

# Optical emission spectroscopy and Langmuir probe diagnostics of CH<sub>3</sub>F/O<sub>2</sub> inductively coupled plasmas

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A CH<sub>3</sub>F:O<sub>2</sub> (50%:50%) inductively coupled discharge, sustained in a compact plasma reactor, was investigated as a function of power (20-400 W) and pressure (9-30 mTorr), using optical emission spectroscopy and Langmuir probe measurements. The electron density increased linearly with power but only weakly with pressure. The effective electron temperature was nearly independent of power and pressure. The gas temperature, obtained from the rotational structure of N<sub>2</sub> (C  $\rightarrow$  B) optical emission, increased from 400 to 900 K as a function of inductive mode power between 75 and 400 W at 10 mTorr. For constant feed gas flow, the absolute H, F, and O atom densities, estimated by optical emission rare gas actinometry, increased linearly with power. The absolute number density ratios H/Ar, F/Ar, and O/Ar, increased, decreased, and remained constant, respectively, with pressure. The H-atom density was estimated to be  $5.4 \times 10^{13}$  cm<sup>-3</sup> at 400 W and 10 mTorr (gas temperature = 900 K), implying a high degree of dissociation of the CH<sub>3</sub>F feedstock gas. The F and O atom number densities were much lower  $(8.3 \times 10^{12} \text{ cm}^{-3} \text{ and } 5.9 \times 10^{12} \text{ cm}^{-3}$ , respectively) for the same conditions, suggesting that most of the fluorine and oxygen is contained in reaction products HF, CO, CO<sub>2</sub>, H<sub>2</sub>O, and OH. The relative number densities of HF, CO, and CO<sub>2</sub> were observed to first rapidly increase with power, and then reach a plateau or decay slightly at higher power. Reaction mechanisms were proposed to explain the observed behavior of the number density of F and HF vs. power and pressure. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4807298]

# I. INTRODUCTION

The transition to devices at the 14 nm technology node has introduced the so-called "FinFET" 3D architecture to reduce gate leakage current and power consumption in the next generation of integrated circuits. This new approach has brought a number of manufacturing challenges. For example, a critical requirement in FinFET gate fabrication is highly anisotropic and selective etching of silicon nitride (Si<sub>3</sub>N<sub>4</sub>) over Si or SiO<sub>2</sub>.<sup>1–3</sup>

Etching of  $Si_3N_4$  using hydrogen-containing fluorocarbon (CH<sub>x</sub>F<sub>y</sub>) plasmas (usually with additional gases, such as O<sub>2</sub>), is currently the process of choice.<sup>2,4–6</sup> Surprisingly few fundamental studies have been reported for this process, even for the simplest and widely used combination of CH<sub>3</sub>F and O<sub>2</sub> feed gases. Understanding the physical and chemical mechanisms of CH<sub>3</sub>F/O<sub>2</sub> plasmas is particularly important for improving selectivity of Si<sub>3</sub>N<sub>4</sub> etching over Si.

A study of CH<sub>3</sub>F/O<sub>2</sub> discharges sustained in a compact inductively coupled plasma (ICP) reactor was reported recently.<sup>7</sup> Using optical emission spectroscopy, an abrupt transition was found in the relative concentration of several species (most notably fluorine atoms) as the O<sub>2</sub> percentage crossed 48%. This was attributed to the presence of a hydrofluorocarbon film on the reactor walls for plasmas with less than 48% O<sub>2</sub>. When the O<sub>2</sub> addition exceeded 48%, the film etching rate by O atoms exceeded the film deposition rate and the surfaces remained film-free at steady-state. With no film present, the reaction of F atoms with the film to form HF stopped, the total F loss rate slowed, and the F number density increased by a factor of 4.

