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Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis

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NOTICE

Project Overview

This research program is an integrated effort to determine the reaction mechanisms responsible for the oxidation of small molecule hydrocarbon structures under conditions representative of combustion environments. The experimental aspects of the work are conducted in an atmospheric pressure flow reactor (APFR) as well as in a new variable pressure flow reactor (VPFR) facility which extends the ranges of parameters available in the APFR, particularly the pressure, (1-15 atm.), the temperature (600 K to 1200 K), and the observation time (10 to 5,000 milli-seconds).

Gas sampling of stable reactant, intermediate, and product species concentrations provide substantial definition of not only the phenomenology of reaction mechanisms, but a much more constrained set of pure kinetic information than can be derived in flames, or shock tubes. Analytical techniques used for detecting hydrocarbons and carbon oxides include gas chromatography, gas chromatography/mass spectrometry for off-line analyses. Non-dispersive infrared and Fourier transform Infrared methods are utilized for continuous on-line sample detection of light hydrocarbons, carbon oxides, and oxygenated species. The VPFR is presently being adapted for resonance absorption measurements of OH, utilizing methods similar to those previously developed utilizing the atmospheric pressure flow reactor (APFR), but with much higher sensitivity.

The modeling aspects of the program emphasize the use of hierarchical mechanistic construction along with path and elemental gradient sensitivity analyses in developing detailed kinetic mechanisms. Kinetic mechanistic studies are utilized for understanding the experimental observations performed as part of this program as well as for developing comprehensive kinetic models for use in general combustion modeling. Modeling using a well defined and validated mechanism for the $CO/H_2/Oxidant$ systems and perturbations of experimental oxidations by small amounts of additives are also used to derive absolute reaction rates and to investigate the compatibility of elementary kinetic rate information.

Chemical issues of particular interest include: the $CO/H_2/O_2$ system and its perturbation (to obtain elementary kinetic data) by small amounts of an added hydrocarbon or hydrocarbon oxygenate; the pyrolysis and oxidation mechanisms of simple aldehydes; the pyrolysis and oxidation mechanisms of simple alcohols; and the pyrolysis and oxidation mechanisms of simple olefins.

Of considerable significance in all of the above is the experimental and mechanistic extension of research on these systems to pressures as high as 15 atmospheres and to temperatures as much as 150 to 250 K lower than was previously possible. This work places strong emphasis on improving understanding of the reactions of molecular oxygen with radicals, the chemistry involving the HO_2 radical, and the interactions of elementary reactions at increased pressure.

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Progress Summary

During the past year, we have had five archival publications appear in the literature and one Ph.D. Thesis completed. Three articles which were submitted in 1991 are presently in press, to appear in 1992. We have also presented and published three preprints at various technical meetings. In summary, the following progress has been achieved:

A. The $CO/H_2/O_2$ System

During the last year, two types of work have been underway. In the APFR, we have noted some very interesting and unique characteristics on how the oxidation rate of CO depends on oxygen concentration at various temperatures. We noted that as temperatures decrease from about 1500 K and above, the overall oxygen dependence decreases from about 0.3 to near zero at about 1038 K, and counter to intuition, becomes negative at still lower temperatures around 1000 K. We have performed additional experiments and modeling of the moist CO oxidation, further extending the work reported in Dryer et al., 1991 a,b to investigate these effects. Our findings are summarized in Roesler et al., 1991 (see Appendix A). We are presently preparing a paper on this work for submittal to Combustion Science and Technology.

Over the past year, the new variable pressure flow reactor (VPFR) has been brought to nearly full operation (Figure 1). The VPFR reactor is fundamentally different from the atmospheric pressure flow reactor (APFR) in that the reaction zone is positioned relative to a fixed sampling location by moving the reactor fuel injection and mixing location. With a fixed location for sampling, the design facilitates further in situ optical diagnostic efforts by allowing simple construction of fixed cross-beam optical access at the sampling location. Quantitative detection of OH in the APFR has been demonstrated through studies of the $CO/H_2O/O_2$, using both laser resonance absorption (Linteris et al., 1991b) and 180 degree-back-scatter, laser induced fluorescence (Linteris et al., 1991a). Progress on adapting the resonance absorption techniques to the new VPFR is described in Section D, below.

