

**LABORATORY STUDIES OF
CHEMICAL AND PHOTOCHEMICAL
PROCESSES RELEVANT TO
STRATOSPHERIC OZONE**

Prepared by

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1. RESEARCH OBJECTIVES

The purpose of this project is to reduce the uncertainty in several key gas-phase kinetic processes which impact our understanding of stratospheric ozone. The main emphasis of this work is on measuring rate coefficients and product channels for reactions of HO_x and NO_x species in the temperature range 200 K to 240 K relevant to the lower stratosphere. The results of these studies will improve models of stratospheric ozone chemistry and predictions of perturbations due to human influences.

2. RESULTS FROM NASA SUPPORTED PROGRAM 1996-1997

The second year's effort has focused on three separate research areas: 1) the construction of the proposed high pressure flow reactor, 2) characterization of the turbulent flow profile, and 3) demonstration of the instrument by measuring $\text{HO}_2 + \text{NO}_2$ and $\text{HO}_2 + \text{NO}$ reaction rate coefficients. We shall discuss our work in each of these areas separately below.

2.1 Instrument Construction

A central theme of the studies suggested in this proposal is the measurement of stratospherically important reaction rate constants under conditions (190-240 K and 50 - 200 torr) characteristic of the stratosphere - especially the lower stratosphere. In order to accomplish these goals, we adopted the turbulent flow reactor technique [Seeley, Jayne and Molina, 1993; Seeley, 1994]. This is a recently demonstrated approach based on a simple extension of the traditional low pressure laminar flow discharge flow method. Our new turbulent flow reactor design is based on an existing low pressure laminar flow reactor [Nelson and Zahniser, 1994; Zahniser, McCurdy, and Stanton, 1989] which required some modification. A simple schematic of the instrument is shown in Figure 1.

The major modification to the low pressure instrument was a change in the detection configuration. In both the low and high pressure configurations, molecules are detected using direct absorption of tunable diode laser radiation in an off axis astigmatic multipass cell invented and developed by Aerodyne Research [Kebabian, 1994; McManus et al., 1994]. The low pressure configuration had the gas flow passing perpendicular to the mirrors. In the new high pressure configuration, a sampling tube with a sonic orifice draws a significant amount (10-35%) of the flow tube flow into a reduced pressure (~5% of the flow tube pressure) multipass cell such that the flow is traversing the length of the cell. Only the center of the flow tube turbulent flow is sampled into the cell.

The new configuration also required a change in the pumping arrangement. The Roots blower used to pump the flow tube in the low pressure configuration is now used to pump the multipass cell. A high pressure, high throughput pump capable of pumping 7 liters s^{-1} between 10 torr and atmospheric pressure was purchased and is used to pump the flow tube.

Another modification necessary was to switch from a low pressure Evenson microwave cavity to a high pressure Beenaker cavity [Beenaker, 1976]. The new microwave cavity allows for the generation of HO_2 radicals at pressures in the range of 10 torr to 760 torr.

A new configuration for cooling the flow tube was also necessary. The nitrogen carrier gas, in addition to the flow tube, had to be cooled due to the large carrier gas flows necessary for

