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Airborne Instruments for the *In Situ* Detection of $ClONO_2$, NO_2, ClO, and BrO in the Stratosphere

Final Technical Report

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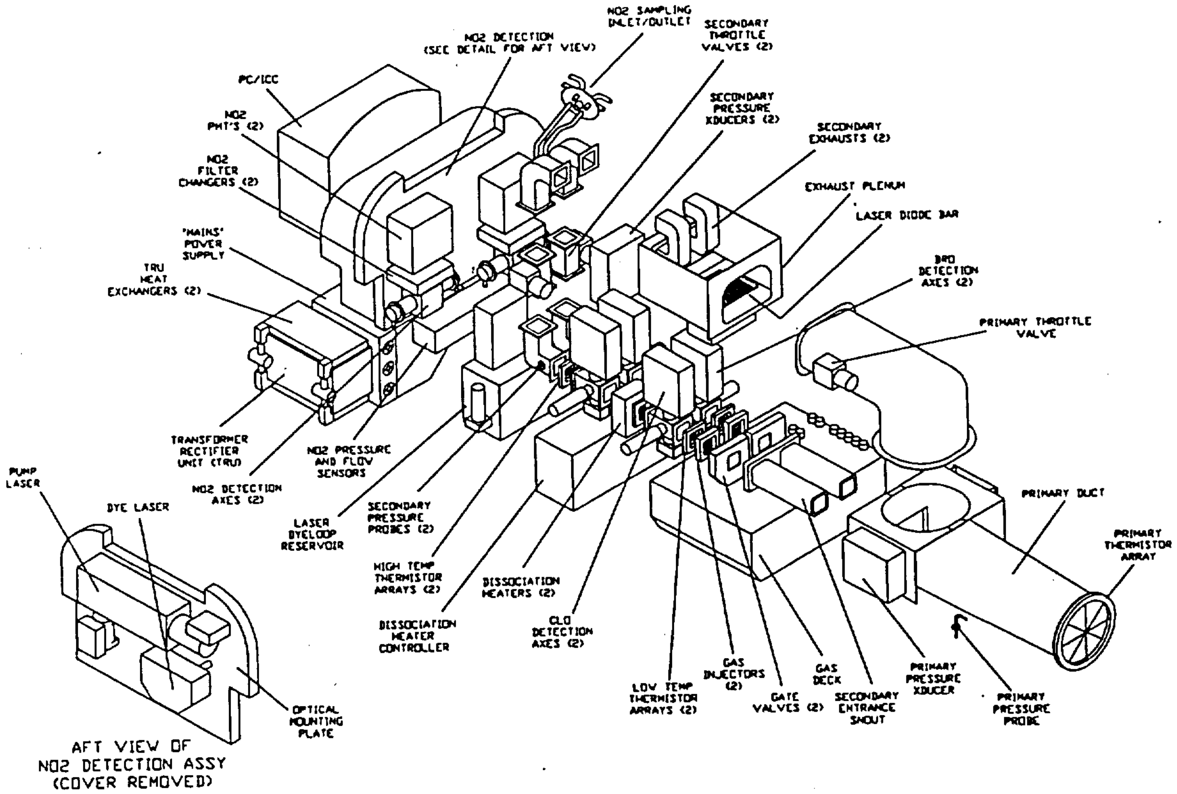
A Final Report: Airborne Instruments for the *In situ* Detection of $ClONO_2$, NO_2, ClO, and BrO in the Stratosphere

The objective of the research supported by this grant was the development of a new instrument to both further the technology of small, lightweight instruments for robotic aircraft and to achieve the ability to detect $ClONO_2$, NO_2, ClO and BrO from the NASA ER-2 aircraft. All of these objectives were accomplished. An exploded schematic of the instrument, developed for the left superpod of the ER-2, is shown below.



The addition of this instrument to the current complement of instruments on the ER-2, in conjunction with the deployment of the ER-2 into the high latitude northern hemisphere summer, allowed the following questions to be addressed:

- Given the addition of *in situ* observations of $ClONO_2$, does the sum of HCl and chlorine nitrate concentrations equal the inorganic chlorine reservoir inferred from the tracer correlation with organic chlorine? Does the simultaneous observation of $ClONO_2$, NO_2, HCl, OH, HO_2, O_3, CH_4, NO, and solar flux yield the same derivatives as calculated from the elementary steps in the network of reactions hypothesized to couple those species?
- Given the addition of *in situ* LIF detection of NO_2 (the rate limiting radical in the dominant nitrogen radical catalyzed destruction mechanism of ozone) in combination with HO_2, ClO, and BrO that rate limit the hydrogen, chlorine and bromine catalytic cycles, respectively, what is the fractional contribution of each of these catalytic cycles to the rate of ozone loss in the high latitude summer? In the midlatitudes and the tropics?

