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Measurements in Ablating Air-Teflon Boundary Layers

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Theoretical descriptions of the detailed structure of an ablating air-Teflon laminar boundary layer predict CF_2 to be a major constituent in the boundary layer. This species has not been observed experimentally. This paper presents spectrally and spatially resolved uv thermal radiation measurements that demonstrate the presence of CF_2 in the stagnation point boundary layer of ablating Teflon cylinder. The experiments were performed in an arc facility which provided subsonic air or nitrogen jets at 2500–4500°K and $\frac{1}{40}$ atmospheric pressure. The state of the freestream was measured by the electron beam fluorescence technique.

I. Introduction

THE detailed structure of laminar ablating air-Teflon boundary layers has been the subject of many investigations.¹⁻⁴ Most of the experimental data has been reviewed in Ref. 3, which includes an analysis developed to describe the structure of the boundary layer. The analysis uses a partial equilibrium model for the air-Teflon chemistry which does not permit the formation of CF_3 and CF_4 within the boundary layer. The validity of the model was based on the excellent agreement between the measured and the theoretically predicted peak intensity of CO_2 radiation, its position in the boundary layer and the integrated intensity across the boundary layer. This theory further predicts the presence of COF_2 as a major radiator in air-Teflon boundary layers. Measurements of absolute intensities by Young, et al.,⁴ were in good agreement with theoretical predictions. The analysis also predicts that CF_2 would be a major species in the boundary layer. This species has not been experimentally observed.

The work presented here was undertaken to demonstrate the existence of CF_2 in the air-Teflon boundary layers by spectrally resolved uv thermal radiation measurements in the stagnation point boundary layer of ablating Teflon cylinders. After demonstrating its presence, the spatial distribution of the CF_2 emission in the boundary layer was measured in order to provide additional information on the chemical processes in the boundary layer. A low-density d.c. arcjet facility was used to provide subsonic air or nitrogen jets at 2500–4500°K and $\frac{1}{40}$ atmospheric pressure. The state of

the freestream gas was measured by use of an electron beam probe. The boundary-layer measurements were made at the stagnation point of a 1 cm diam by 1-cm long Teflon cylinder. By measuring on the axis of the jet, the problems of interference by the jet's mixing boundaries, the cold nozzle wall boundary layers and other jet nonuniformities were eliminated. In addition, the stagnation point provided both a laminar boundary layer and sufficient heat transfer for steady-state ablation to be rapidly reached over a wide range of arc operating conditions.

II. Experimental Apparatus

A. Arcjet

The AERL low-density arcjet is a d.c.-battery-powered facility which produces a subsonic air jet at temperatures from 2500–4500°K and at a pressure of $\frac{1}{40}$ atmosphere. The input power is variable over the range of 30–80 kw. The air mass flow was approximately 1.5 g/sec and the flow velocity was 10^5 cm/sec. A schematic diagram of the arc is presented in Fig. 1. Nitrogen is introduced around the circumference of the 2% thoriated tungsten cathode. It flows around the cathode and into the anode section. This swirling flow stabilizes the arc by constricting the arc to the anode centerline. Oxygen is introduced downstream of the anode by means of twelve radial holes circumferentially placed at the entrance to the plenum chamber. The gases mix within the plenum chamber and the hot air exits through the 1.9-cm-diam nozzle. All internal components are water-cooled and, with the exception of the cathode, are constructed of copper. The arc is enclosed in the low pressure chamber, which is evacuated by a 500-cfm pumping system using a Stokes mechanical pump.

The gas power was determined by subtracting the wall losses from the arc input power. These losses were obtained by measuring the temperature rise ΔT and the flow rate of the coolant water, $\dot{m}_{\text{H}_2\text{O}}$, through the arc. The enthalpy per unit mass of gas H was then given by

$$H = (VI - S\dot{m}_{\text{H}_2\text{O}}\Delta T)/\dot{m}_{\text{air}} \quad (1)$$

where V and I are the arc operating voltage and current,

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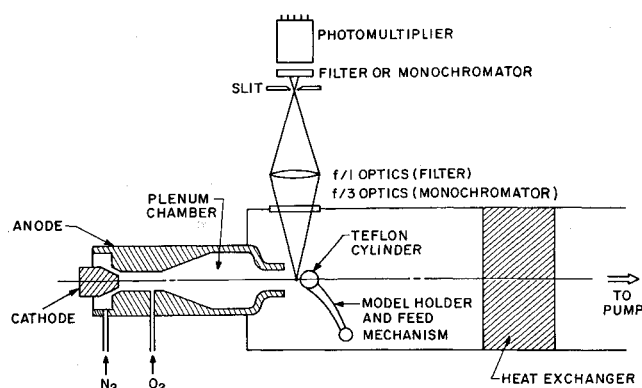