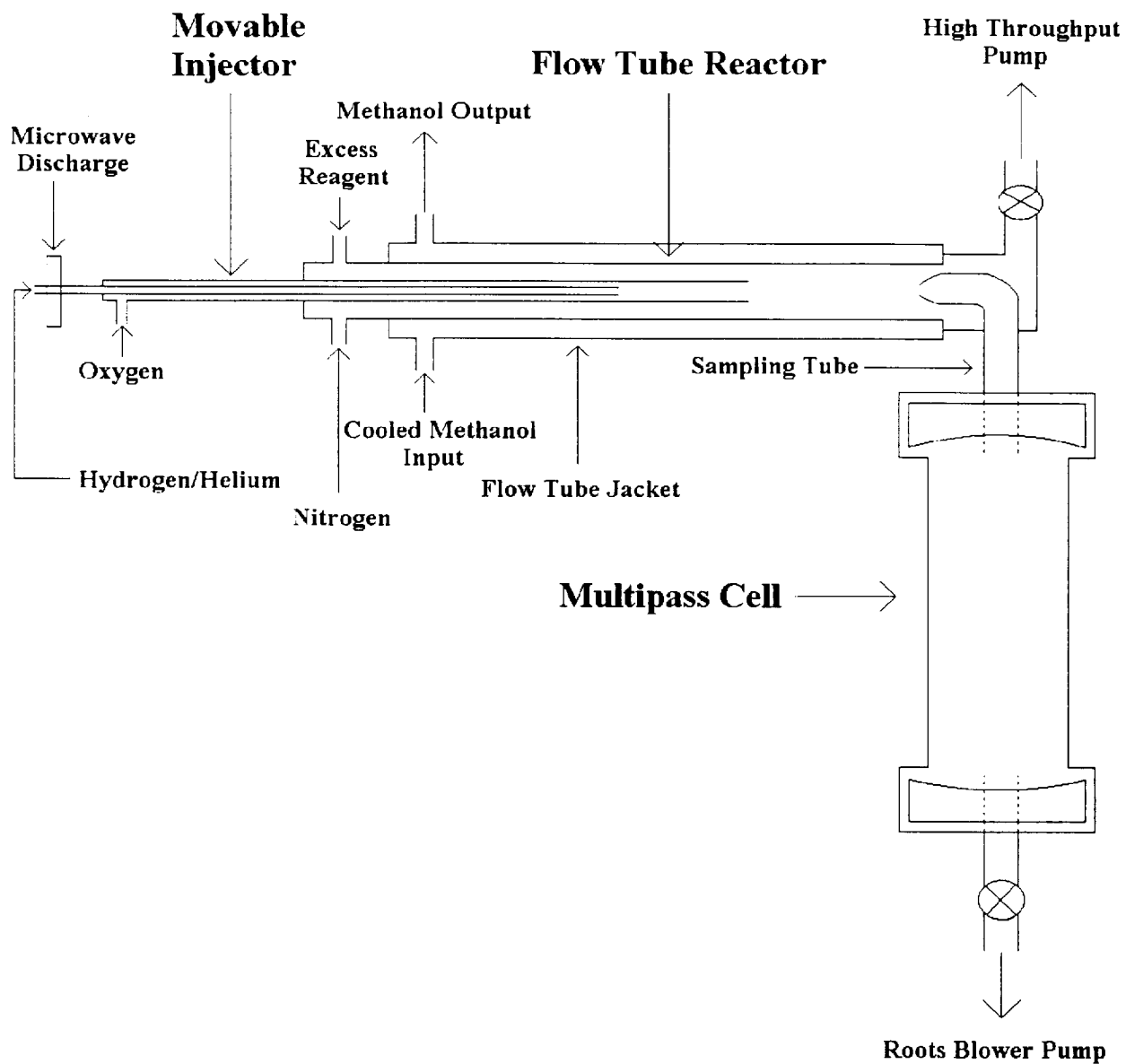


Figure 1. Simple schematic of the high pressure turbulent flow reactor with tunable diode laser absorption detection with an astigmatic Herriott multipass cell.

turbulent flow. The nitrogen was cooled by passing it through a coil of copper tubing immersed in liquid nitrogen and subsequently warmed to the appropriate temperature (200 - 295 K) prior to introduction to the flow tube by passing it through an additional length of copper tubing wrapped with heating tape. The gas temperature is measured by a thermocouple immediately prior to entering the flow tube. The flow tube is cooled by chilled methanol which is pumped through the stainless steel jacket which surrounds the flow tube. The methanol is pumped out of a reservoir which consists of a flat bottom stainless steel container with fifteen 0.75" dia. x 12" long copper tubes which have been soldered to the bottom of the container. These copper tubes sit in a dewar filled with liquid nitrogen. The reservoir has heating pads wrapped around it for temperature regulation. The temperature of the methanol is measured with thermocouples just prior to entering the jacket and just after exiting it. Thermocouples are attached to the end of the injector and the tip of the sampling tube to measure the gas inside the flow tube. It is the temperature of the gas in the flow tube as measured by these two thermocouples which is used as the reaction temperature and in the data analysis. The temperature of the methanol and the temperature of the gas in the flow tube are adjusted to match as closely as possible.

The final major change to the instrument was to modify the data acquisition system by changing both the hardware and the software. Two computers are now used with one devoted to determining the reactant concentration and the other used to record those concentrations along with the temperatures, pressures, and gas flows and to determine flow velocities, Reynolds numbers, etc. A new computer program was implemented for this second computer and, in addition to recording concentrations and flow tube parameters, it has a graphical component which allows for viewing of the data and parameters and does fitting of the data. A new AD board is also in use.