Here, studies of  $CH_3F/O_2$  (50%/50%) plasmas in the same ICP reactor are presented. Under these conditions, the walls remain film-free. A Langmuir probe was used to obtain electron energy probability functions (EEPFs) and electron number densities. Optical emission spectra in the 200–940 nm range, combined with rare gas actinometry, provided absolute number densities of H, F, and O atoms, as well as estimates of relative densities of HF, CO, and CO<sub>2</sub> as a function of power and pressure. Reaction mechanisms were proposed to explain the observed behavior of F and HF density as a function of power and pressure.

#### **II. EXPERIMENTAL**

A schematic of the ICP source is illustrated in Figure 1. Plasma was ignited in a 1.4'' ID alumina tube, surrounded by a 4'' OD co-axial stainless steel (SS) cylindrical enclosure. Teflon tubing around the outer wall of the alumina tube provided water cooling (DI water at 20 °C). The ICP coil (3turn, 1/4'' OD copper tubing) was also water-cooled. A slotted 316 SS cylindrical sleeve that can serve as a "boundary electrode" to control ion energy distributions<sup>8,9</sup> was grounded in this study. Gas was fed into the reactor through a 1/8'' SS tube that was co-axial with the discharge tube (Figure 1). The reactor was pumped by a 300 l/s turbomolecular pump backed by a roughing pump. The base pressure

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FIG. 1. Schematic of the compact inductively coupled plasma source.

was  $\sim 2 \times 10^{-7}$  Torr. Reactor operating pressure was measured by a capacitance manometer at the top flange. A pressure rise (few mTorr) was observed after plasma ignition, due to gas dissociation and gas heating. Flow rates were regulated by mass flow controllers (MKS model 1179A). For gas temperature ( $T_g$ ) measurements, small amounts (2.5%) of N<sub>2</sub> were added to the feed gas. To determine the density of gas-phase species, optical emission actinometry was performed, with a trace rare gas (TRG) mixture containing 40% Ne, 20% Ar, 20% Kr, and 20% Xe added to the feed gas. Unless stated otherwise, the total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025.

A radio frequency (RF) amplifier (ENI model A-300) driven by a function generator (Hewlett Packard model 3325A) was employed to supply power to the coil at a frequency of 13.56 MHz, through an impedance-matching network. In-line Bird-meters measured forward and reflected powers, the reflected power was nearly zero. Optical emission spectra were recorded with three spectrometers (Ocean Optics model HR4000 with 1.7 Å resolution) covering the wavelength ranges of 200-427 nm, 578-775 nm, and 764-916 nm. Spectra between 382 and 458 nm were obtained by using the second order dispersion of the 764–916 nm range spectrometer in combination with a glass filter to block the first order dispersion, giving a resolution of 0.85 A. Light was collected along the axis of the plasma, without any intervening optical elements (Figure 1). Signal integration and averaging times were adjusted based on the intensity level and shape of the peaks of interest. The total acquisition time of a spectrum was between 4 and 8 s.

A Langmuir probe (Scientific Systems, Smart Probe) was used to obtain the plasma potential  $(V_p)$ , electron density  $(n_e)$ , effective electron temperature  $(T_e^{eff})$ , and EEPF. A cylindrical tungsten probe tip (0.15 mm diameter and 3.0 mm

exposed length) was used to acquire I-V characteristics. The probe tip was cleaned by a bias voltage of 40 V every 10 s while it is exposed to the plasma. A compensation electrode and RF chokes minimized distortions due to the RF oscillations of the plasma potential. The second derivative of the probe current (I'') was plotted vs. probe voltage (V), and  $V_p$  was determined as the x-axis intercept. EEPFs were produced from semilog plots of AI'' vs. electron energy,  $\varepsilon$ , where  $\varepsilon = V_p - V$ .  $A = (8me^{-3}S_p^{-2})^{1/2} = 4.2 \times 10^{13} S_p^{-1}$  with m, e, and  $S_p$  being electron mass, electron charge, and probe tip area in m<sup>2</sup>, respectively. A 5-point adjacent-average smoothing was used. Plasma parameters were calculated by the following formulas:<sup>10,11</sup>

$$n_e = \int_{0}^{\infty} \varepsilon^{\frac{1}{2}} f(\varepsilon) d\varepsilon, \qquad (1)$$

$$T_e^{eff} = \frac{2}{3n_e} \int_{0}^{\infty} \varepsilon^{\frac{3}{2}} f(\varepsilon) d\varepsilon, \qquad (2)$$

where  $f(\varepsilon)$  is the EEPF. Because of unknown ion composition (particularly the density of H<sup>+</sup>) and therefore large uncertainty in the effective ion mass, ion density was not extracted from the ion current.