Vermeersch, 1991, fully details the basic VPFR apparatus design and operation, reports a number of experiments initially performed on the H_2/O_2 reaction system, and compares these experimental results with the computations performed with the mechanism of Yetter et al., 1991. Results, including the location of the explosion limit, and reaction profiles were in general agreement with the model for stoichiometric conditions and pressures to 9 atm (Vermeersch et al., 1991), although departures appear to increase with increasing pressure. Measured ignition delays were significantly different than expected. We are continuing to perform further analysis on these results and expect to perform more experiments pending modifications in the techniques we utilize to heat the carrier gas in the VPFR. A new electrical resistance heater system has been developed and has been installed in early February 1992. The combination of previous plasma heating methods with this new resistance heating source will permit us to extend investigation of ignition characteristics to lower temperatures.

This year, we have initiated studies of the moist CO/O_2 system at higher pressures. These studies are motivated by our interest in further extending our comprehensive CO modeling work to higher pressure conditions, and in developing sufficient knowledge of this reaction to utilize it in "seeded" reaction studies. The issue of interest is that the HO_2 reactions are substantially increased in importance at higher pressure conditions. Once having further developed the HO_2 segments of the system to satisfactorily reproduce the H_2/O_2 and moist CO oxidation, we will utilize results of studies in which these reactions are perturbed by small amounts of hydrocarbon additions to study reactions of hydrocarbons and hydrocarbon fragments with radical species (see Yetter and Dryer, 1992, Appendix B). Our initial work on the moist CO system at 3 atm. shows considerable disparity with predictions using

the present moist CO oxidation model (Figure 2). We believe these disparities are related to inadequacies in the HO$_2$ chemistry in the current model.

B. Formaldehyde Pyrolysis and Oxidation

A first paper summarizing experimental atmospheric pressure flow reactor studies has been published (Hochgreb et al., 1990) and an additional paper which reports experimental work on and interpretation of the decomposition of trioxane at flow reactor conditions in the APFR is presently in press (Hochgreb and Dryer, 1992, Appendix C). Additional work to that reported in Hochgreb, 1991 is in progress on revisions in and comprehensive comparisons of the mechanism appearing there with shock tube, stirred reactor, and flame data (Hochgreb and Dryer, 1991).

C. Methanol and Ethanol Oxidation Studies

Efforts devoted to developing a detailed kinetic model for the interpretation of ethanol oxidation experiments (Norton, 1989; Norton and Dryer, 1990b) have been extended, and a paper reporting this work is presently in press (Norton and Dryer, 1992, see Appendix D). The importance of including all three isomeric forms of the C$_2$H$_5$O radical in the mechanism construction is demonstrated in this paper through comparison of numerical results with experimental work performed in the APFR.

We are currently continuing to work experimentally on both the methanol (Norton and Dryer, 1989; Norton and Dryer, 1990a) and ethanol systems in the VPFR, specifically to perform additional measurements, utilizing Fourier Transform Infrared Spectroscopy (FTIR) for stable species and resonance absorption for OH (see Section D below), under both atmospheric and high pressure conditions. These data, together with our previous work, will be utilized to extend the mechanistic studies to a wider range of parameters and to develop a more comprehensive mechanism for these oxidations at shock tube, static reactor and flame conditions.

D. OH Measurements in the VPFR

One of the main design features of the Variable Pressure Flow Reactor is that the sampling point is fixed, while the point at which fuel is injected is moveable, in contrast to the more common arrangement of a fixed fuel injector with a moving sample probe. This greatly simplifies optical diagnostics, which can then provide information over a wide range of reaction times within a single experiment.

The sampling point itself consists of four ports at 90 degree radial positions (Figure 1). Because of the hazards involved in the design and operation of windows in high pressure environments, all optical signals are conducted to the interior of the pressure vessel by fiber optics. A small pressure vessel (Figure 3) is connected to the main shell, and contains the fiber positioner, detector, beamsplitter and a small chopper. The opposite port is equipped with a flange attachment with a 1" mirror on a gimbal mount. The light source is a Coherent 699-21 CW ring dye laser pumped by a Coherent I-100-20 argon ion laser. The dye laser is equipped with a lithium iodate intracavity doubling crystal to provide approximately 3 mW of ultraviolet radiation. The lasers are located in a separate laboratory adjacent to the VPFR, and the UV beam is coupled to a 20m length of 50μm core silica fiber. A single detector (EG&G Photon Devices UV-444B with a PMI OP-27 amplifier) alternately detects the signal and reference beams, as in Figure 3. This arrangement allows for the detection of the difference in signal and reference intensities, which is more sensitive than simply detecting the individual beams and ratioing them.