2.2 Flow Speed Measurements

The gas flow in the turbulent regime separates into a fast flowing turbulent core surrounded by a slow flowing laminar layer at the flow tube wall. The flow speed profile across the flow tube diameter was measured to confirm this picture and to determine an expression which can be used to calculate a characteristic flow speed for the turbulent core at a given Reynolds number. A pitot tube/mechanical manipulator was designed and built to measure the flow speeds across the end of the flow tube from top to bottom. The pitot tube was ~1mm wide allowing for 17 measurements to be made across the 2.5 cm ID flow tube. The pitot tube

extended ~3 cm into the flow tube. The pitot tube pressure differential was measured by a 1 torr differential capacitance manometer. The distance from entrance of the carrier gas to the end of the flow tube is ~75 cm. This distance is insufficient to attain fully developed turbulent flow. In addition, the injector has an OD of ~1.3 cm and therefore the flow profile will experience a large perturbation at the tip of the injector. Two teflon disks with slots cut into them in a symmetric pattern and a ~1.3 cm hole in the center were slid onto the injector. One of the disks is at the very tip of the injector and the other disk is ~10 cm behind it. These disks serve to induce symmetric and turbulent flow after the injector tip. Several design iterations were required to get the final relatively symmetric flow profiles. Flow profiles were measured at different injector position distances from the pitot tube (i.e. sampling tube position in the flow tube). A typical series of profile measurements are shown in Figure 2. Flow profiles were also measured at different Reynolds numbers and at two different temperatures. A characteristic flow speed for a given profile was determined by area weighted averaging of the individual flow speed measurements of the profile. All the individual measurements appear to be within the turbulent core and eddy diffusion (eddy diffusion coefficient = 5-25 cm²/s) should help reduce any concentration gradients present in the cross sectional area of the flow tube due to the slightly slower flow speeds as one goes from the center of the flow tube to the edges. A plot of the characteristic flow speed as a function of Reynolds number is shown in Figure 3. A fit to this plot over the turbulent region (Reynolds number > 3000) yields the expression: $u_{\text{eff}}/u_{\text{ave}} = 1 + 25.7 \cdot \text{Re}^{-0.661}$ where u_{eff} is the flow speed calculated as described above, u_{ave} is the average flow speed of all the gas, and Re is the Reynolds number. This expression is used to determine the flow speed, and hence reaction time, for the kinetic measurements.

2.3 Kinetic Measurements Using Instrument

Kinetic measurements of the HO₂ + NO₂ and HO₂ + NO reactions are ongoing. Preliminary measurements of the HO₂ + NO reaction rate coefficient at 100 torr and 293 K have been made and a value of $8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined. This value agrees with the recommended value from the NASA evaluation [DeMore et al., 1997] although there may be a slight correction necessary due to secondary chemistry. This is currently being investigated. Measurements of the HO₂ + NO₂ reaction rate coefficients have been made at pressures of 50, 100, 150, and 200 torr. These measurements are shown in Figure 4 and are in good agreement with the current pressure dependent rate coefficient recommendation from the NASA evaluation [DeMore et al., 1997]. Measurements of these two reactions at other pressures and lower temperatures are underway. HO₂ wall losses at temperatures of 233 K and 200 K and 100 torr have been measured to be $20 \pm 3 \text{ s}^{-1}$ and $23 \pm 3 \text{ s}^{-1}$, respectively. These wall losses are a fraction of the largest first order losses (70 - 80 s⁻¹) measured in the previously completed kinetic

measurements. Huge HO₂ wall losses at these temperatures have previously limited the temperature range of HO₂ kinetic measurements made in a flow tube.