Under the present experimental conditions, at a typical gas temperature of  $\sim 600 \text{ K}$  and pressure of 10 mTorr, the Knudsen number, Kn (ratio of neutral mean free path-to-tube ID), was  $\sim 0.3$  for a typical molecule like O<sub>2</sub>, and hence gas flow was in the transition regime. Assuming continuum flow, then for 10 sccm, and an upstream pressure of 10 mTorr, the downstream pressure at the end of the discharge tube would be 9.0 mTorr. If flow were molecular (Knudsen), the downstream pressure would be 5.2 mTorr under these conditions. It follows that the average of the upstream and downstream pressures would be between 9.5 and 7.6 mTorr. Hence the effective pressure was about 8.5 mTorr at an upstream pressure of 10 mTorr. Since the pump was throttled to achieve higher pressures (as opposed to increasing flow rates), above 10 mTorr the effective pressure was even closer to the upstream pressure. Because of the relatively small corrections involved, only measurements for the upstream pressures are reported in this work.

#### **III. RESULTS AND DISCUSSION**

# A. Electron energy probability functions and plasma parameters

EEPFs between ~2 and 35 eV, derived from Langmuir probe measurements, are presented in Figure 2 for different powers and pressures. EEPFs exhibit a bi-Maxwellian character with a relatively high  $T_e$  for  $\varepsilon = 2-15$  eV, and a cooler  $T_e$  for  $\varepsilon = 15-35$  eV, due to energy losses in high-threshold inelastic electron-neutral collisions. As power increases (Figure 2(a)), the EEPF tends toward a Maxwellian distribution (straight line on the semilog plot), due to the higher frequency of electron-electron thermalizing collisions. As expected, the high energy tail of the EEPF between 10 and



FIG. 2. EEPFs for different powers (at 10 mTorr) and pressures (at 300 W). The total flow rate was 10 sccm, with  $CH_3F:O_2:TRG = 1:1:0.025$ . TRG = trace rare gas.

25 eV decays faster at higher pressures due to more frequent inelastic collisions between electrons and neutrals (Figure 2(b)).

 $T_e^{eff}$  and  $n_e$  are presented in Figures 3 and 4 as a function of power and pressure, respectively. The electron density increases linearly with power in the inductive plasma mode, and reaches  $2.6 \times 10^{11}$  cm<sup>-3</sup> at 400 W for a pressure of 10 mTorr. (It should be noted that the plasma transitioned from capacitive to inductive mode of operation around 50 W, see below.)  $T_e^{eff}$  is ~5.5–6 eV, independent of power. This suggests a nearly constant gas number density as a function of power. Below we show that the gas temperature roughly doubles between 150 and 400 W at 10 mTorr. Thus, we would expect the number density to decrease and  $T_e$  to increase. The fact that  $T_e$  remains constant with power can be explained by the formation, at higher powers, of many species that are easier to ionize than CH<sub>3</sub>F and O<sub>2</sub>, largely



FIG. 3. Electron density and effective electron temperature as a function of power at 10 mTorr. The total flow rate was 10 sccm, with  $CH_3F:O_2:TRG = 1:1:0.025$ . TRG = trace rare gas.