The initial set of optical experiments is the detection and quantitative determination of the hydroxyl radical (OH), which is of great importance to combustion reactions. The method used is

resonant absorption on the $A^2\Sigma^+(v=0) \rightarrow X^2\Pi(v=1)$ band at approximately 308 nm. This method was chosen over the more commonly used technique of laser induced fluorescence (LIF) for two reasons. First, the LIF measurement requires foreknowledge of the collisional quenching cross-section of the electronically excited OH radical. While efforts have been made to quantify this parameter, it is a strong function of the composition of the bath gas and pressure. Because this composition varies during the course of the reaction, and the experiments are carried out over a range of pressures, it is difficult to obtain a quantitative measure of the concentration of OH using LIF. Because a major emphasis of this research is to use the information obtained to compare to calculations of detailed kinetic models, such a quantitative result is required.

Typically, experiments are carried out at a roughly constant initial mole fraction as the pressure is varied. Thus, the detection limit of a species of interest is more appropriately determined in terms of mole fraction, rather than concentration. This has the effect of increasing the sensitivity of the diagnostic as the pressure is increased due to the density effect. However, the increased density also increases the effects of pressure broadening on an absorption line profile, thus decreasing the line center absorption coefficient for a given concentration. These two effects are roughly compensating, and affect both absorption and LIF measurements. However, the LIF signal is also reduced by the effects of increased collisional deexcitation. Thus, while an absorption measurement maintains a roughly constant detection limit in terms of mole fraction, the LIF technique will suffer an approximately linear degradation of its detection limit as pressure is raised. For these two reasons, absorption was chosen as the initial optical diagnostic for development in the VPFR.

Absorption is a line of sight measurement, and thus its accuracy in obtaining accurate quantitative results depends on the accuracy of the assumption that the concentration (or mole fraction) of the species to be measured is constant over the optical path. A set of measurements in the atmospheric pressure flow reactor (APFR) at Princeton using a radially positionable LIF probe indicated that the OH concentration was constant to within experimental scatter over at least the central 90% of the reactor tube diameter. Because of the similarity of the two reactors with respect to the geometry of their reaction tubes and range of Reynolds number conditions, this result is valid for the VPFR as well.

The measurement of the OH radical is, as stated earlier, of great kinetic importance for the development and validation of chemical kinetic models. However, other radical species are of at least comparable importance to combustion chemistry, and are impossible or extremely difficult to measure using conventional gas sampling probes. For this reason, additional optical diagnostics, using the same optical porting as the OH measurements, are under development. In particular, both the methyl radical (CH_3) and the formyl radical (HCO) can be measured spectroscopically in the UV and visible wavelength range, respectively. Because absorption measurements do not typically require large amounts of incident light intensity, and polyatomic radicals exhibit broad absorption bands, a conventional light source with a spectrograph detector can perform these measurements more easily and in a much more cost effective manner than laser diagnostics. The equipment required for such a measurement would be a medium power xenon light source coupled to a fiber optic to provide UV, visible and NIR radiation. The return beam would be focussed onto another fiber optic, taken from the pressure vessel and coupled to a ¼m monochrometer/spectrograph with a cooled, high dynamic range photodiode array detector. These more conventional optics can supply spectrographic information for the aforementioned radicals, as well as several other species simultaneously for considerably less than the cost of a single laser. Because of the greater power stability of the conventional light source over that of a dye laser, the sensitivity of this diagnostic technique should be at least as great as the laser's. The obvious disadvantage is the lower spectral resolution of the spectrograph as compared to the laser; however this is not an important issue with the broadened spectroscopic features of polyatomic species.

Finally, the OH diagnostic described above could still be used in conjunction with LIF measurements to obtain valuable spectroscopic information. First, because simultaneous absorption and

LIF measurements can be made, and stable gas species mole fractions are determined by conventional gas sampling, the effect of bath gas composition and pressure on quenching rates could be determined simply in a series of experiments. Also, once this information is obtained, along with broadening coefficients as a function of pressure and temperature, LIF could be used as a secondary diagnostic for OH, especially as the pressure increases such that the linewidth of the rotational line becomes comparable with the scanning range of the dye laser.