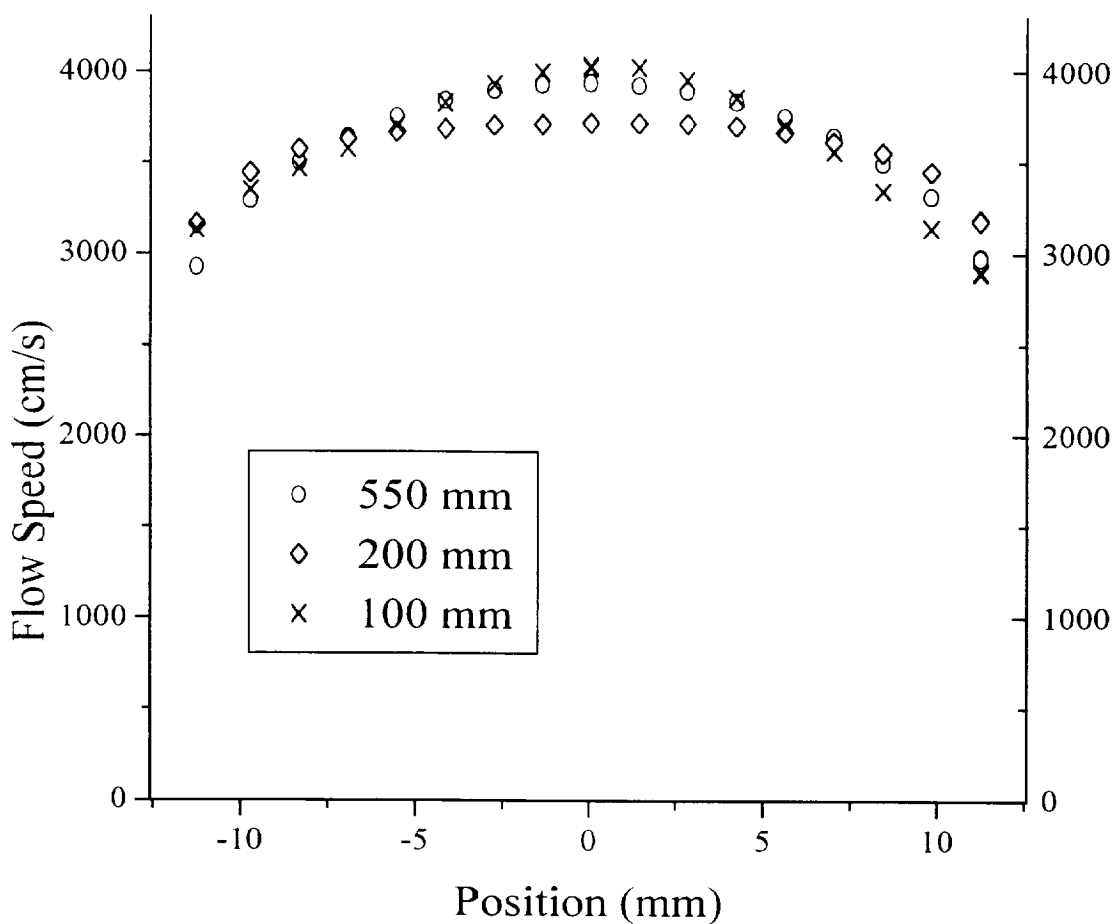


Figure 2. The one dimensional flow speed profile across the flow tube diameter in the vertical direction (i.e. the flow speed as a function of vertical position in the flow tube) at different injector positions in the flow tube. The circles, diamonds, and crosses are for the injector 550, 200, and 100 mm, respectively, from the tip of the pitot tube. These measurements were made with a bulk flow velocity of 3220 cm/s, a Reynolds number of 7250, and a pressure of 100 torr.