Fig. 1 Schematic of low-density arcjet and associated optical system.

respectively, and S is the specific heat of water. Assuming the gas to be in thermochemical equilibrium, an energy balance temperature for the gas can be directly deduced from the preceding calculated enthalpy.

B. Model Holder and Injection Mechanism

The model holder was designed to move the Teflon cylinder into the jet after steady-state conditions had been obtained in the operation of the arc. This was done to avoid severe ablation of the Teflon cylinder during the time taken for the cooling system to reach steady state, approximately 7 sec. For the spectral scans of the ablating boundary layer, it was necessary to maintain the entrance slit of the monochromator focused at a fixed point relative to the cylinder. Therefore, a model holder was equipped with a variable speed motor drive which mechanically fed the cylinder toward the arc nozzle exit at the same rate as the measured ablation rate.

C. Spectrometric System

The optical system is shown schematically in Fig. 1. For the freestream density measurements, an $f/1$ Cassagrain optical system with an S-13 photomultiplier detector was

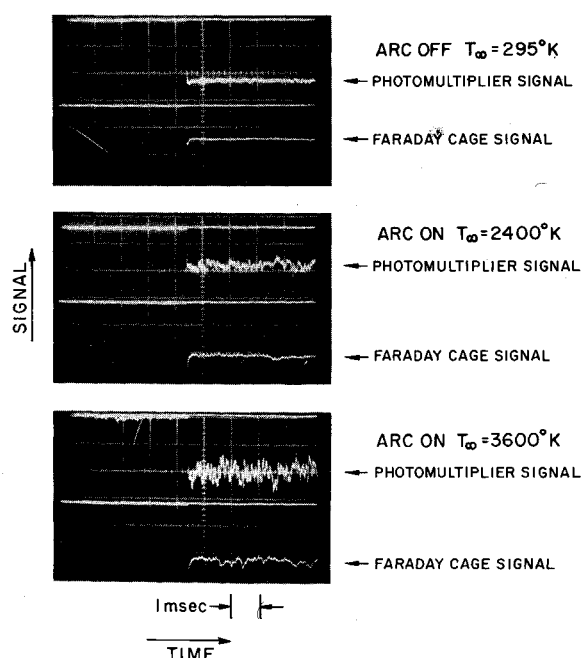


Fig. 2 Electron beam current and photomultiplier response to the $N_2(2+)$ emission at the jet centerline. The electron beam was chopped at 100 Hz with a 50% duty cycle.

used to measure the electron beam excited fluorescence through selected narrow band pass filters. The species concentration and boundary-layer measurements were made with an $f/3$ reflecting optical system which directed the emission to a Jarrell Ash Elbert 0.25-m double pass grating monochromator. The resolution along the jet axis was 0.140 mm when using a 100μ monochromator entrance slit. This slit width gave a triangular spectral resolution function with a full width at half height of $3.2 \text{ \AA}$.

For the spectral measurements from 2000 to 5500 $\text{\AA}$, the emission signal was detected by an S-13 photomultiplier. A photomultiplier with an S-20 surface was used for spectral measurements in the range of 5000–8000 $\text{\AA}$. The photomultiplier signals were displayed on an X-Y recorder. The optical windows were all made of quartz. The optical, detector and recording system was calibrated as a unit by use of a tungsten lamp with its filament located on the arc axis at the model location.

