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~~REPORT ON~~
~~"FRENCH ACTIVITIES RELEVANT TO THE STUDY~~
~~OF THE OZONE LAYER (1983-1985)"~~

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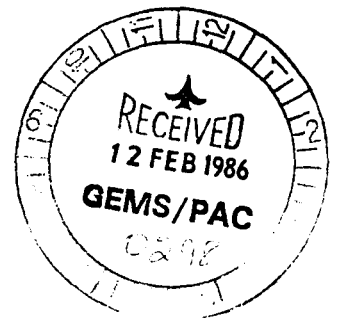
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REPORT ON

"FRENCH ACTIVITIES RELEVANT TO THE STUDY

OF THE OZONE LAYER (1983-1985)"



This document presents a summary of the activities which have been developed by the French laboratories in 1984-1985 in relation with the study of the ozone layer. More than 80 scientists from laboratories (CNRS, University, operational Organizations) have contributed to this effort which is mainly sponsored by the Centre National de la Recherche Scientifique, the Ministère de l'Environnement and the Centre National d'Etudes Spatiales. Three types of activities - laboratory studies, experimental field studies and modelization - are considered hereafter.

1. LABORATORY MEASUREMENTS

Significant results on stratospheric chemistry related to ozone have been obtained at the CNRS - CRCCHT Orléans, and at the Universities of Bordeaux and Lille, during the last two years.

At the CNRS Orléans the following reactions have been studied using the discharge flow method : $\text{Br} + \text{HO}_2$, $\text{Cl} + \text{CH}_3\text{CN}$, $\text{OH} + \text{CH}_3\text{CN}$, and $\text{OH} + \text{ClO}$.

For the reaction $\text{Br} + \text{HO}_2$, the rate constant measured at 298 K, $7.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is much lower than the value previously estimated, but nearly 3.5 times higher than the experimental determination of Posey et al (1981). The present result leads to the conclusion that HO_2 and H_2CO would have a similar efficiency in trapping Br atoms in the stratosphere (HO_2 and H_2CO are the only species which trap Br atoms in the stratosphere).

The rate constant of the reaction $\text{Cl} + \text{CH}_3\text{CN}$, measured in the range 295 - 720 K confirms that this reaction is negligible in the stratosphere for both Cl and CH_3CN species. The activation energy obtained, $5570 \text{ cal.mole}^{-2}$, is unexpectedly high compared to those measured for similar reactions of Cl atoms with methyl containing molecules.

The rate constant of the reaction $\text{OH} + \text{CH}_3\text{CN}$, measured at a pressure near one torr is in agreement with previous values obtained at higher pressures. Therefore a pressure independent rate constant for $\text{OH} + \text{CH}_3\text{CN}$ can be used in modeling the stratosphere at any altitude.

For the reaction $\text{OH} + \text{ClO}$, a rate constant of 1.94×10^{-11} has been measured at 298 K in agreement with the more recent data of Hills and Howard (1984). Due to the possible occurrence of the channel $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ (a) in competition with the channel $\text{OH} + \text{ClO} \rightarrow \text{Cl} + \text{HO}_2$ (b), the branching ratio $k_a / (k_a + k_b)$ has been measured and found to be 0.98 ± 0.07 at 298 K. This additional data implies that reaction $\text{OH} + \text{ClO}$ is negligible in stratospheric ozone chemistry.

Also, very recently, the oxidation reaction of SO_2 by OH has been studied by the discharge flow method at the CNRS Orleans. The effect of O_2 has been confirmed and the rate constant for the reaction of the adduct HSO_3 with O_2 has been measured to be $(3.5 \pm 1) \times 10^{-13}$ at 298 K. This result confirms the HO_x conservation in the atmospheric oxidation of SO_2 .

At the University of Bordeaux studies have been carried out on several reactions involved in the oxidation processes of chlorofluoromethyl radicals resulting from the photolysis of CFM's or their reactions with $\text{O}(^1\text{D})$. Using the Laser Photolysis Time Resolved Mass Spectrometry technique, the following reactions have been studied : $\text{CFCl}_2 + \text{O}_2$ (in the range 0.2 - 12 Torr), $\text{CX}_3\text{O}_2 + \text{NO}$ ($\text{CX}_3 = \text{CF}_3, \text{CF}_2\text{Cl}, \text{CFCl}_2$ and CCl_3) and $\text{CFCl}_2\text{O}_2 + \text{NO}_2$. The rate constants have been determined at 298 K for the reactions $\text{CFCl}_2 + \text{O}_2$, $\text{CFCl}_2\text{O}_2 + \text{NO}$ and $\text{CFCl}_2\text{O}_2 + \text{NO}_2$, and in the range 230 - 430 K for the reactions $\text{CX}_3\text{O}_2 + \text{NO}$. The data obtained show that the successive oxidation of CX_3 radicals by O_2 and NO is fast compared to the initial photolysis of CFM's. However in contrast to the CH_3O_2 radical, the reaction $\text{CX}_3\text{O}_2 + \text{NO}_2 \xrightarrow{(+M)} \text{CX}_3\text{O}_2\text{NO}_2$ would be fast enough in the lower stratosphere to form the peroxyxynitrate to a significant extent. Therefore the halogenated peroxyxynitrates may have an influence as a temporary reservoir for ClO_x and NO_x in the lower stratosphere.

