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

Progress Report
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Design and construction of an *in situ* sensor for the detection of stratospheric $ClONO_2$, ClO, BrO, and NO_2, was conceived as a two-year program. The experiment has two novel components: a resistive silicon thermal dissociation heater used to fragment $ClONO_2$ into ClO and NO_2 and a laser-induced fluorescence sensor for NO_2. These two new components are integrated into an experiment that uses technology developed in our labs for the ER-2 ClO and ER-2 HO_x instruments. During the first year we reconstructed our laboratory prototypes for $ClONO_2$ and NO_2 detection and made substantial improvements in the calibration apparatus. Results from these laboratory experiments have been used to refine the design of the flight instrument. During this year we began the design of all of the long-lead items required to produce a flight instrument: including the design and fabrication of the air flow system used to direct stratospheric air to our halogen sensors, design and prototyping of an aircraft-compatible thermal dissociation heater, and development and test of a new high powered laser system. Finally, we have designed and released for fabrication several subsystems.

The elementary step of our technique is the gas-phase thermal dissociation of $ClONO_2$, producing ClO and NO_2. Detection of ClO is accomplished by chemical titration with nitric oxide (NO) converting ClO to Cl, followed by Cl atom detection using resonance fluorescence. Prior laboratory experiments demonstrated the potential of the thermal dissociation-resonance fluorescence technique to produce a signal proportional to $ClONO_2$ under a wide range of conditions (pressure, concentration of $ClONO_2$, flow velocity); however, the proportionality constant was 20–30% lower than expected, raising concerns about the accuracy of the technique. In this early phase of our work we improved the purity of our $ClONO_2$ sample, and tested several other hypotheses that were consistent with the low yield. At the same time, we developed our NO_2 prototype. Because ClO and NO_2 are produced 1:1 in the thermal dissociation step, we view simultaneous detection of both fragments as the most rigorous possible test of our apparatus. The results are shown in Figures 1–3. We find that NO_2 is produced in proportion to the $ClONO_2$ dissociated and that the proportionality constant is one, exactly as expected (Figure 1). Furthermore, upon conversion of ClO to Cl, theory predicts a

doubling of the NO_2, which is exactly what we observe (Figure 2); however, we still observe a low yield of Cl atoms (Figure 3). These results show that (i) the dissociation event is a simple gas-phase process, (ii) ClO and NO_2 are produced 1:1 without any loss of ClO on the surface of the heaters, and (iii) the yield is independent of pressure, velocity, or composition of the buffer gas. We have developed a calibration approach that will provide direct calibration at elevated temperatures, which will pinpoint the 20–30% difference in ClO yield from $ClONO_2$ dissociation.