Preprints removed

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Figures

Fig. 1. Schematic of Variable Pressure Flow Reactor.

Fig. 2. Moist CO Oxidation Data for a Stoichiometric CO/O_2 Reaction at Three Atmospheres Pressure and 1038 K.

Fig. 3. Schematic of Pressure Shell Arrangement for Optical Experiments.
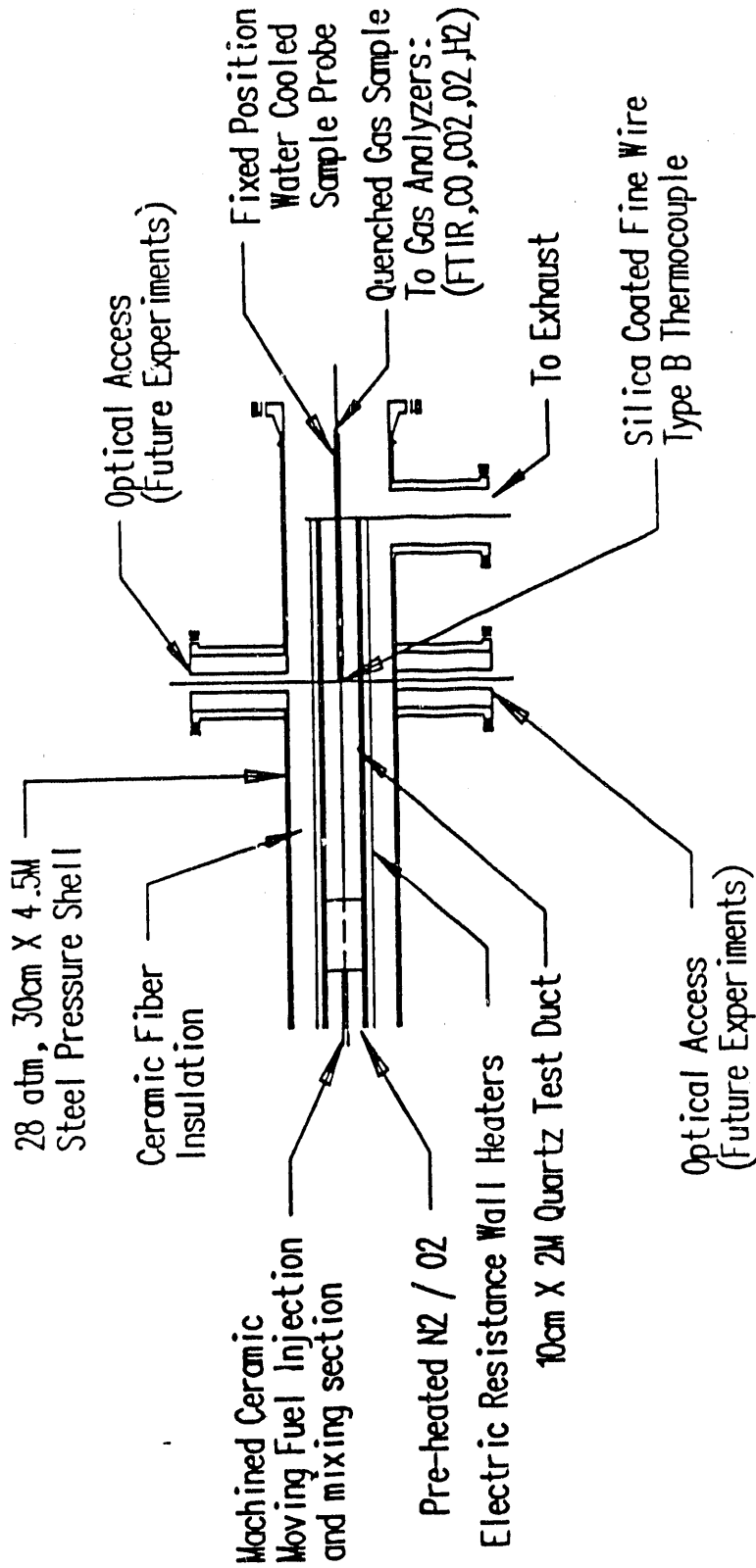
Fig. 4. Layout of VPFR Optics.