FIG. 4. Electron density and effective electron temperature as a function of pressure at 300 W. The total flow rate was 10 sccm, with  $CH_3F:O_2:TRG = 1:1:0.025$ . TRG = trace rare gas.

compensating for the reduced number density from gas heating so that the total ionization rate, and correspondingly  $T_e$ , do not change much with power. The electron density,  $n_e$ , slowly increases with pressure from  $1.7 \times 10^{11}$  cm<sup>-3</sup> at 10 mTorr to  $3.1 \times 10^{11}$  at 40 mTorr.  $T_e^{eff}$  decreases from 5.2 eV at 10 mTorr to 4.3 eV at 20 mTorr, as expected, and then barely changes between 20 and 40 mTorr. The pressure-independent behavior of  $T_e$  at higher pressure could be due to higher gas temperature; unfortunately gas temperature measurements could not be made at pressures higher than  $\sim 10 \text{ mTorr}$  (see below).

#### B. Gas temperature measurements

A small amount (2.5%) of N<sub>2</sub> was added to the feed gas to measure gas temperatures by optical emission spectroscopy. The recorded rotational structure of the (1,0) and (1,3)emission bands of the second positive system of N<sub>2</sub> ( $C^3\Pi_u$ )  $\rightarrow B^{3}\Pi_{g}$ ) was compared with simulated bands with the rotational temperature of the ground electronic state as the adjustable parameter.<sup>12,13</sup> The ground state rotational temperature of N<sub>2</sub> approaches  $T_g$  as long as thermal equilibrium is maintained between translational and rotational levels,<sup>12,14</sup> which should be the case here. To obtain clean  $C^3\Pi_{\mu}$  $\rightarrow B^{3}\Pi_{g}$  emission bands, spectra recorded without added N<sub>2</sub> were subtracted from those with added N2, under otherwise the same experimental conditions.  $T_g$  values determined by this method as a function of power at 10 mTorr are presented in Figure 5. The error bars in Figure 5 correspond to differences in temperature found by using the (1,0) and (1,3) rovibronic bands.  $T_g$  increases from about 400 K at 75 W to 900 K at 400 W. Unfortunately, gas temperature measurements could not be reliably obtained at pressures higher than  $\sim 10$  mTorr because intense OH and other molecular emissions obstructed the N<sub>2</sub> emission bands (even after taking the difference between spectra with and without N<sub>2</sub>).

### C. Optical emission spectroscopy

A sample optical emission spectrum of a  $CH_3F/O_2$  plasma at 300 W (10 mTorr, 10 sccm) is shown in Figure 6, covering the 200–450 and 580–900 nm wavelength ranges.



FIG. 5. Gas temperature as a function of power (at 10 mTorr). The total flow rate was 10 sccm, with  $CH_3F:O_2:N_2 = 1:1:0.05$ .

The OH(A<sup>2</sup> $\Sigma \rightarrow X^2\Pi$ ) band system at 306.4 nm was one of the most intense features. Several intense bands of the third positive system of CO(b<sup>3</sup> $\Sigma^+ \rightarrow a^3\Pi$ ) were observed in the UV at 283.3 (0,0), 297.7 (0,1), 313.4 (0,2), 330.5 (0,3), 349.3 (0,4), 266.5 (1,0), 279.3 (1,1), 324.2 (1,4), 341.9 (1,5), and 361.2 (1,6) nm. Doublet features ascribed to CO<sub>2</sub><sup>+</sup> were observed at 288.3 and 289.6 nm.<sup>15</sup> The CF(A<sup>2</sup> $\Sigma^+ \rightarrow X^2\Pi_r$ ) and CF(B<sup>2</sup> $\Delta \rightarrow X^2\Pi_r$ ) band systems were also observed near 202.6 and 230.8 nm, and the (0-0) band of CH(A<sup>2</sup> $\Delta \rightarrow X^2\Pi$ ) at 431.3 nm was also found.