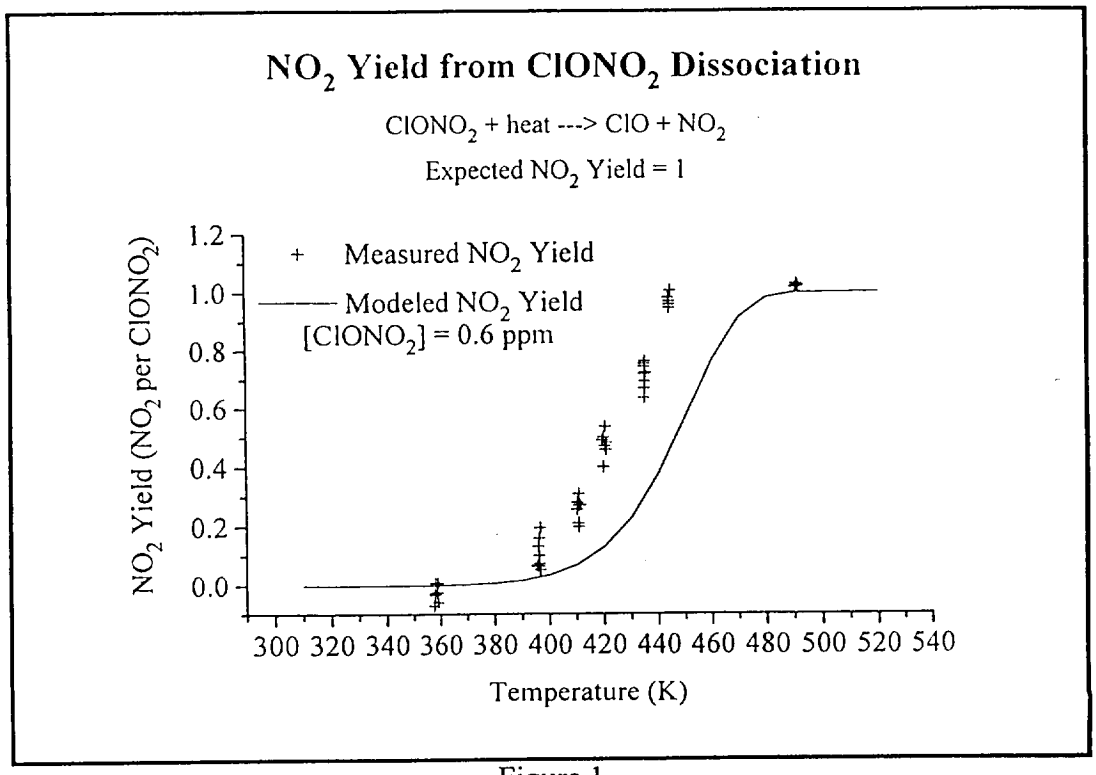

Figure 1

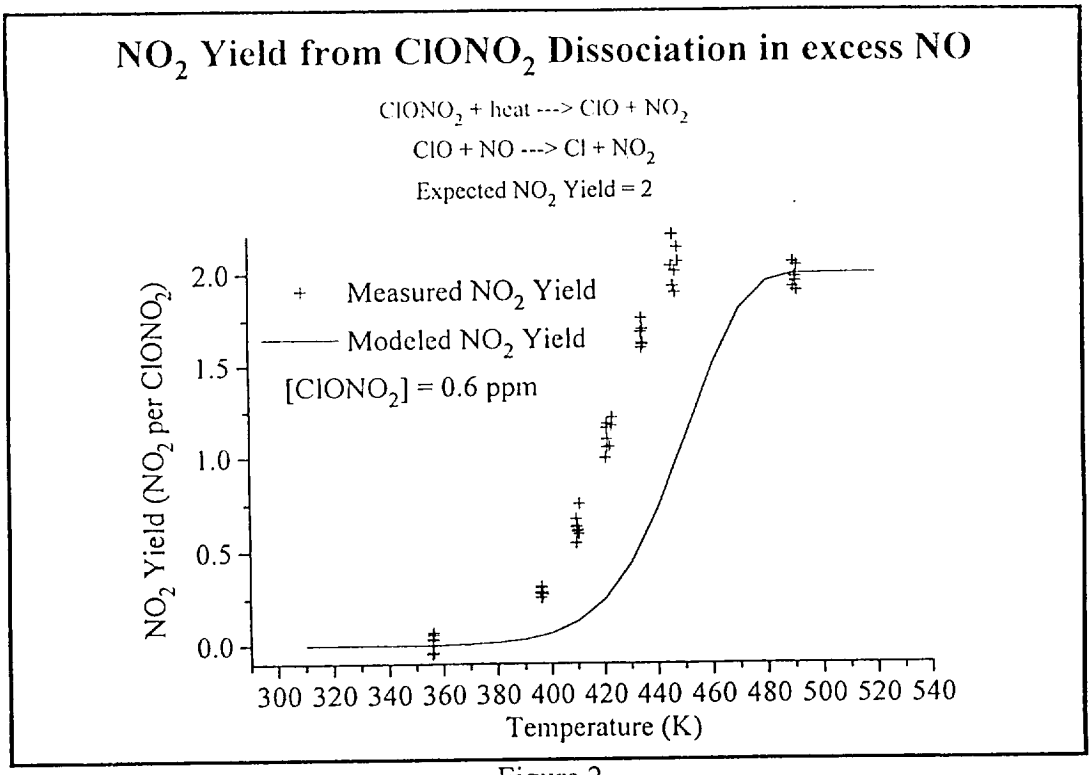

Figure 2

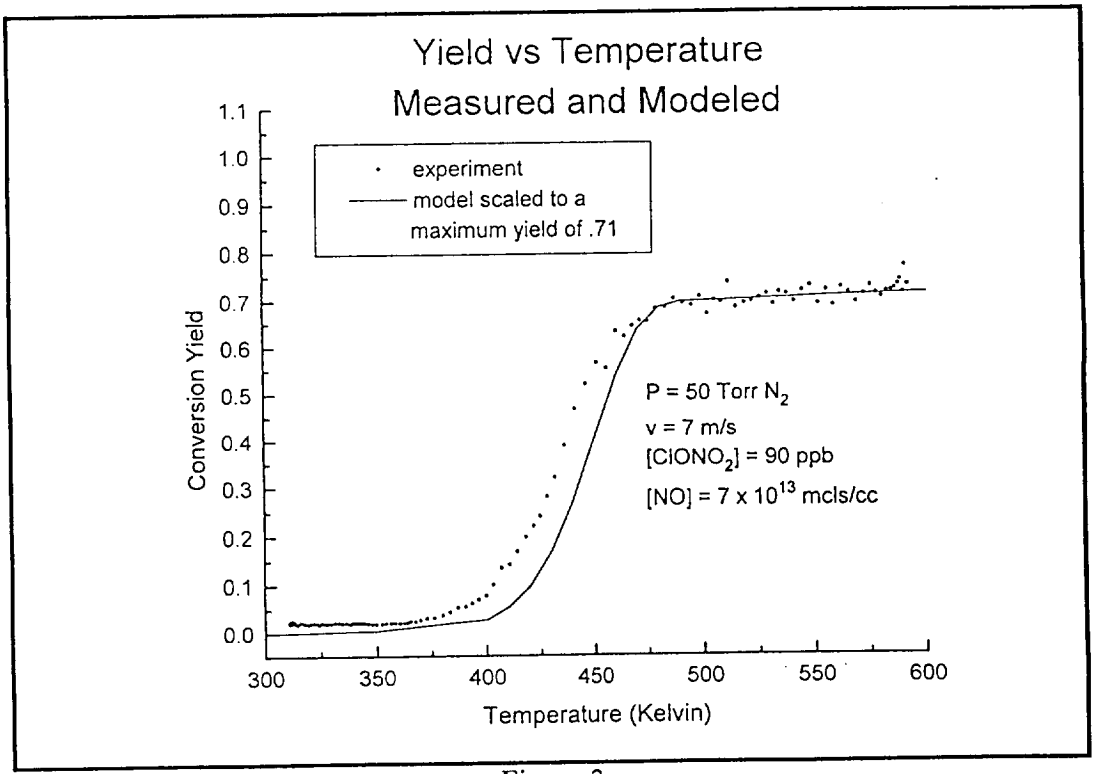

Figure 3

In parallel, rapid progress has been made toward the development of an airborne instrument with sufficient sensitivity, precision, and reliability to produce high quality measurements. To date, we have a mechanical design layout describing the geometry of all the major components. Electrical designs for all the major subsystems are underway. Fabrication drawings for about two thirds of the machined parts have been released. About one third of the electrical subsystems are in fabrication. More specifically, we have: (i) developed new electrical and mechanical designs for the chlorine and bromine detection systems, which reduce the weight of those subsystems substantially; (ii) redesigned significant portions of our data acquisition system to reduce weight and to support the complex control algorithms required for this instrument; (iii) incorporated a state-of-the-art diode-pumped solid-state laser, increasing the power of our dye laser system by a factor of ten over that of our laboratory prototype; and (iv) devoted considerable attention to the design and safe operation of the 3000 W resistive heaters that we plan to use to thermally dissociate $ClONO_2$.