Experimental Apparatus

28 atm, 30cm X 4.5M
Steel Pressure Shell

Ceramic Fiber
Insulation

Machined Ceramic
Moving Fuel Injection
and mixing section

Pre-heated N2 / O2

Electric Resistance Wall Heaters

10cm X 2M Quartz Test Duct

Optical Access
(Future Experiments)

Optical Access
(Future Experiments)

Fixed Position
Water Cooled
Sample Probe

Quenched Gas Sample
To Gas Analyzers:
(FTIR,CO,CO2,O2,H2)

To Exhaust

Silica Coated Fine Wire
Type B Thermocouple

Figure 1

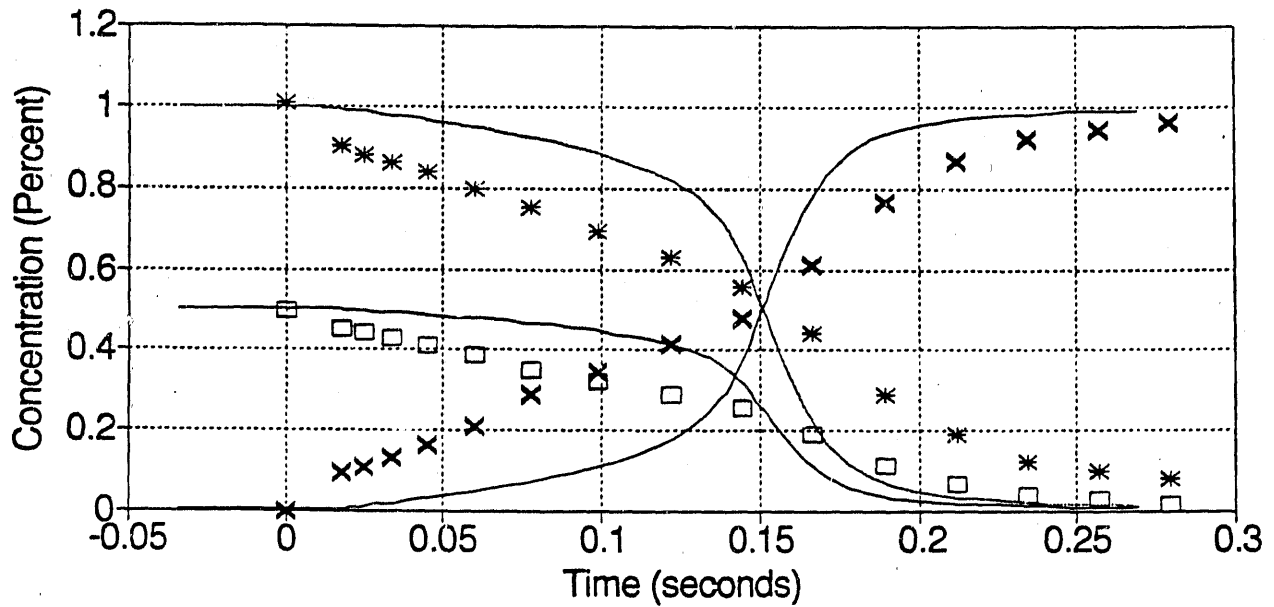# CO/H2O/O2 P=3ATM
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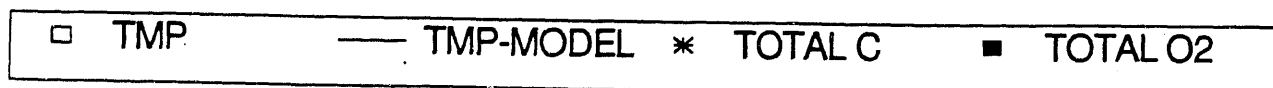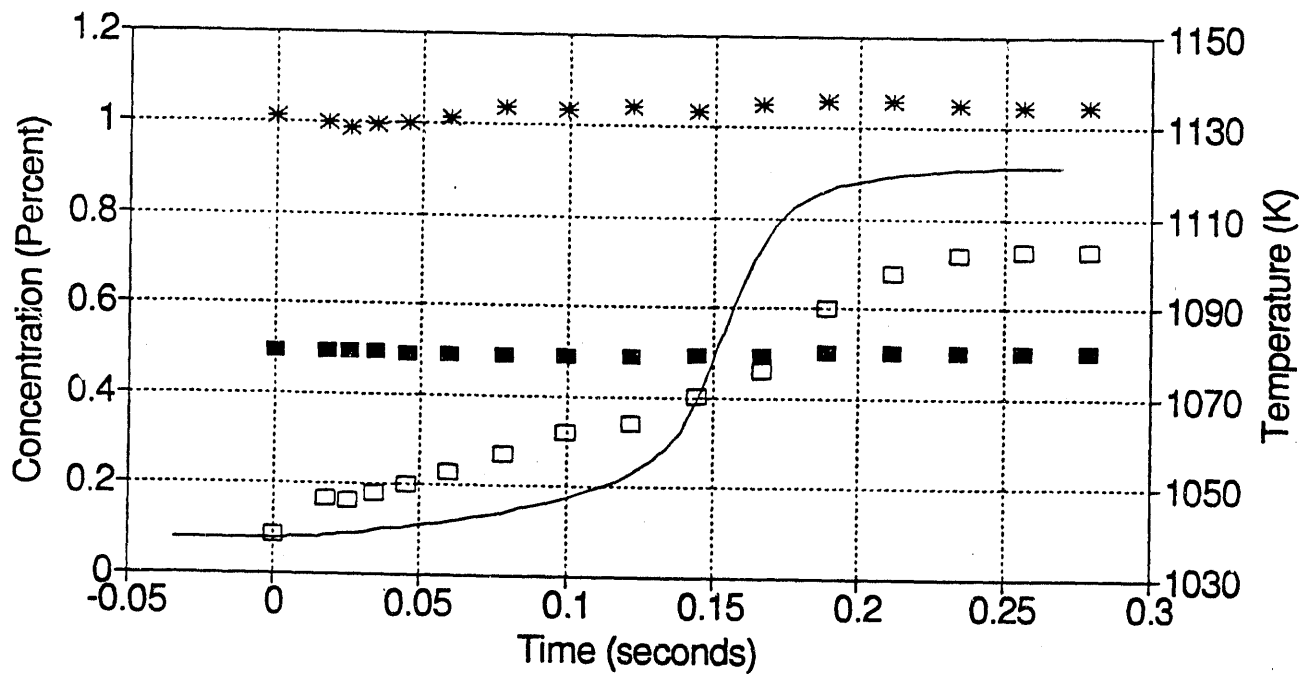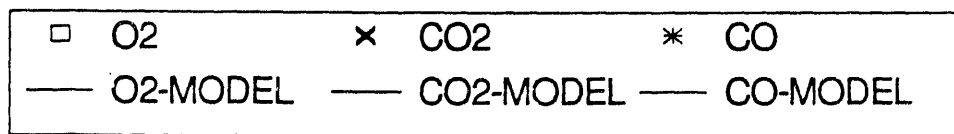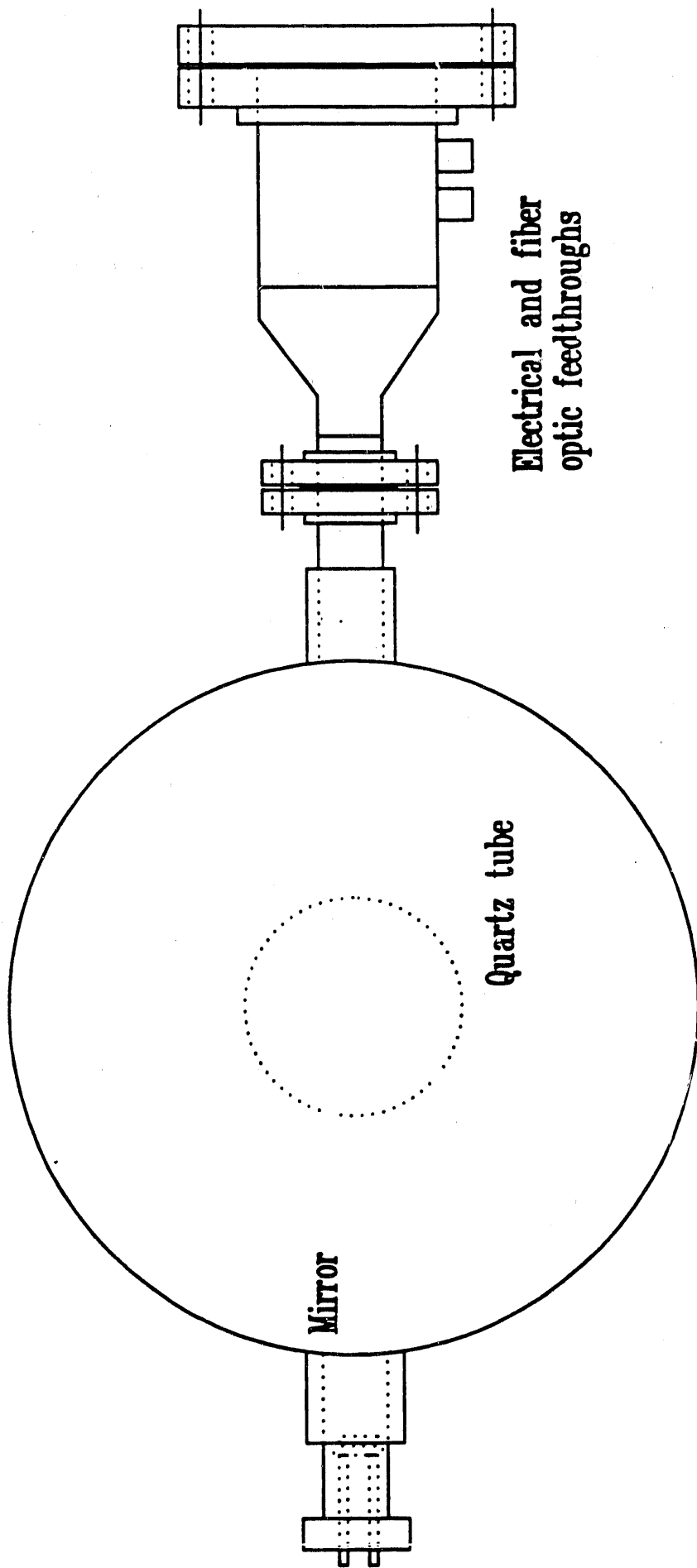