HF (B<sup>1</sup> $\Sigma \rightarrow X^{1}\Sigma$ ) and HF<sup>+</sup>(A<sup>2</sup> $\Sigma^{+} \rightarrow X^{2}\Pi$ ) emissions were found near 255 and 390 nm, respectively.<sup>16</sup> Noticeably absent was the C<sub>2</sub>(d<sup>3</sup> $\Pi_{g} \rightarrow a^{3}\Pi_{u}$ ) Swan band at 436 nm. This band (along with the bands at 467, 518, and 550 nm, which were not accessible with the spectrometers used in this study) is often observed in hydro-fluorocarbon containing plasmas. C, H $\gamma$ , H $_{\delta}$ , and H $_{\alpha}$  atomic emission lines were observed at 247.7, 433.9, 410.2, and 656.3 nm, respectively. F emission lines emerged at various wavelengths, including 624.0, 634.9, 685.6, 690.2, 703.7, 712.8, 731.1 739.9, 775.5, and 780.0 nm, and atomic oxygen peaks were visible near 777 nm and at 844.6 nm.

# D. Actinometry and estimates of relative and absolute number densities

Optical emission actinometry was used to estimate species number densities.<sup>17–20</sup> In actinometry, the measured emission intensity,  $I_X$ , from the species of interest with an unknown number density  $n_X$  is divided by the intensity,  $I_A$ , of an appropriate trace rare gas (the actinometer) with a known concentration,  $n_A$ , to cancel out the effect of changing electron density and EEPF, as operating conditions vary. If the excited state of the species of interest and the actinometer are formed predominantly by electron-impact from their ground states, and the cross sections for these processes have similar threshold energies and energy dependences (ratio of the cross sections nearly independent of energy), then the number density ratio is given by

$$\frac{n_X}{n_A} = a_X \frac{I_X}{I_A} \frac{\gamma_A}{\gamma_X},\tag{3}$$

where  $\gamma_X$  and  $\gamma_A$  are relative sensitivities of the spectrometer at the wavelengths at which the species and the actinometer emit.  $a_X$  is a proportionality constant that includes the rate coefficients,  $k_X$  and  $k_A$ , for electron impact excitation from the ground states, and branching ratios,  $b_X$  and  $b_A$  for the emitting states at the monitored wavelengths

$$a_X = \frac{k_A b_A}{k_X b_X}.$$
 (4)

At the low pressures and electron densities in the present study, the excited states decay solely by photon emission and not by collisions with neutral species or electrons.



FIG. 6. Optical emission spectrum (300 W, 10 mTorr). The total flow rate was 10 sccm, with  $CH_3F:O_2:TRG = 1:1:0.025$ . TRG = trace rare gas.

Actinometry can provide estimates of relative changes in the concentration of the species of interest as plasma conditions vary, provided that the emission of the particular species results primarily from electron impact on that species, and not through dissociative excitation from a larger molecule. Absolute number density ratios  $n_X/n_A$  can be obtained if the proportionality constant  $a_X$  can be computed from electron impact cross sections, or produced from calibrations (see below), and the ratio  $\gamma_A/\gamma_X$  is known for the spectrometer used. If, in addition, the gas temperature is known or can be measured, one can determine  $n_A$  and therefore the absolute number density of the species of interest,  $n_X$ .

For H, F, and O atoms, the Ar 750.3 nm line (energy of the  $2p_1$ , Paschen notation, excited state = 13.48 eV) was used for actinometry, while for HF, HF<sup>+</sup>, C, CO, CO<sub>2</sub><sup>+</sup>, CF, CH, and OH, the Xe 834.7 nm line (energy of the  $2p_3$  excited state = 11.05 eV) was used. As seen in Figure 7, the relative emission intensities of the Ar 750.3 nm and Xe 834.7 nm lines show very similar behavior as a function of power. A transition from the capacitively coupled mode to the inductively coupled mode of plasma operation is evident near 50 W.