Concerning the chlorofluoromethoxy radicals CX_2ClO , theoretical calculations have shown that they would decompose rapidly into CX_2O and Cl even at the low stratospheric temperatures.

At the University of Lille, an additional measurement of the rate constant of the reaction $\text{OH} + \text{HNO}_3$ has been made using the discharge flow method. The value obtained is $0.95 \times 10^{-13} \exp(843/T)$, in the range 253 - 373 K. At the stratospheric temperatures, this value is somewhat lower than the recommended value but higher than the recent discharge flow measurement of Connell and Howard.

Spectroscopic studies have been carried out at the Laboratoire de Spectrométrie Moléculaire et Atmosphérique in Reims which cover two wavelength ranges :

- Measurements of the ozone absorption cross sections from 240 nm to 340 nm which have been taken into account in the general review performed by R.D. Hudson for the International Ozone Commission.
- Measurements of the molecular oxygen and ozone cross sections from 200 nm to 240 nm in the atmospheric window. They have been performed using a multipath absorption cell (up to 2 km optical path). The results are in good agreement with those obtained by Johnston et al. in the laboratory and Herman and Mentall by direct measurements in the stratosphere.

2. FIELD EXPERIMENTS

In 1983-1985 the experimental studies conducted in France on the ozone layer are related to three major types of activities :

- spaceborne experiments and essentially the Spacelab 1 mission ;
- coordinated campaigns involving balloon borne, air-borne and groundbased instruments : MAP/GLOBUS, BIC, STRAT0Z III ;
- development of groundbased observations and laboratory experiments.

2.a) Spaceborne experiments

Two experiments with a large french participation were flown in 1983 on board of the Spacelab 1 mission, which were directly related to the study of the stratosphere :

- trace constituents measurements from 20 to 140 km altitude using the sun occultation technique and the grid spectrometer jointly developed by the Office National d'Etudes et de Recherches Aérospatiales and the Belgian Institute for Space Aeronomy (IAS) : HCl, HNO₃, H₂O, CH₄, CO₂...

- solar spectrum measurements in the UV and visible spectral ranges with an instrument jointly developed by the Service d'Aéronomie du CNRS, the IAS in Belgium and the Heidelberg Observatory in the FRG.

The ONERA team was also involved in the ground validation of the LIMS data and in their theoretical analysis. A. Chedin and N. Scott from the Laboratoire de Météorologie Dynamique du CNRS studied new algorithms for the inversion of the TOVS data on board of the NOAA operational satellites. This work is being performed in collaboration with S. Müller and S. Cayla from the Centre National de Recherche Météorologique in Toulouse who have developed a method to reconstitute the 20-ozone fields from the same data.

2.b) Coordinated campaigns - Balloon and airborne experiments

Several french teams were involved in the international campaigns which have used large stratospheric balloons to intercompare instruments during the last two years :

- MAP/GLOBUS in september 1983 when 13 Gondolos were launched from Aire sur l'Adour in the south of France by the CNES including NO₂ measurements by absorption spectrometer in the visible (J.P. Pommereau, Service d'Aéronomie du CNRS), ozone measurements by an in situ chemiluminescent sonde (P. Aïmedieu and A. Matthews, Service d'Aéronomie du CNRS), ozone, NO₂ and NO₃ measurements by star occultation using visible spectrometry (P. Rigaud, Laboratoire de Physique et Chimie de l'Environnement du CNRS).

These measurements were associated to groundbased observations from the Observatoire de Haute Provence (Dobson spectrometer, IR spectrometer and lidar) and the Observatoire de Bordeaux (microwave spectrometer).

- BIC (Balloon Intercomparison Campaign) in June 1983 organized by NASA in Palestine (Texas) to intercompare various instruments devoted to trace species measurements, with the participation of J.P. Pommereau, Service d'Aéronomie du CNRS (NO₂ and Ozone measurements) and N. Louisnard, ONERA (H₂O, HNO₃, NO, NO₂, HCl, O₃ measurements with the grid spectrometer).

The results of these campaigns are presently being analyzed.

Other balloon borne experiments were also performed which include measurements of :

- NO₃ and O₃ in the 600 nm range and of the solar flux penetration in the Herzberg Continuum by P. Rigaud, J.P. Naudet and Pirre from the LPCE Orléans ;
- optical properties of the aerosol particles in the stratosphere using various spectrometers and polarimeters (J. Lenoble, R. Santer, M. Herman from the Laboratoire d'Optique Atmosphérique in Lille) ;
- fine structure of the stratospheric flow (wave propagation turbulent layers) by J. Barat, C. Sidi and C. Cot from the Service d'Aéronomie du CNRS.

