. Knable, J. Phys. Chem., 88 (15), 3305-8 (1984).

F. J. Lovas, National Bureau of Standards

1. The Microwave and Millimeter-Wave Spectra of Hypochlorous Acid, H. E. G. Singbeil, W. D. Anderson, R. W. Davis, M. C. L. Gerry, E. A. Cohen, H. M. Pickett, F. J. L., and R. D. Suenram, J. Mol. Spectrosc., 103 (2), 466-85 (1984).

2. Millimeter Wave Spectrum of Chlorine Nitrate, R. D. Suenram and F. J. L., J. Mol. Spectrosc., 105 (1/2), 351-9 (1984).

Table 5 (continued)

J. E. Lovelock, University of Reading, England

1. Atmospheric Halocarbons and Stratospheric Ozone, J. E. L., Nature, 252, 292-4 (1974).

2. Long-range Transport of Photochemical Ozone in Northwestern Europe, R. A. Cox, A. E. J. Eggleton, R. G. Derwent, J. E. L., and D. H. Pack, Nature, 255, 118-21 (1975).

3. Natural Halocarbons in the Air and Sea, J. E. L., Nature, 256, 193-4 (1975).

4. Photochemical Oxidation of Halocarbons in the Troposphere, R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. L., Atmos. Environ., 10 (4), 305-8 (1976).

5. Halocarbon Behavior from a Long Time Series, D. H. Pack, J. E. L., G. Cotton, and C. Curthoys, Atmos. Environ., 11 (4), 329-44 (1977).

6. The Electron Capture Detector Theory and Practice, J. E. L., J. Chromatogr., 99, 3-12 (1974).

7. Methyl Chloroform in the Troposphere as an Indicator of OH Radical Abundance, J. E. L., Nature, 267, 32 (1977).

8. Fluorotrichloromethane and Tetrachloromethane Data in the British Isles 1970-1975, J. E. L. and D. H. Pack, Health Saf. Lab. Environ. Q. - U. S. Energy Res. Dev. Adm., (April), 3-20 (1976).

9. Electron-Capture Detector: Theory and Practice. II. J. E. L. and A. J. Watson, J. Chromatogr., 158, 123-38 (1978).

10. See 7 under D. M. Cunnold, et al.

11. See 33 under R. A. Rasmussen.

12. See 5 under P. G. Simmonds.

L. R. Martin and H. S. Judeikis, Aerospace Corporation

1. Measurement of Chlorine Atom Diffusion, H. S. J. and M. Wun, J. Chem. Phys., 68 (9), 4123-7 (1978).

2. Chlorine Atom and ClO Wall Reaction Products, L. R. M., A. G. Wren, and M. Wun, Int. J. Chem. Kinet., 11 (5), 543-57 (1979).

3. Surface Reactions of Chlorine Molecules and Atoms with Water and Sulfuric Acid at Low Temperatures, A. G. Wren, R. W. Phillips, and L. U. Tolentino, J. Colloid Interface Sci., 70 (3), 544-57 (1979).

4. Heterogeneous Reactions of Cl and ClO in the Stratosphere, L. R. M., H. S. J., and M. Wun, J. Geophys. Res., 85 (C10), 5511-18 (1980).

Table 5 (continued)

K. Moe

1. Simultaneous Measurements of Total Ozone and Aerosol Extinction, K. M., L. Muth, and P. Crooimans, ms. for presentation at International Ozone Symposium, Boulder, Colo., 1980.