D. Electron Beam

The electron gun produced about 80 keV energy electrons which entered the arc test chamber through a drift tube with a 1.75-mm-diam exit orifice. The electron beam was directed normal to the arcjet and intersected the jet centerline 1.27 cm downstream of the nozzle exit. The beam current was variable from 0 to 250 μ amps and was measured by a shielded Faraday cage. For the experiments in hot air jets, the presence of freestream plasma can influence the current values measured by the Faraday cage. To prevent interference of the Faraday cage signal by the freestream plasma, a thin aluminum foil (0.01-mm thickness) was placed over the entrance to the cage. The collector was connected directly to an oscilloscope and the signal monitored throughout an experiment. The grid of the electron gun was pulsed at 50% duty cycle to permit the use of phase-sensitive detection, thus minimizing the contribution of background thermal radiation during the electron fluorescence measurements. The duration of the electron beam pulse could be varied between 200 μ sec and 10 msec.

III. Experimental Results

A. Freestream Density Measurements

The use of the electron beam fluorescence technique has been described elsewhere.⁵⁻⁷ The molecular nitrogen density was determined from emission intensity measurements of the N_2 second positive system, $C^3\Pi \rightarrow B^3\Pi$. This transition was

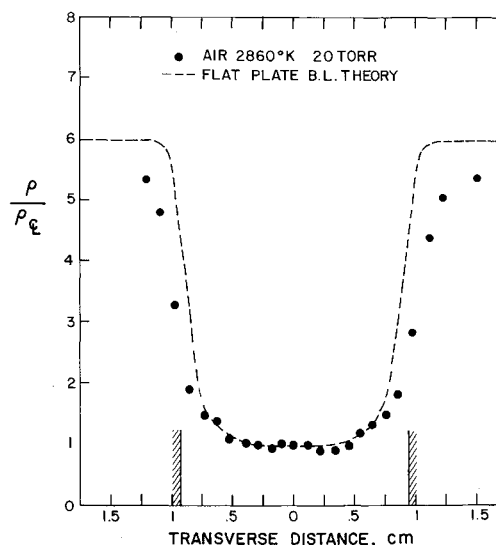


Fig. 3 Measurement of the radial density profile in the arcjet.

chosen rather than the first negative system because of the large collision quenching cross section⁸ for the $B^2\Sigma$ state of N_2^+ by ground state N_2 . The collision quenching rate of the $N_2(2+)$ system by N_2 is two orders of magnitude smaller than the corresponding rate for the $N_2^+(1-)$ system. In air the quenching rate is determined by the oxygen concentration. The rate constants experimentally determined by Brocklehurst⁸ indicate that quenching of the second positive system should not be important for air densities less than $10^{17}/\text{cm}^3$, and this was verified experimentally.

Figure 2 shows some oscillographs of the photomultiplier and beam current signals for the beam excited radiation from $N_2(2+)$ system at various arc input power levels. A 3370 Å interference filter with a half-width of 140 Å was used to isolate the second positive system. The electron beam current was simultaneously measured by the shielded Faraday cage, and the output is displayed with the optical signal on the lower beam of the dual beam oscilloscope. From the magnitude of the photomultiplier output when the electron beam is off, one can observe that the signal due to thermal radiation was negligible compared to the electron fluorescence. Since the diffusion of the secondary electrons from the main beam is small at these pressures, the spatial resolution of the optical system was determined by the electron beam diameter and the limiting slit dimension in the system. Furthermore, the upper state of the $N_2(2+)$ system has a lifetime of 2.7×10^{-8} sec, which is small compared to the characteristic flow times for a flow velocity of 10^5 cm/sec in the jet. These two factors permit the local measurements of density and density fluctuations in the jet. Over the range of jet gas temperature from 2400° to 3600°K, the measured gas density agreed to within 10% with the magnitude deduced from the arc energy balance temperature and the measured pressure.

The response time of the fluorescence detection and recording system was 10^{-4} sec, thus permitting measurement of density fluctuations up to 10 KHz in the arcjet. Measurements at comparable intensities with cold jets indicated no observable fluctuation in the electron beam system. Therefore, estimates of the point density fluctuation could be made from the measured fluctuations in the electron fluorescence signals for the hot jets. From results similar to those shown in Fig. 2, maximum density fluctuations of $\pm 10\%$ peak to peak were observed for a range of jet temperatures between 2400 to 3600°K.