Airborne instruments have also been flown during 1983 and 1984 to study the latitudinal variation of several trace species. These include a grid spectrometer (F. Karcher, CNRM Toulouse) and an in situ instrument to measure ozone and carbon monoxide (A. Flarenco, Laboratoire d'Aérodologie Toulouse).

One flight took place during the MAP/GLOBUS campaign in September 1983 allowing comparisons of NO₂ and HCl integrated column measurements. In June 1984, the STRATOS III campaign led to the observation of the latitudinal repartition (60° N to 60° S) of the integrated content of several stratospheric trace species : HNO₃, HCl, H₂O, CO, CH₄, O₃, NO, NO₂ and N₂O. These data will also complete the seasonal variations as already observed during the former STRATOS experiments in 1976, 1978 and 1980.

2.c) Ground based observations

In 1984 the geophysical station of the Observatoire de Haute Provence has been integrated in the newly developed network of automated Dobson spectrophotometers for Umkehr measurements of the ozone vertical distribution. In complement to these, routine lidar observations of the stratospheric aerosols and Brewer Mast sonde ozone soundings are performed on a routine basis. The station will be operated continuously during the next 5 years under the joint responsibility of the Service d'Aéronomie du CNRS and the Laboratoire de Spectroscopie Moléculaire in Reims. The corresponding data are sent to the World Ozone Center in Toronto.

Other measurements related to the study of the ozone layer are performed at the Observatoire de Haute Provence. They include :

- lidar measurements of the ozone vertical distribution from the ground up to 50 km (J. Pelon and G. Mégie, Service d'Aéronomie du CNRS) using various types of laser sources adapted to the altitude range of interest. They allow the study of the ozone distribution at various spatial and temporal scales going from the short term variations at the tropopause level (stratosphere-troposphere exchange processes) to long term evolution in the upper stratosphere. In addition lidar measurements of the stratospheric temperature are also performed on a routine basis (A. Hauchecorne and M. L. Chanin, Service d'Aéronomie CNRS) providing informations on planetary and gravity waves activity.
- infrared spectrometer observations of various trace species (O_3 , HCl, HF, NO, CH_4) leading to the determination of the altitudes profiles (P. Marché and P. Jouve, Laboratoire de Spectroscopie Moléculaire in Reims).

Measurements of the ozone vertical distribution from 40 to 80 km are also performed using a microwave spectrometer at the Observatoire de Bordeaux (J. de la Noe), reinforcing and complementing thus the overall groundbased activity in France.

Evidence for a daytime variation of the NO_2 total content has been brought by J. M. Flaud and C. Camy Peyret (Laboratoire de Physique Moléculaire et d'Optique Atmosphérique in Orsay) using a Fournier transform spectrometer at $3.4 \mu\text{m}$. Tentative nighttime measurements are presently underway using the moon as a source.

Finally, and of importance for the study of the dynamics of the stratosphere, ST radars are presently being developed in France with a two fold objectives :

- wind profiling and study of short term fluctuations related to wave activity in the lower stratosphere (M. Crochet, Laboratoire de Sondages Electromagnétiques de l'Environnement Terrestre in Toulon) ;
- high spatial (30 m) observations of turbulent layers in the lower stratosphere in relation with the already noted in situ measurements of Barat et al. (F. Bertin, Centre de Recherches en Physique de l'Environnement, Issy-Les-Moulineaux).

3. MODELLING

2D and 3D modelling work on stratospheric dynamics and trace gases distribution is being performed at the EERM in cooperation with ONERA.

The 2D model results have been compared to the zonally averaged monthly mean cross sections derived from LIMS data. The model reproduces the main features of the observations for O_3 and NO_2 . At solstice a large hemispheric dissymetry exists in both the measured and the calculated NO_2 concentrations which is consistent with the existence of N_2O_5 . The calculated HNO_3 profiles are too high above

10 mb compared to the measurements. It is not clear at the present time if this difference must be attributed to inadequacies in the rate of the chemical reactions which control the partitioning between HNO_3 and other NO_x species or to an overprediction of the total nitrogen concentration.

The 3D model contains now a detailed parameterization of the ozone photochemistry based on relaxation coefficients inferred from the 2D photochemical model, along with a more comprehensive radiative code for the IR, UV and visible radiations. Results from a 6 months integration show the model ability to reproduce the main characteristics of the ozone distribution. For instance, the distribution of the total ozone column is characterized by a minimum at the equator, a belt of maxima in the SH at 50° - 60° latitude, a region of large gradients at midlatitudes and ozone maxima above the continents in the NH.

Before this model can be used for climatic sensitivity studies a simulation of at least a full seasonal cycle is needed for a more comprehensive model validation.

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