D. G. Murcray and A. Goldman, University of Denver

1. Measurements of Stratospheric Halocarbon Distributions Using Infrared Techniques, W. J. Williams, J. J. Kosters, A. G., and D. G. M., Geophys. Res. Lett., 3 (7), 379-82 (1976).
2. Statistical-Band-Model Analysis and Integrated Intensity for the 10.8 μm Band of CF_2Cl_2, A. G., F. S. Bonomo, and D. G. M., Geophys. Res. Lett., 3 (6), 308-12 (1976).
3. Measurements of Stratospheric Fluorocarbon Distribution Using Infrared Techniques, W. J. Williams, J. J. Kosters, A. G., and D. G. M., Geophys. Res. Lett., 3 (7), 379-82 (1976).
4. Measurement of Stratospheric Mixing Ratio Altitude Profile of HCl Using Infrared Absorption Techniques, W. J. Williams, J. J. Kosters, A. G., and D. G. M., Geophys. Res. Lett., 3 (7), 383-5 (1976).
5. Statistical Band Model Analysis and Integrated Intensity for the 11.8 μm Band of $CFCl_3$, A. G., F. S. Bonomo, and D. G. M., Appl. Opt., 15 (10), 2305-7 (1976).
6. Upper Limit for Stratospheric $ClONO_2$ from Balloon-Borne Infrared Measurements, D. G. M., A. G., W. J. Williams, F. H. Murcray, F. S. Bonomo, C. M. Bradford, G. R. Cook, P. L. Hanst, and M. J. Molina, Geophys. Res. Lett, 4 (6), 227-30 (1977).
7. Identification of the ν_3 Vibration-Rotation Band of CF_4 in Balloon-Borne Infrared Solar Spectra, A. G., D. G. M., F. J. Murcray, G. R. Cook, J. W. Van Allen, F. S. Bonomo, and R. D. Blatherwick, Geophys. Res. Lett., 6 (7), 609-12 (1979).
8. Stratospheric Distribution of Chlorine Nitrate, D. G. M., A. G., F. H. Murcray, F. J. Murcray, and W. J. Williams, Geophys. Res. Lett., 6 (11), 857-9 (1979).
9. Handbook of High Resolution Infrared Spectra of Atmospheric Interest, D. G. M. and A. G., CRC Press, 1981.
10. Observation of New Emission Lines in the Infrared Solar Spectrum Near 12.33, 12.22, 7.38 μm, F. J. Murcray, A. G., F. H. Murcray, C. M. Bradford, and D. G. M., Astrophys. J., 247, 97-9 (1981).
11. Analysis of the ν_2 and $2\nu_2-\nu_2$ Ozone Bands from High-Resolution Infrared Spectra, A. G., J. R. Gillis, D. G. M., A. Barbe, and C. Secroun, J. Mol. Spectrosc., 96 (2), 279-87 (1982).

Table 5 (continued)

D. G. Murcray and A. Goldman, University of Denver (continued)

12. Analysis of the $\nu_1 + \nu_2 + \nu_3$ Band of O_3, A. Barbe, C. Secroun, A. G., and J. R. Gillis, J. Mol. Spectrosc., 100 (2), 377-81 (1983).

13. Atmospheric Transmission in the 750-2000 cm^{-1} Region, D. G. M., J. Quant. Spectrosc. Radiat. Transfer, 32 (5), 381-96 (1984).

14. High Resolution IR Laboratory Spectra, D. G. M., F. J. Murcray, A. G., F. S. Bonomo, and R. D. Blatherwick, Appl. Opt., 23 (20), 3502 (1984).

R. W. Nicholls, York University

1. The Absorption Cross Sections and f-Values for the v" = 0 Progression of Bands and Associated Continuum for the ClO ($A^2\pi_i \leftarrow X^2\pi_i$) System, M. Mandelman and R. W. N., J. Quant. Spectrosc. Radiat. Transfer, 17 (4), 483-91 (1977).

M. Pagano and E. Parzen, State University of New York at Buffalo

1. Statistical Time Series Analysis of Worldwide Total Ozone for Trends, E. P., M. P., and H. J. Newton, draft ms.

W. H. Parkinson and D. E. Freeman, Harvard University

1. Herzberg Continuum Cross Section of Oxygen in the Wavelength Region 193.5-204.0 nm: New Laboratory Measurements and Stratospheric Implications, A. S. C. Cheung, K. Yoshino, W. H. P., and D. E. F., Geophys. Res. Lett., 11 (6), 580-2 (1984).

2. Herzberg Continuum Cross Section of Oxygen in the Wavelength Region 193.5-204.0 nm and Band Oscillator Strengths of the (0,0) and (1,0) Schumann-Runge Bands, A. S. C. Cheung, K. Yoshino, W. H. P., and D. E. F., Can J. Phys., 62 (12), 1752-62 (1984).

L. F. Phillips, University of Canterbury, N. Z.

1. Upper Limit for the Atomic Oxygen Yield in the 308 nm Photolysis of HOCl, P. J. D. Butler and L. F. P., J. Phys. Chem., 87 (1), 183-4 (1983).

J. N. Pitts, Jr., and O. C. Taylor, University of California at Riverside

1. Fluorocarbons in the Los Angeles Basin, N. E. Hester, E. R. Stephens, and O. C. T., J. Air Pollut. Control Assoc., 24 (6), 519-5 (1974).

2. Relative Rate Constants for the Reaction of $O(^1D)$ Atoms with Fluorocarbons and N_2O, J. N. P., H. L. Sandoval, and R. Atkinson, Chem. Phys. Lett., 29 (1), 31-4 (1974).

Table 5 (continued)

J. N. Pitts, Jr., and O. C. Taylor, University of California at Riverside (continued)

3. Reactions of Electronically Excited $O(^1D)$ Atoms with Fluorocarbons, H. L. Sandoval, R. Atkinson, and J. N. P., J. Photochem., 3 (4), 325-7 (1974).