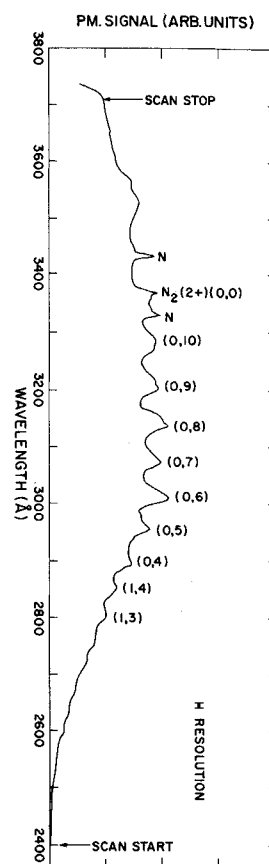
The radial density profile of the jet was measured by monitoring the $N_2(2+)$ electron excited fluorescence as the optical system was traversed along the electron beam, i.e., across the jet. The results of such a scan for the case of 2800°K freestream are shown in Fig. 3. The effects of collisional quenching with oxygen concentration have been folded into the data points. Also shown in Fig. 3 is the theoretical density profile predicted from flat plate equilibrium boundary-layer calculations for the same nozzle exit conditions. The effect of finite optical aperture has been included in the calculated profile. The experimental results show a constant density core of approximately 1.5 cm for the arc conditions of interest. This limited the cylinder dimension to 1 cm long by 1 cm in diameter.

B. Thermal Radiation Measurement in Air-Teflon Boundary Layer

1. Detection of CF_2

To investigate the presence of CF_2 in the ablating Teflon boundary layer, uv thermal radiation spectra were taken at the stagnation point of the ablating Teflon cylinder. For the spectral scans, the entrance slit of the monochromator, 0.1 mm, was focused at a fixed point relative to the ablating cylinder throughout the measurement. This was accomplished by mechanically feeding the cylinder at the same rate as the measured steady-state ablation rates. The time to

Fig. 4 Composite spectral scan of the thermal emission in the air-Teflon boundary layer for $T_\infty = 2600^\circ\text{K}$. The optical slit was focused 0.1mm in front of the stagnation point and the spectral resolution was 3.2 Å.



reach steady-state ablation was measured to be 2 sec for the 2600°K freestream temperature and less than $\frac{1}{2}$ sec for the 3500°K freestream temperature. Following this incubation time, the ablation rate at a given freestream temperature was observed to be constant until the cylinder diameter had been reduced by more than 40%. The measured ablation rates were 0.056 mm/sec, 0.125 mm/sec, and 0.17 mm/sec for the freestream temperature of 2600°, 2850°, and 3500°K.

For a given ablation rate, the range of wavelength that could be covered by the scanning monochromator depended upon the monochromator scanning rate and the maximum tolerable change in the radius of curvature. The monochromator was scanned at 16 Å/sec. For the freestream temperature of 2600°K, a scan of 400 Å could be covered while the cylinder diameter decreased by 10% of its original dimension. Therefore, the entire wavelength range for the expected CF_2 radiation was covered by a composite of runs at the same freestream condition. The wavelength range of consecutive runs was overlapped to determine the effect of the variations in the radius of curvature of the model.

Figure 4 shows a composite of the recorded photomultiplier output for wavelength range of 2400–3700 Å for a freestream temperature of 2600°K. The monochromator entrance slit of 100 μ resulted in a spectral resolution of 3.2 Å and a spatial resolution of 0.140 mm. The wavelength scan was initiated 10 sec after the cylinder was introduced into the freestream to ensure that steady-state ablation had been achieved. The overlapping of the wavelength between consecutive runs indicated that the variation of radius of curvature of the cylinder had a negligible effect on the magnitude of the emission intensity. The $N_2(2+)[0, 0]$ band head and the atomic nitrogen lines serve as an internal check on the wavelength calibration during the experiment. Also shown in Fig. 4 are the wavelength location for CF_2 emission band heads as identified by Venkateswarlu.⁹ The observed spectra demonstrate the presence of CF_2 in the air-Teflon boundary layer.

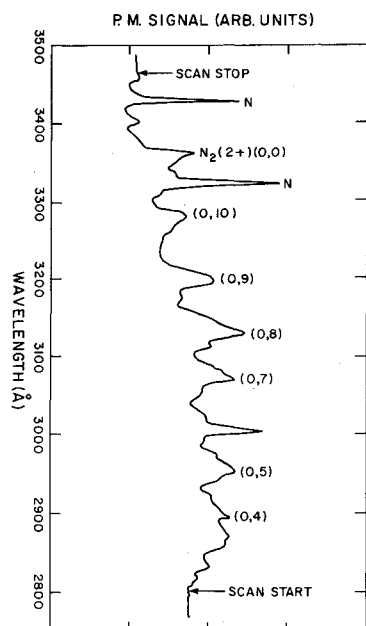


Fig. 5 Composite spectral scan of the thermal emission in the N_2 -Teflon boundary layer for the same ablation rate as in Fig. 4.