- Does the loss rate of ozone observed on tracer surfaces match the sum of the rate limiting steps determined directly from observations of HO_2, ClO, BrO, and NO_2?
- Does the free radical catalytic system transition from hydrogen-halogen control to nitrogen radical controling the high latitude summer hemisphere? If the system does transition to nitrogen control, how does the transition take place? Does the transition depend in a critical way on aerosol loading? On temperature? On insolation?
- What is the quantitative impact of the absence of nighttime reservoir formation on the inorganic partitioning of species? On the free radical concentrations?
- How is the photochemical structure of the middle-upper troposphere modified in the summer, high latitude period? What are the dominant features of the transition from catalytic destruction of ozone in the lower stratosphere to catalytic production of ozone in the troposphere?
- What are the dominant chemical sources of HO_x in the middle-upper troposphere during high latitude summer? Are proposed sources such as $BrONO_2 + H_2O$ of quantitative importance?
- What is the $[ClO]/[Cl_y]$ ratio and the $[HO_2]/[HO_x]$ ratio as a function of NO_2 concentration? NO_x concentration? NO_y concentration?
- Given the addition of LIF detection of NO_2, does the observed $[NO]/[NO_2]$ ratio match that calculated from the elementary steps? Does the observed $[NO_x]/[NO_y]$ ratio match that calculated from the elementary steps? Do the derivatives match?
- Penetration into the high latitudes of the northern hemisphere with multiple flights covering a period of six months provides the opportunity to explore a large dynamic range in species concentrations, temperatures, daylight-to-darkness ratios, and terminator transit periods. Do the diurnal patterns in species concentrations reveal missing processes?
- By what mechanism and in what pattern is material exchanged between high latitudes and the topics during northern hemisphere summer?
- What are the initial conditions of the species concentrations that constitute the arctic vortex for the winter that *follows* the POLARIS campaign?
- What conclusions can be drawn regarding the degree of ozone destruction within the arctic vortex by halogen catalysis during the *previous* winter by investigating the remnants of the vortex in April?

The instrument flew as an integral part of the NASA Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission. That mission took place in 1997. Using the instrument developed under this grant, the following steps have been accomplished. Publications of these results from the POLARIS mission will appear in a special issue of *Journal of Geophysics—Atmospheres* in Fall 1999.

1. ***In situ* measurements of $ClONO_2$: A new thermal dissociation resonance fluorescence instrument on board the NASA ER-2 aircraft.** The partitioning of inorganic chlorine species has remained a prominent question in stratospheric chemistry. Specifically, the lack of an *in situ* measurement of $ClONO_2$ has been a severe hindrance to achieving closure on key questions about inorganic chlorine partitioning. We describe a new instrument for the measurement of $ClONO_2$ using a novel thermal dissociation resonance fluorescence technique that has flown on the NASA ER-2 aircraft. The $ClONO_2$ molecule is measured by first heating a flowing

airstream up to 250°C, thermal dissociating $ClONO_2$ in the gas phase into ClO and NO_2, and then titrating the ClO fragment with NO to form chlorine atoms. The chlorine atoms are then detected using atomic resonance fluorescence. Laboratory calibrations and aircraft measurements indicate that the technique can be described using simple gas phase processes and that the instrument has the ability to measure $ClONO_2$ reliably down to a detection threshold of 10 parts per trillion in short integration times (35 seconds).

2. **The coupling of $ClONO_2$, ClO and NO_2 in the lower stratosphere from *in situ* observations using the NASA ER-2 aircraft.** The first *in situ* measurements of $ClONO_2$ in the lower stratosphere, acquired using the NASA ER-2 aircraft during the Polar Ozone Loss in the Arctic Region in Summer (POLARIS) mission, are combined with simultaneous measurements of ClO, NO_2, temperature, pressure and the calculated photolysis rate coefficient (J_{ClONO2}) to examine the balance between production and loss of $ClONO_2$. The observations demonstrate that the $ClONO_2$ photochemical steady state approximation, $[ClONO_2]^{PSS} = k \times [ClO] \times [NO_2] / J_{ClONO2}$, is in good agreement with the direct measurement, $[ClONO_2]^{MEAS}$. For the bulk of the data (80%), where $T > 220K$ and latitudes > 45°N, $[ClONO_2]^{PSS} = 1.15 \pm 0.36\ (1\sigma) \times [ClONO_2]^{MEAS}$, while for $T < 220K$ and latitudes < 45°N the result is somewhat less at 1.01 ±0.30. The cause of the temperature and/or latitude trend is unidentified. These results are independent of solar zenith angle and air density, thus there is no evidence in support of a pressure-dependent quantum yield for photodissociation of $ClONO_2$ at wavelengths > 300 nm. These measurements confirm the mechanism by which active nitrogen ($NO_x = NO + NO_2$) controls the abundance of active chlorine ($Cl_x = ClO + Cl$) in the stratosphere.
3. ***In situ* measurements of $ClONO_2$, HCl and ClO: The inorganic chlorine budget of the northern hemisphere lower stratosphere.** We present simultaneous *in situ* measurements of $ClONO_2$, ClO, HCl, and Cl_y inferred from organic chlorine source species made on board the NASA ER-2 aircraft during the POLARIS campaign. These data indicate that the sum of the measured inorganic chlorine species ($ClO + ClONO_2 + HCl$) is within 10% of the total inorganic chlorine inferred from measurements of organic chlorine source gases. These measurements provide evidence that there are no significant reservoirs of inorganic chlorine missing from our current description of the inorganic chlorine budget.
4. **The ratio of $ClONO_2$/HCl in the summer lower stratosphere: Does homogeneous phase photochemistry explain the observations?** *In situ* measurements of $ClONO_2$ and HCl in the summer lower stratosphere from POLARIS are used with simultaneous measurements of O_3, OH, CH_4, and calculated photodissociation rates (J_{NO2} and J_{ClON2}) to test our understanding of the homogeneous photochemical processes that control the partitioning of inorganic chlorine between $ClONO_2$ and HCl. If these two species are in diurnal, photochemical steady state and the known principal production and loss mechanisms for HCl are correct, the ratio of $ClONO_2$/HCl should be proportional to $[O_3]^2/[CH_4]$, among other terms. Instantaneous steady-state calculations and calculations along back trajectories demonstrate that the partitioning of $ClONO_2$ and HCl is in agreement with known photochemistry for these data.