4. Tropospheric and Stratospheric Chemical Sinks for Commercial Fluorocarbons, J. N. P. and R. Atkinson, Trans. Amer. Geophys. Union, 55 (12), 1153 (1974).

5. Mechanisms of Photochemical Air Pollution, J. N. P. and B. J. Finlayson, Angew. Chem. Int. Ed. Engl., 14 (1), 1-15 (1975).

6. Fluorocarbon Air Pollutants. II. N. E. Hester, E. R. Stephens, and O. C. T., Atmos. Environ., 9 (6-7), 603-6 (1975).

7. Fluorocarbon Air Pollutants, Measurements in Lower Stratosphere, N. E. Hester, E. R. Stephens, and O. C. T., Environ. Sci. Technol., 9 (9), 875-6 (1975).

8. The Photostability of Fluorocarbons, S. Japar, J. N. P., and A. M. Winer, draft ms.

9. Background and Vertical Atmospheric Measurements of Fluorocarbon-11 and Fluorocarbon-12 over Southern California, L. Zafonte, N. E. Hester, E. R. Stephens, and O. C. T., Atmos. Environ., 9, 1007-9 (1975).

10. Rate Constants for the Reaction of OH Radicals with CHF_2Cl, CF_2Cl_2, $CFCl_3$, and H_2 Over the Temperature Range 297-434 K, R. Atkinson, D. A. Hansen, and J. N. P., J. Chem. Phys., 63 (5), 1703-6 (1975).

11. Tropospheric and Stratospheric Sinks for Halocarbons: Photooxidation, $O(^1D)$ Atom and OH Radical Reactions, R. Atkinson, G. M. Brewer, J. N. P., and H. L. Sandoval, J. Geophys. Res., 81 (33), 5765-70 (1976).

12. Fluorocarbon Air Pollutants. III. Fluorocarbon Measurements in the Lower Stratosphere, N. E. Hester, E. R. Stephens, and O. C. T., draft ms.

13. Ultraviolet and Infrared Absorption Cross Sections of Gas Phase HO_2NO_2, R. A. Graham, A. M. Winer, and J. N. P., Geophys. Res. Lett., 5 (11), 909-11 (1978).

J. A. Pyle, Rutherford Appleton Laboratory

1. The Water Vapour Budget of the Stratosphere Studied Using LIMS and SAMS Satellite Data, R. L. Jones, J. A. P., J. E. Harries, A. M. Zavody, J. M. Russell, III, and J. C. Gille, draft ms.

R. A. Rasmussen, Oregon Graduate Center (Formerly Washington State University)

1. Halocarbon Measurements in the Alaskan Troposphere and Lower Stratosphere, E. Robinson, R. A. R., J. Krasnec, D. Pierotti, and M. Jakubovic, Atmos. Environ., 11 (3), 215-23 (1977).

Table 5 (continued)

R. A. Rasmussen, Oregon Graduate Center (Formerly Washington State University) (continued)

2. Detailed Halocarbon Measurements Across the Alaskan Tropopause, E. Robinson, R. A. R., J. Krasnec, D. Pierotti, and M. Jakubovic, Geophys. Res. Lett., 3 (6), 323-6 (1976).

3. Global and Regional N_2O Measurements, R. A. R. and D. Pierotti, Pure Appl. Geophys., 116 (2-3), 405-13 (1978).

4. Interlaboratory Comparison of Atmospheric Nitrous Oxide Measurements. R. A. R. and D. Pierotti, Geophys. Res. Lett., 5 (5), 353-5 (1978).

5. Interlaboratory Comparison of Fluorocarbon Measurements, R. A. R., Atmos. Environ., 12 (12), 2505-8 (1978).

6. Nitrous Oxide Measurements in the Eastern Tropical Pacific Ocean, D. Pierotti and R. A. R., draft ms.

7. F-11 and N_2O in the North American Troposphere and Lower Stratosphere, W. D. Saunders, E. Robinson, D. R. Cronn, R. A. R., and D. Pierotti, Water Air Soil Pollut., 10 (4), 421-39 (1978).

8. The Sahara as a Possible Sink for Trace Gases, D. Pierotti, L. E. Rasmussen, and R. A. R., Geophys. Res. Lett., 5 (12), 1001-4 (1978).

9. Concentration Distribution of Methyl Chloride in the Atmosphere, R. A. R., L. E. Rasmussen, M. A. K. Khalil, and R. W. Dalluge, J. Geophys. Res., 85 (C12), 7350-6 (1980).

10. Measurements of $CHFCl_2$ (Freon 21) in Background Tropospheric Air, S. A. Penkett, N. J. D. Prosser, R. A. R., and M. A. K. Khalil, Nature, 286, 793-5 (1980) (8/21/80).