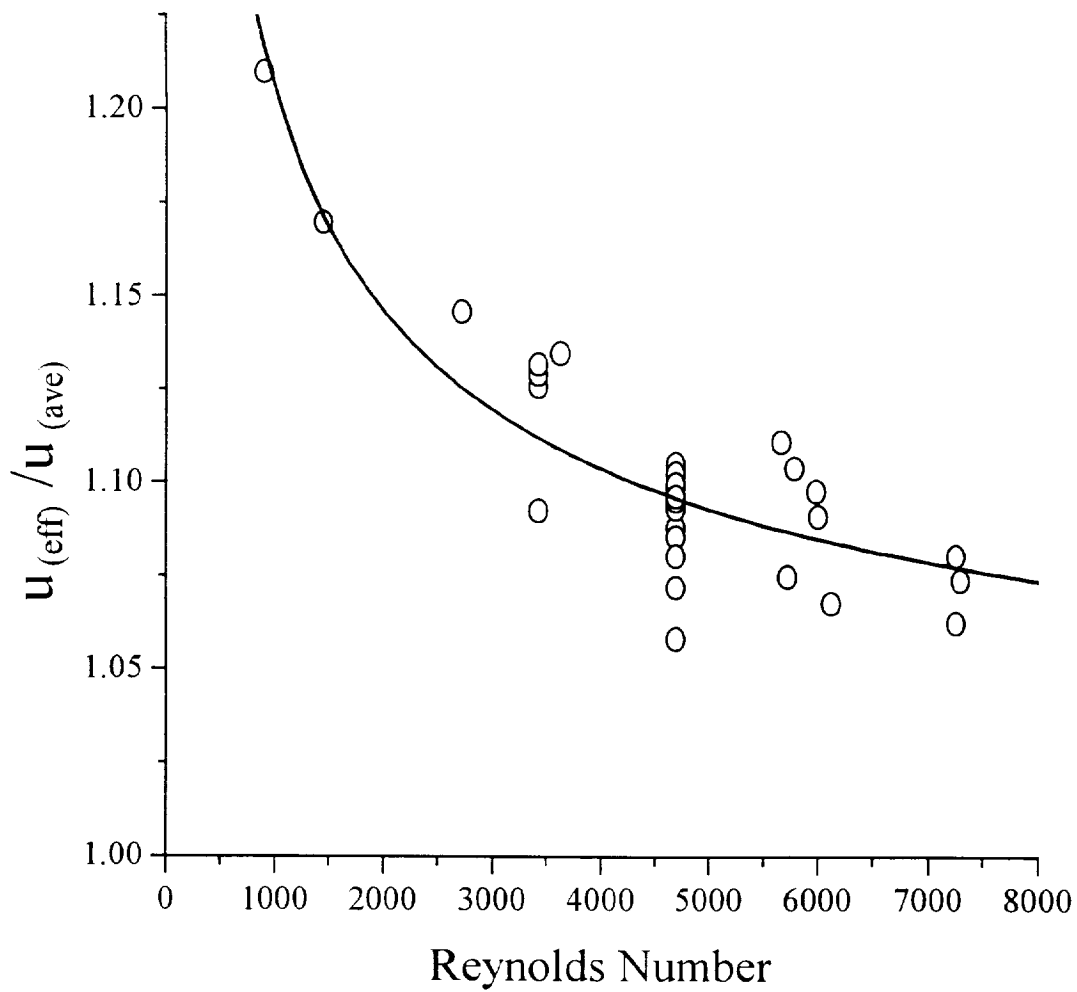


Figure 3. Ratio of the effective flow speed to the bulk flow speed ($u_{(eff)}/u_{(ave)}$) as a function of Reynolds number. The line plotted is the fit to the data and described by the expression:
 $u_{(eff)}/u_{(ave)} = 1 + 25.7 \cdot Re^{-0.661}$.