Similar spectra were obtained for freestream temperatures of 2860° and 3500°K.

The boundary-layer theory of Ref. 3 also predicts that COF_2 should be present in the air-Teflon boundary close to the body with a similar concentration to that of CF_2 . Young et al.⁴ have observed infrared emission from COF_2 in the air-Teflon boundary layer. Since COF_2 can also radiate in the uv, experiments were conducted to verify that the observed radiation was CF_2 rather than COF_2 . Similar spectral scans were carried out with decreasing oxygen content in the heated jet. Figure 5 shows a spectrum for a pure nitrogen jet with power setting such that the ablation rate is similar to that of the 2600°K air jet. Only ablation rates were matched because the nitrogen jet was not in thermochemical equilibrium and therefore comparison of the freestream parameters is not meaningful. For equivalent ablation rates, the spectra

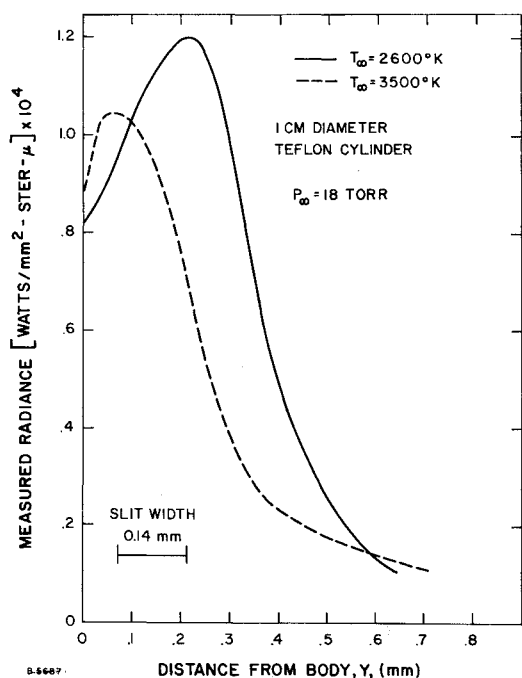


Fig. 6 CF_2 concentration profile measurements.

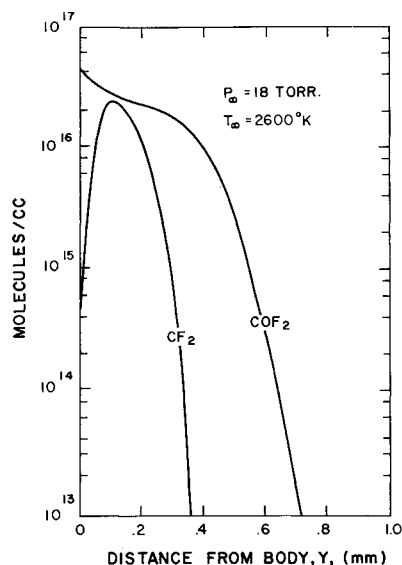


Fig. 7 Theoretical CF_2 and COF_2 concentration profiles.

observed were sufficiently similar in intensity and character for both air and nitrogen jets to confirm that the observed radiation was due to CF_2 and not COF_2 .

The entire optical, electronic, recording system and the monochromator were calibrated with a tungsten lamp of known temperature. Thus, the absolute intensity of the observed radiation could be directly obtained from the photomultiplier output with the aid of the spectral calibration curves. The contribution of the background radiation and surface reflection was estimated by substituting the Teflon cylinder with a polished copper cylinder of the same size. In the wavelength regime where the CF_2 emission was observed, the radiation with the nonablating copper cylinder was negligible compared to that measured with the ablating cylinders.