11. Atmospheric Halocarbons: Measurements and Analyses of Selected Trace Gases, R. A. R. and M. A. K. Khalil, Proc. NATO Adv. Study Inst. Atm. Ozone, October 1-13, 1979, pp. 209-31.

12. $CHClF_2$ (F-22) in the Earth's Atmosphere, R. A. R., M. A. K. Khalil, S. A. Penkett, and N. J. D. Prosser, Geophys. Res. Lett., 7 (10), 809-12 (1980).

13. Atmospheric Trace Gases in Antarctica, R. A. R., M. A. K. Khalil, and R. W. Dalluge, Science, 211, 285-7 (1981).

14. Sources of Atmospheric Trace Gases in the Southern Hemisphere, M. A. K. Khalil and R. A. R., Atmos. Environ., 15 (7), 1331-4 (1981).

15. Interlaboratory Comparison of Fluorocarbons 11, 12, Methyl Chloroform, and Nitrous Oxide Measurements, R. A. R. and M. A. K. Khalil, Atmos. Environ., 15 (9), 1559-68 (1981).

Table 5 (continued)

R. A. Rasmussen, Oregon Graduate Center (Formerly Washington State University) (continued)

16. Atmospheric Measurements of CF_4 and Other Fluorocarbons Containing the CF_3 Group, S. A. Penkett, N. J. D. Prosser, R. A. R., and M. A. K. Khalil, J. Geophys. Res., 86 (C6), 5172-8 (1981).

17. Atmospheric Trace Gases Over China, R. A. R., M. A. K. Khalil, and J. S. Chang, Environ. Sci. Technol., 16 (2), 124-6 (1982).

18. Increase in the Concentration of Atmospheric Methane, R. A. R. and M. A. K. Khalil, Atmos. Environ., 15 (5), 883-6 (1981).

19. Atmospheric Methane (CH_4): Trends and Seasonal Cycles, R. A. R. and M. A. K. Khalil, J. Geophys. Res., 86 (C10), 9826-32 (1981).

20. Atmospheric Methyl Chloride, M. A. K. Khalil and R. A. R., Chemosphere, 10 (9), 1019-23 (1981).

21. Decline in the Atmospheric Accumulation Rates of CCl_3F, CCl_2F_2, and CH_3CCl_3, M. A. K. Khalil and R. A. R., J. Air Pollut. Control Assoc., 31 (12), 1274-5, (1981).

22. Global Atmospheric Distribution and Trend of CH_3CCl_3, R. A. R. and M. A. K. Khalil, Geophys. Res. Lett., 8 (9), 1005-7 (1981).

23. Increase of $CHClF_2$ (F-22) in the Earth's Atmosphere, M. A. K. Khalil and R. A. R., Nature, 292, 823-4 (1981).

24. Trends of Atmospheric Methane in the Southern Hemisphere, P. J. Fraser, M. A. K. Khalil, and R. A. R., Geophys. Res. Lett., 8 (10), 1063-6 (1981).

25. Differences in the Concentrations of Atmospheric Trace Gases in and Above the Tropical Boundary Layer, R. A. R. and M. A. K. Khalil, Pure Appl. Geophys., 119 (5), 990-7 (1982).

26. Latitudinal Distributions of Trace Gases in and Above the Boundary Layer, R. A. R. and M. A. K. Khalil, Chemosphere, 11 (3), 227-35 (1982).

27. Methane and Carbon Monoxide in Snow, R. A. R., M. A. K. Khalil, and S. D. Hoyt, J. Air Pollut. Control Assoc., 32 (2), 176-8 (1982).

28. Atmospheric Methyl Iodide, R. A. R., M. A. K. Khalil, R. Gunawardena, and S. D. Hoyt, J. Geophys. Res., 87 (C4), 3086-90 (1982).

29. Oceanic Source of Carbonyl Sulfide (OCS), R. A. R., M. A. K. Khalil, and S. D. Hoyt, Atmos. Environ., 16 (6), 1591-4 (1982).

30. Increases in the Atmospheric Concentrations of Halocarbons and N_2O, R. A. R. and M. A. K. Khalil, draft ms.

Table 5 (continued)

R. A. Rasmussen, Oregon Graduate Center (Formerly Washington State University) (continued)

31. Carbonyl Sulfide and Carbon Disulfide from the Eruptions of Mount St. Helens, R. A. R., M. A. K. Khalil, R. W. Dalluge, S. A. Penkett, and B. Jones, Science, 215, 665-7 (1982).

32. See 7 under D. M. Cunnold, et al.

33. Atmospheric Lifetime Experiment. 2. Calibration, R. A. R. and J. E. Lovelock, J. Geophys. Res., 88 (C13), 8369-78 (1983).