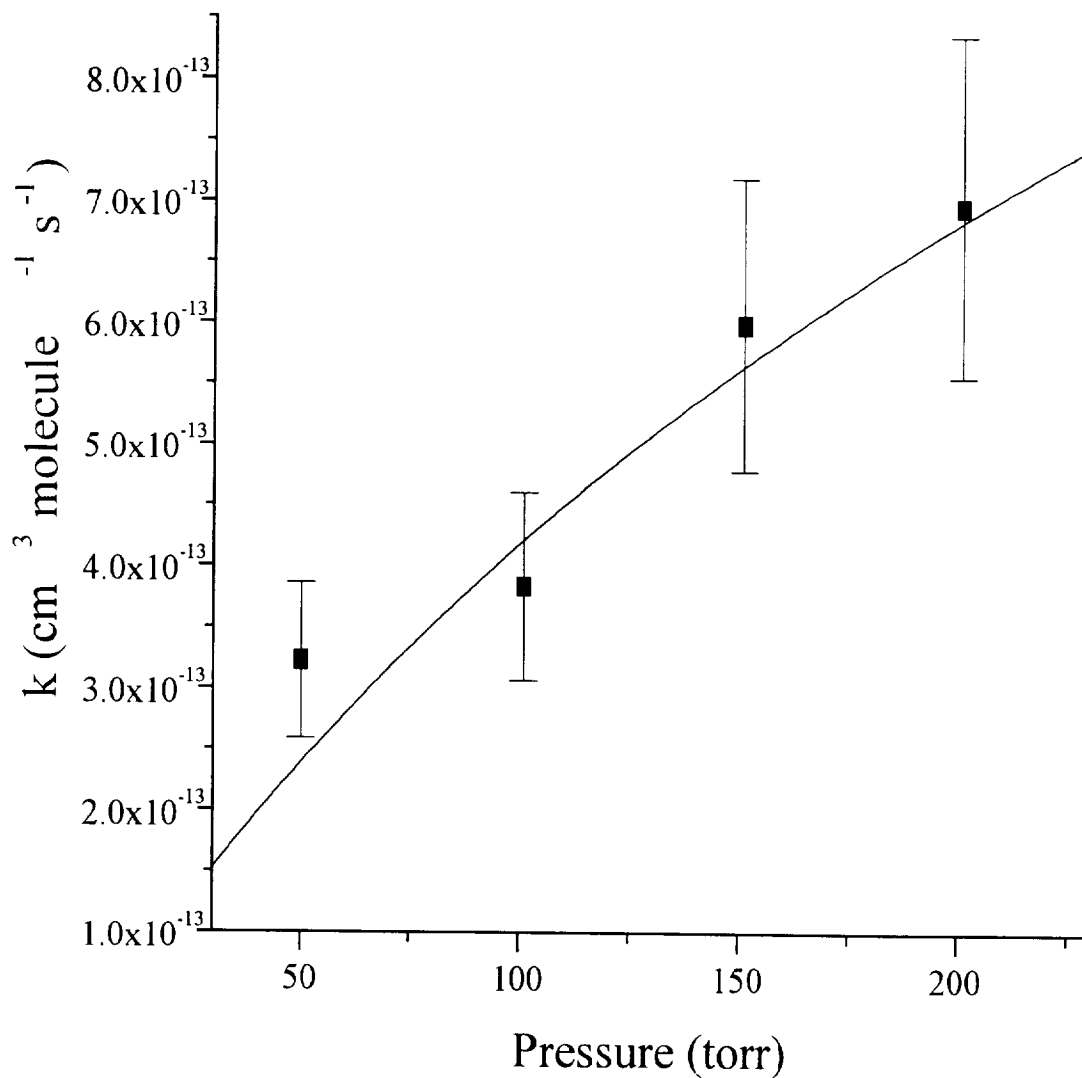


Figure 4. Measured rate coefficients for the $\text{HO}_2 + \text{NO}_2$ reaction at 50, 100, 150, and 200 torr and 293 K plotted along with a line representing the pressure dependent rate coefficient recommendation from the NASA evaluation [DeMore et al., 1997].

2.4 Archival Publications Prepared Under the Current Contract

Molina, M.J., L.T. Molina and C.E. Kolb, "Gas-Phase and Heterogeneous Chemical Kinetics of the Troposphere and Stratosphere," *Ann. Rev. Phys. Chem.* **47**, 327 (1996)

Tao, F.M., K. Higgins, W. Klemperer and D.D. Nelson, "Structure, Binding Energy, and Equilibrium Constant of the Nitric Acid-Water Complex." *Geophys. Res. Lett.* **23**, 1797 (1996).

Nelson, D.D., J.T. Wormhoudt, M.S. Zahniser, C.E. Kolb, M.K.W. Ko and D.K. Weisenstein, "OH Reaction Kinetics and Atmospheric Impact of 1-Bromopropane." *J. Phys. Chem.* **101**, xxx (1997).

2.5 General References

Seeley, J.V., J.T. Jayne and M.J. Molina, "High Pressure Fast-Flow Technique for Gas Phase Kinetics Studies," *Int. J. Chem. Kinet.* **25**, 571 (1993).

Nelson, D.D. and M.S. Zahniser, "A Mechanistic Study of the Reaction of HO₂ Radical with Ozone," *J. Phys. Chem.* **98**, 2101 (1994).

Zahniser, M.S., K.E. McCurdy and A.C. Stanton, "Quantitative Spectroscopic Studies of the HO₂ Radical: Band Strength Measurements for the ν_1 and ν_2 Vibrational Bands." *J. Phys. Chem.* **93**, 1065 (1989).

Seeley, J.V. "Experimental Studies of Gas Phase Reactions Using the Turbulent Flow Tube Technique," Ph.D. Thesis, MIT (1994).

DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb and M.J. Molina, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling," Evaluation Number 12, Report No. JPL 97-4, National Aeronautics and Space Administration, Jet Propulsion Laboratory, Pasadena, CA (1997).

Kebabian, P.L., "Off-Axis Cavity Absorption Cell," U.S. Patent #5,291,265, March 1, 1994.

Beenaker, C.I.M., *Spectrochim. Acta* **31B**, 483 (1976).

McManus, J.B., P.L. Keabian, M.S. Zahniser, "Astigmatic Mirror Multiple Pass Absorption Cells for Long Pathlength Spectroscopy," *Applied Optics* **34**, 3336 (1995).

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