#### E. Important species number densities

Absolute H-to-Ar number density ratios  $(n_H/n_{Ar})$  were estimated from the Balmer H<sub> $\alpha$ </sub> emission line at 656.3 nm (upper level energy = 12.03 eV), divided by the intensity of the Ar 750.4 nm line. Proportionality constants were computed in Ref. 18 from cross section data reported by Lin and co-workers for Ar  $2p_1$  (Ref. 21) and by Lavrov and Piva<sup>22</sup> for H<sub> $\alpha$ </sub>. The EEPF was assumed to be Maxwellian above the thresholds for excitation, with  $T_e = 6 \text{ eV}$ , corresponding to  $k_{Ar}/k_{H\alpha} \approx 0.7$ .<sup>20</sup> The branching ratios were  $b_{Ar} = 0.996$  and  $b_{H\alpha} = 0.442$ . The spectral response ratio,  $\gamma_{Ar}/\gamma_{H\alpha} = 0.51$  for the spectrometer employed.

For F, the 703.4 nm  $(3p^2P^0 \rightarrow 3s^2P)$  emission line was chosen (upper state energy = 14.75 eV),<sup>13,23,24</sup> along with the Ar 750.4 nm line. To estimate absolute  $n_F/n_{Ar}$  values, a

proportionality constant  $a_F = 2.84$  was taken from a prior study that measured absolute F-atom concentrations using a titration method.<sup>13,24</sup> The spectral response ratio  $\gamma_{Ar}/\gamma_F$  was 0.61 for this case.

The excited state of  $O(3p^3P)$  emitting at 844.6 nm (upper level energy = 10.94 eV) was used to estimate absolute O-to-Ar number density ratios,  $n_O/n_{Ar}$ . The O(3p<sup>3</sup>P) state can be populated by direct electron impact excitation, dissociative excitation, electron impact excitation from metastable states, and cascading transitions from upper levels. For O number densities around  $\sim 10^{13} \text{ cm}^{-3}$  and a characteristic plasma dimension of  $\sim 10$  cm, the rate coefficient for populating the  $3p^{3}P$  state through cascade transitions, enhanced by radiation trapping, was about 3 times larger than that for direct excitation.<sup>25</sup> In the present case, however, the characteristic plasma dimension is  $\sim 2 \text{ cm}$ , which is roughly equal to the mean free path of a cascading transition photon. Therefore, the cross section for direct excitation of the  $3p^{3}P$  state should give a better estimate. Excitation by electron impact of metastable species is less important. Dissociative excitation from  $O_2$  can be very important at low powers and/or high pressures, and generally under circumstances favoring low degrees of dissociation. It is therefore necessary to correct for this effect. A rate coefficient ratio of  $k_{Ar}/k_{O(direct)} = 0.62$  was obtained from Figure 10 in Ref. 23. The branching ratio  $b_{Ar}/b_O = 1$ , hence  $a_O = 0.237$ . The spectral response correction  $\gamma_{Ar}/\gamma_O$  was 2.5 for the spectrometer employed.

Emission intensities of HF, HF<sup>+</sup>, C, CO, CO<sub>2</sub><sup>+</sup>, CF, CH, and OH were divided by the emission intensities of the Xe 834.6 nm line for the particular condition. This line is a better match for the average threshold energy of e-impact excitation of these species, to at least partially remove the dependence of the emission intensity on the plasma parameters. Figure 8 presents absolute number density ratios ( $n_{H/}$  $n_{Ar}$ ,  $n_F/n_{Ar}$  and  $n_O/n_{Ar}$ ) as a function of power at 10 mTorr. Normalized emission intensity ratios for C and molecular species as a function of power are shown in Figure 9. The



FIG. 7. Normalized I(Ar) and I(Xe) emission intensities at 750.4 nm and 834.7 nm, respectively, as a function of power (at 10 mTorr). The total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025. TRG = trace rare gas.



FIG. 8.  $n_H/n_{Ar}$ ,  $n_F/n_{Ar}$ , and  $n_O/n_{Ar}$  absolute number density ratios vs. power at 10 mTorr. The  $n_H/n_{Ar}$  values are 5 times those listed on the ordinate axis, e.g.,  $n_H/n_{Ar} = 100$  at 400 W. The total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025. The absolute number density of Ar is also shown. The thick solid line is  $n_F/n_{Ar}$  computed from Eq. (12). TRG = trace rare gas.