34. See 8 under D. M. Cunnold, et al.

35. See 9 under D. M. Cunnold, et al.

36. See 10 under D. M. Cunnold, et al.

37. See 5 under P. G. Simmonds.

38. Increase and Seasonal Cycles of Nitrous Oxide in the Earth's Atmosphere, M. A. K. Khalil and R. A. R., Tellus, 35B (3), 161-9 (1983).

39. Interlaboratory Comparison, Preparation, and Stability of $CHCl_2F$ (F-21) Samples and Standards, R. A. R., M. A. K. Khalil, G. Crescentini, F. Mangani, A. R. Mastrogiacomo, and F. Bruner, Anal. Chem., 55 (11), 1834-6 (1983).

A. R. Ravishankara and P. H. Wine, Georgia Institute of Technology

1. The Kinetics of the Reaction of OH with ClO, A. R. R., F. L. Eisele, and P. H. W., J. Chem. Phys., 78 (3), 1140-4 (1983).

2. Absorption Cross Sections for NO_3 between 565 and 673 nm, A. R. R. and P. H. W., Chem. Phys. Lett., 101 (1) 73-8 (1983).

3. Kinetics of the Reaction $NO_2 + NO_3 + M$ at Low Pressures and 298°K, C. A. Smith, A. R. R., and P. H. W., J. Phys. Chem., 89 (8), 1423-7 (1985).

4. Kinetics of the Reactions of $O(^3P)$ and $O(^1D)$ with Cl_2, P. H. W., J. M. Nicovich, and A. R. R., J. Phys. Chem., in press.

C. Sandorfy, University of Montreal

1. Vacuum Ultraviolet and Photoelectron Spectra of Fluorochloro Derivatives of Methane, J. Doucet, P. Sauvageau, and C. S., J. Chem. Phys., 58 (9), 3708-16 (1973).

2. Vacuum Ultraviolet Absorption Spectra of Fluoromethanes, P. Sauvageau, R. Gilbert, P. P. Berlow, and C. S., J. Chem Phys., 59 (2), 762-5 (1973) (7/15/73).

Table 5 (continued)

C. Sandorfy, University of Montreal (continued)

3. Vacuum Ultraviolet Absorption Spectra of Chlorofluoromethanes from 120 to 65 nm, R. Gilbert, P. Sauvageau, and C. S., J. Chem. Phys., 60 (12), 4820-4 (1974).

4. Vacuum Ultraviolet and Photoelectron Spectra of Fluoroethanes, P. Sauvageau, J. Doucet, R. Gilbert, and C. S., J. Chem. Phys., 61 (1), 391-5 (1974).

5. On the Hydrogen Bond Breaking Ability of Fluorocarbons Containing Higher Halogens, T. DiPaolo and C. S., Can. J. Chem., 52 (21), 3612-22 (1974).

6. Fluorocarbon Anaesthetics Break Hydrogen Bonds, T. DiPaolo and C. S., Nature, 252, 471 (1974).

7. Photoelectron and Far-Ultraviolet Absorption Spectra of Chlorofluoro-Derivatives of Ethane, J. Doucet, P. Sauvageau, and C. S., J. Chem. Phys., 62 (2), 355-9 (1975).

8. Photoelectron and Far-Ultraviolet Spectra of CF_3Br, CF_2BrCl, and CF_2Br_2, J. Doucet, R. Gilbert, P. Sauvageau, and C. S., J. Chem. Phys., 62 (2), 366-9 (1975).

9. Photoelectron and Vacuum Ultraviolet Spectra of a Series of Fluoroethers, A. H. Hardin and C. S., J. Fluorine Chem., 5 (5), 435-42 (1975).

10. Ultraviolet Absorption of Fluorocarbons, a Review, C. S., Atmos. Environ., 10 (5), 343-51 (1976).

R. J. Saykally, University of California, Berkeley

1. Tone-Burst Modulated Color Center Laser Spectroscopy, C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. S., Opt. Lett., 8 (6), 310-12 (1983).

2. Color Center Laser Optogalvanic Spectroscopy of a Planar Hollow Cathode Plasma, M. H. Begemann, J. Pfaff, and R. J. S., draft ms.

3. Visible Laser Optogalvanic Spectroscopy of a Hollow Cathode Plasma, J. Pfaff, M. H. Begemann, and R. J. S., draft ms.

P. G. Simmonds

1. See 7 under D. M. Cunnold, et al.

2. See 8 under D. M. Cunnold, et al.

3. See 9 under D. M. Cunnold, et al.

4. See 10 under D. M. Cunnold, et al.

Table 5 (continued)

P. G. Simmonds (continued)

5. The Atmospheric Lifetime Experiment. 6. Results for Carbon Tetrachloride Based on 3 Years Data, P. G. S., R. A. Rasmussen, J. E. Lovelock, F. N. Alyea, D. M. Cunnold, R. G. Prinn, and B. C. Lane, J. Geophys. Res., 88 (C13), 8427-41 (1983).