Figure 2

Cross-section of VPFR with optical access

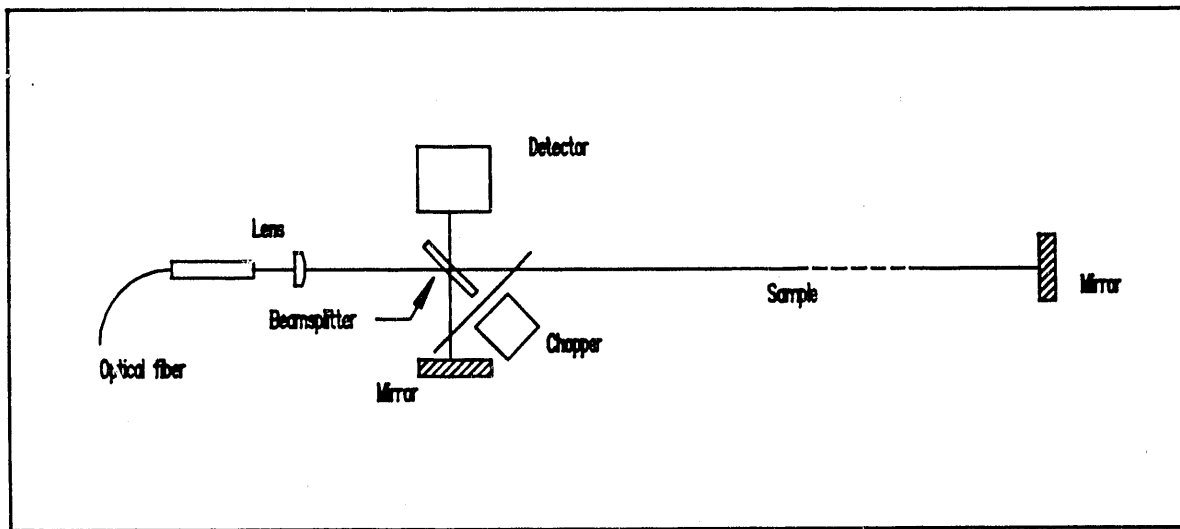Quartz tube

Mirror

Electrical and fiber optic feedthroughs

Figure 3

Detector

Lens

Beamsplitter

Optical fiber

Mirror

Chopper

Sample

Mirror

Figure 4

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