2. Spatial distribution measurement

To determine the CF_2 concentration profile in the boundary layer, spatially resolved measurements of the absolute intensity were made with the monochromator set at 3075 ± 1.6 Å to monitor the CF_2 (0, 7) system. The imaged slit width at the body was 0.14 mm. The profiles were obtained by fixing the slit image location and allowing the cylinders to ablate at a known rate. The measured intensity profiles for freestream temperatures of 2600° and 3500°K are presented in Fig. 6. The concentration profiles of CF_2 and COF_2 predicted by the partial equilibrium theory of Greenberg et al.³ are presented in Fig. 7. In this theory, the laminar boundary-layer equations are coupled to the Teflon surface through heat and mass balances, using a constant ablation temperature of 1000°K for Teflon. Chemical nonequilibrium effects are taken into account by a partial equilibrium chemistry model, which does not allow the formation of CF_3 and CF_4 . The external flowfield for the cylindrical geometry was properly incorporated, but the azimuthal pressure gradient in the boundary layer was neglected in these preliminary calculations. The individual transport properties of all the elements were set equal, and all Lewis and Prandtl numbers were taken as unity. The measured profiles show good spatial agreement with the predicted profile.

The partial equilibrium theory predicts that the CF_2 exists close to the surface in the region of relatively low temperature. The calculated profiles for freestream temperatures of 2600° and 3300°K are shown in Fig. 8. The peak of the observed CF_2 fluorescence coincides approximately with calculated temperatures of 1800°K as seen from Figs. 6 and 8. Comparison of the observed emission with that based on the available f numbers for CF_2 ^{10,11} and the calculated temperature

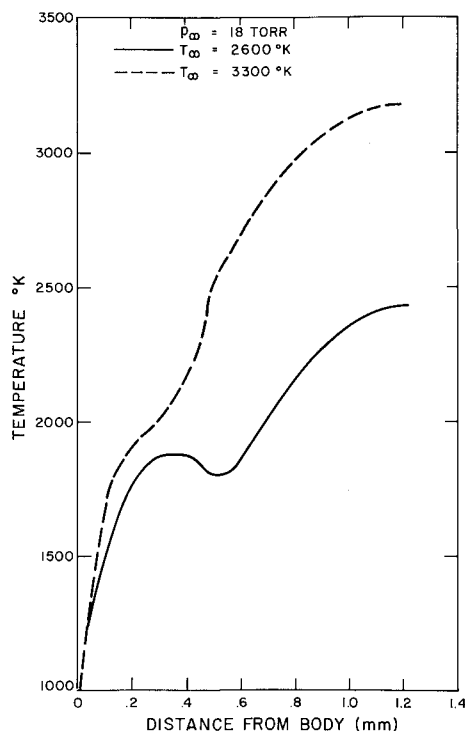


Fig. 8 Theoretical temperature profiles in the air-Teflon stagnation point boundary layer.

and concentration profiles indicate that the observed radiation was approximately two orders of magnitude larger than predicted. This discrepancy may result from the chemiluminescent reaction $\text{CF} + \text{F} \rightarrow \text{CF}_2 + h\nu$ or some nonequilibrium processes in the boundary layer.

IV. Conclusion

Spectrally and spatially resolved uv radiation measurements at the stagnation point of an ablating Teflon cylinder have confirmed the existence of CF_2 in the air-Teflon boundary layer. The spatially resolved profiles of the absolute radiation intensity of the $\text{CF}_2(0,7)$ emission at $3075 \text{ \AA}$ showed the CF_2 to be concentrated near the ablating body. Good spatial agreement exists between the measured and predicted CF_2 concentration profile. The magnitude of the observed radiation intensity is approximately two orders of magnitude greater than that calculated from available f numbers and the pre-

dicted concentration. This large discrepancy in radiation may suggest the possibility of a chemiluminescent reaction such as $\text{CF} + \text{F} \rightarrow \text{CF}_2 + h\nu$ or some nonequilibrium processes in the air-Teflon mixture. It must be pointed out that the theory employed is the simplest which contains the relevant chemistry. The assumption of the absence of CF_3 and CF_4 may not be applicable at these pressure levels.

The state of the freestream gas was measured by the electron beam fluorescence technique. The gas densities deduced from the magnitude of the electron luminescence of the $\text{N}_2(2+)$ system agreed within 10% with those deduced from arc energy balance temperatures and measured pressure. The point density fluctuation in the jet was measured to be of the order $\pm 10\%$ of the mean.

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