P. M. Solomon and R. L. deZafra, State University of New York at Stony Brook

1. Chlorine Oxide in the Stratospheric Ozone Layer: Ground-Based Detection and Measurement, A. deS. Parrish, R. L. deZ., P. M. S., J. W. Barrett, and E. R. Carlson, Science, 211, 1158-61 (1981).
2. A Quasi-Continuous Record of Atmospheric Opacity at $\lambda = 1.1$ mm over 34 Days at Mauna Kea Observatory, R. L. deZ., A Parrish, P. M. S., and J. W. Barrett, Int. J. Infrared Millimeter Waves, 4 ( ), 757-65 (1983).
3. A Measurement of Stratospheric HO_2 by Ground-Based Millimeter-Wave Spectroscopy, R. L. deZ., A. Parrish, P. M. S., and J. W. Barrett, J. Geophys. Res., 89 (D1), 1321-6 (1984).
4. Diurnal Variation of Stratospheric Chlorine Monoxide: A Critical Test of Chlorine Chemistry in the Ozone Layer, P. M. S., R. L. deZ., A. Parrish, and J. W. Barrett, Science, 224, 1210-14 (1984).
5. An Observed Upper Limit on Stratospheric Hydrogen Peroxide, R. L. deZ., A. Parrish, J. Barrett, and P. M. S., draft ms.

D. H. Stedman, University of Michigan

1. Measurement Techniques for the Ozone Layer, D. H. S., Res./Dev., January, 1976, pp. 22-4, 26.

T. C. Steimle, University of Oregon

1. Double Enhancement of the Multiphoton Ionization of Nitric Oxide, T. C. S. and H. T. Liou, Chem. Phys. Lett., 100 (3), 300-4 (1983).

G. M. Stokes, Battelle, Pacific Northwest Laboratories

1. Daytime Variation of Atmospheric NO_2 from Ground-Based Infrared Measurements, J. M. Flaud, C. Camy-Peyret, D. Cariolle, J. Laurent, and G. M. S., Geophys. Res. Lett., 10 (11), 1104-7 (1983).
2. See 2 under R. Zander.
3. Presentation of Twentieth Century Atmospheric CO_2 Record in Smithsonian Spectrographic Plates, G. M. S. and J. C. Barnard, draft ms.

Table 5 (continued)

F. Stuhl, University of Bochum

1. The Ultraviolet Absorption of Some Halogenated Methanes and Ethanes of Atmospheric Interest, C. Hubrich and F. S., J. Photochem., 12 (2), 93-107 (1980).

N. D. Sze, Atmospheric and Environmental Research, Inc. (Formerly Environmental Research & Technology, Inc.)

1. Measurement of Fluorocarbons 11 and 12 and Model Validation: An Assessment, N. D. S. and M. F. Wu, Atmos. Environ., 10 (12), 1117-25 (1976).
2. Heterogeneous Photodecomposition of Halogenated Compounds in the Troposphere, T. Y. Kong and N. D. S., EOS Trans. Am. Geophys. Union, 50 (8), 811 (1978).
3. Stratospheric Fluorine: A Comparison Between Theory and Measurements, N. D. S., Geophys. Res. Lett., 5 (9), 781-3 (1978).
4. Is CS_2 a Precursor for Atmospheric COS? N. D. S. and M. K. W. Ko, Nature, 278, 731-2 (1979).
5. CS_2 and COS in the Stratospheric Sulfur Budget, N. D. S. and M. K. W. Ko, Nature, 280, 308-10 (1979).
6. Coupled Effects of Atmospheric N_2O and O_3 on the Earth's Climate, W. C. Wang and N. D. S., Nature, 286, 589-90 (1980).
7. Atmospheric Ozone: Comparison of Observations with Two-Dimensional Model Calculation, M. K. W. Ko, M. Livshits, and N. D. S., Proc. Quadrennial Int. Ozone Symp. (Boulder, CO), A84-A92 (1980).
8. Photochemistry of COS, CS_2, CH_3SCH_3, and H_2S: Implications for the Atmospheric Sulfur Cycle, N. D. S. and M. K. W. Ko, Atmos. Environ., 14 (11), 1223-39 (1980).
9. The Effects of the Rate for OH + HNO_3 and HO_2NO_2 Photolysis on Stratospheric Chemistry, N. D. S. and M. K. W. Ko, Atmos. Environ., 15 (7), 1301-7 (1981).
10. A 2-Dimensional Calculation of Atmospheric Lifetimes for N_2O, CFC-11, and CFC-12, M. W. K. Ko and N. D. S., Nature, 297, 317-19 (1982).
11. Atmospheric Sodium Chemistry. I. The Altitude Region 70-100 km, N. D. S., M. K. W. Ko, W. Swider, and E. Murad, Geophys. Res. Lett., 9 (10), 1187-90 (1982).
12. Effect of Recent Rate Data Revision on Stratospheric Modeling, M. K. W. Ko and N. D. S., Geophys. Res. Lett., 10 (4), 341-4 (1983).
13. Atmospheric Ozone: Response to Combined Emissions of CFCs, N_2O, CH_4, NO_x, and CO_2, N. D. S., M. K. W. Ko, and W. C. Wang, draft ms.

Table 5 (continued)

N. D. Sze, Atmospheric and Environmental Research, Inc. (Formerly Environmental Research & Technology, Inc.) (continued)

14. The Seasonal and Latitudinal Behavior of Trace Gases and Ozone as Simulated by a Two-Dimensional Model of the Atmosphere, M. K. W. Ko, N. D. S., M. Livshits, M. B. McElroy, and J. A. Pyle, *J. Atmos. Sci.*, in press.

15. Diurnal Variation of ClO: Implications for the Stratospheric Chemistries of $ClONO_2$, HOCl, and HCl, M. K. W. Ko and N. D. S., *J. Geophys. Res.*, in press.

16. A Zonal Mean Model of Stratospheric Tracer Transport in Isentropic Coordinates: Numerical Simulation for N_2O and HNO_3, M. K. W. Ko, K. K. Tung, D. Weisenstein, and N. D. S., *J. Geophys. Res.*, 90 (D1), 2313-29 (1985).

G. A. Takacs, Rochester Institute of Technology

1. Heats of Formation and Bond Dissociation Energies of Some Simple Sulfur- and Halogen-Containing Molecules, G. A. T., *J. Chem. Eng. Data*, 23 (2), 174-5 (1978).

2. Photoabsorption Spectra of Gaseous Methyl Bromide, Ethylene Dibromide, Nitrosyl Bromide, Thionyl Chloride, and Sulfuryl Chloride, A. P. Uthman, P. J. Demlein, T. D. Allston, M. C. Withiam, M. J. McClements, and G. A. T., *J. Phys. Chem.*, 82 (20), 2252-7 (1978).

3. Atmospheric Photodissociation Lifetimes for Nitromethane, Methyl Nitrite, and Methyl Nitrate, W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, and G. A. T., *Int. J. Chem. Kinet.*, 12 (4), 231-40 (1980).

4. Laboratory Investigations Concerning Atmospheric Chlorine, M. J. McClements, W. D. Taylor, M. C. Withiam, T. D. Allston, G. Fazekas, and G. A. T., draft ms.

5. Photoabsorption Spectra of Gaseous CH_3SO_2Cl, CCl_3SCl, SO_2ClF, and $(CH_3O)_2SO$, R. Kozlowski, G. B. Fazekas, M. C. Withiam, K. Bloomer, R. Sampson, T. D. Allston, and G. A. T., *J. Photochem.*, 18 (2), 117-23 (1982).

6. See 11 under C. J. Howard.

B. A. Thrush, University of Cambridge, England

1. The Rates of Reaction of HO_2 with HO and O_2 Studied by Laser Magnetic Resonance, J. P. Burrows, G. W. Harris, and B. A. T., *Nature*, 267, 233-4 (1977).

2. Laser Magnetic Resonance Spectroscopy and its Application to Atmospheric Chemistry, B. A. T., *Acc. Chem. Res.*, 14 (4), 116-22 (1981).

3. The Absolute Intensity of the $_3$ Band of HO_2, J. W. Buchanan, B. A. T., and G. S. Tyndell, *Chem. Phys. Lett.*, 103 (2), 167-8 (1983).

Table 5 (continued)

G. C. Tiao, University of Chicago (Formerly University of Wisconsin), and G. Reinsel, University of Wisconsin

1. Statistical Analysis of Stratospheric Ozone Data for the Detection of Trend, G. R., G. C. T., M. N. Wang, R. Lewis, and D. Nychka, Atmos. Environ., 15 (9), 1569-77 (1981).

2. A Statistical Analysis of Total Ozone Data from the Nimbus-4 BUV Satellite Experiment, G. R., G. C. T., and R. Lewis, J. Atmos. Sci., 39 (2), 418-30 (1982).

3. Analysis of Total Ozone Data for the Detection of Recent Trends and the Effects of Nuclear Testing During the 1960's, G. R., Geophys. Res. Lett., 8 (12), 1227-30 (1981).

4. Analysis of Upper Stratospheric Ozone Profile Data from the Ground-Based Umkehr Method and Nimbus-4 Satellite Experiment, G. R., G. C. T., R. Lewis, and M. Bobkoski, J. Geophys. Res., 88 (C9), 5393-402 (1983).

5. Use of Statistical Methods in the Analysis of Environmental Data, G. C. T., Am. Stat., 37 (4), 459-70 (1983).

6. Analysis of Upper Stratospheric Ozone Profile Data for Trends and the Effects of Stratospheric Aerosols, G. R., G. C. T., J. J. DeLuisi, C. L. Mateer, A. J. Miller, and J. E. Frederick, J. Geophys. Res., 89 (D3), 4833-40 (1984).

W. A. Traub and K. V. Chance, Smithsonian Astrophysical Observatory at Harvard University

1. Stratospheric HF and HCl Observations (15 June 1981), W. A. T. and K. V. C., Geophys. Res. Lett., 8 (10), 1075-7 (1981).

2. Q Branches in the Rotational Spectrum of HOCl, K. V. C. and W. A. T., J. Quant. Spectrosc. Radiat. Transfer, 29 (1), 81-4 (1983).

3. The Torsional Spectrum of Chlorine Nitrate, K. V. C. and W. A. T., J. Mol. Spectrosc., 95 (2), 306-12 (1982).

4. An Upper Limit for Stratospheric Hydrogen Peroxide, K. V. C. and W. A. T., J. Geophys. Res., 89 (D7), 11655-60 (1984).

G. S. Watson, P. Bloomfield, and G. W. Oehlert, Princeton University

1. Stratospheric Ozone - Observations and Data Analysis, G. S. W., Am. Stat., 36 (3, Pt. 2), 312-16 (1982).

2. A Frequency Domain Analysis of Trends in Dobson Total Ozone Records, P. B., G. W. O., M. L. Thompson, and S. Zeger, J. Geophys. Res., 88 (C13), 8512-22 (1983).

3. The Association of Ozone with Meteorological Variables, P. B., M. L. Thompson, G. S. W., and S. Zeger, draft ms.

Table 5 (continued)

G. S. Watson, P. Bloomfield, and G. W. Oehlert, Princeton University (continued)

4. A Statistical Analysis of Umkehr Measurements of 32-46 km Ozone, P. B., M. L. Thompson, and S. Zeger, J. Appl. Meteorol., 21 (12), 1828-37 (1982).
5. Methods of Analysis of Stratospheric Ozone Data, G. S. W., draft ms.
6. Trends in Dobson Total Ozone: An Update through 1982, G. W. O., draft ms.
7. Direct Analysis of Umkehr N-Values for Trends, G. W. O., draft ms.
8. Relative Trends in Atmospheric Temperature Profiles, G. W. O., draft ms.

R. P. Wayne, University of Oxford, England

1. Relative Rate Constants for the Reactions of $O(^1D)$ Atoms with Fluorocarbons and with N_2O, R. G. Green and R. P. W., J. Photochem., 6 (5), 371-4 (1977).
2. Vacuum Ultra-violet Absorption Spectra of Halogenated Methanes and Ethanes, R. G. Green and R. P. W., J. Photochem., 6 (5), 375-7 (1977).

J. R. Wiesenfeld, Cornell University

1. Production of Atomic Oxygen Following Flash Photolysis of $ClONO_2$, S. M. Adler-Golden and J. R. W., Chem. Phys. Lett., 82 (2), 281-4 (1981).

R. Zander, University of Liege, Belgium

1. Recent Observations of HF and HCl in The Upper Stratosphere, R. Z., Geophys. Res. Lett., 8 (4), 413-16 (1981).
2. Simultaneous Detection of FC-11, FC-12, and FC-22, through 8 to 13 Micrometers IR Solar Observations from the Ground, R. Z., G. M. Stokes, and J. W. Brault, Geophys. Res. Lett., 10 (7), 521-4 (1983).
3. Concentrations of Hydrogen Chloride and Hydrogen Fluoride Above the Jungfraujoch and Haute Provence in September 1983, R. Z., G. Roland, L. Delbouille, A. J. Sauval, and P. Marche, draft ms.

R. Zellner, University of Goettingen, F. R. G.

1. H_2 Formation in the Reaction of $O(^1D)$ with H_2O, R. Z., G. Wagner, and B. Himme, J. Phys. Chem., 84 (24), 3196-8 (1980).
2. Pressure and Temperature Dependence of the Reaction $ClO + NO_2 (+ N_2) \rightarrow ClONO_2 (+ N_2)$, V. Handverk and R. Z., Ber. Bunsenges. Phys. Chem., 88 (4), 405-9 (1984).
3. See 5 under Brasseur.

Index to Table 3 by Investigator and Project Number

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number
(continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number
(continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

(continued)

Index to Table 3 by Investigator and Project Number (continued)

---

*(c) indicates completed project