FIG. 9. Normalized emission intensity ratios for HF/Xe, HF<sup>+</sup>/Xe, CO/Xe,  $CO_2^+/Xe$ , CF/Xe, CH/Xe, OH/Xe, and C/Xe, as a function of power at 10 mTorr. Emission intensity ratios for HF and HF<sup>+</sup> are expected to scale approximately with the relative number density ratios for  $n_{HF}/n_{Xe}$ , while those for CO and  $CO_2^+$  mainly scale with relative number density ratios  $n_{CO}/n_{Xe}$  and  $n_{CO2}/n_{Xe}$ , respectively. The total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025. TRG = trace rare gas.

pressure dependence of absolute number density ratios, and normalized emission intensity ratios, at a constant power of 300 W are shown in Figures 10 and 11, respectively.

The relatively small change in " $n_H/n_{Ar}$ " between ~20 and 40 W in Figure 8 indicates that H emission in this capacitively coupled regime is due to dissociative excitation of CH<sub>3</sub>F and not due to electron impact excitation of H. If it were mainly the latter, then  $I_H/I_{Ar}$  should roughly double (i.e., the electron number density and electron impact dissociation rate should double). This is reasonable in the capacitively coupled region where there are very few H atoms. H emission through dissociative excitation of a H-containing species such as H<sub>2</sub>O, OH, or CH<sub>x</sub> is less likely, since as seen in Figure 9,  $I_{OH}/I_{Xe}$  and  $I_{CH}/I_{Xe}$  values increase strongly between 20 and 40 W.

If the data between 40 and 20 W are extrapolated to 0 W, a value of about 4 is obtained for dissociative excitation of CH<sub>3</sub>F to produce H emission, relative to Ar. Above 75 W (in the inductive mode of operation),  $I_H/I_{Ar}$  increases with



FIG. 10.  $n_{H}/n_{Ar}$ ,  $n_{F}/n_{Ar}$ , and  $n_{O}/n_{Ar}$  absolute number density ratios vs. pressure at 300 W. The total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025. TRG = trace rare gas. The thick solid line is  $n_{F}/n_{Ar}$  computed from Eq. (15).



FIG. 11. Normalized emission intensity ratios for HF/Xe, HF<sup>+</sup>/Xe, CO/Xe,  $CO_2^+/Xe$ , CF/Xe, CH/Xe, OH/Xe, and C/Xe, as a function of pressure at 300 W. Emission intensity ratios for HF and HF<sup>+</sup> are expected to scale approximately with the relative number density ratios for  $n_{HF}/n_{Xe}$ , while those for CO and  $CO_2^+$  mainly scale with relative number density ratios  $n_{CO}/n_{Xe}$  and  $n_{CO2}/n_{Xe}$ , respectively. The total flow rate was 10 sccm, with CH<sub>3</sub>F:O<sub>2</sub>:TRG = 1:1:0.025. TRG = trace rare gas.

power in a manner which suggests that the predominant excitation mechanism is electron impact of ground state H, and not dissociative excitation. For example, between 100 and 400 W,  $I_H/I_{Ar}$  (minus a zero-power extrapolated value of 4) increased by a factor of 2.6, while  $I_{OH}/I_{Xe}$  and  $I_{CH}/I_{Xe}$ increased by factors of only 1.3 and 1.5. (it should be noted that H emission from dissociative excitation of CH<sub>3</sub>F, normalized to Ar emission, would *decrease* with increasing power).

To correct for dissociative excitation from CH<sub>3</sub>F, a value between 0 and 4 should be subtracted from the  $n_H/n_{Ar}$  values in Figure 9. Thus, at 400 W,  $n_H/n_{Ar} = 99$  to 103. The CH<sub>3</sub>F:Ar feed gas ratio was 200:1, so the total-H:Ar ratio was 600:1. The conditions are such that flow conductance is mainly limited by the conductance of the discharge tube. In the transitional flow regime, a long tube conductance,  $C_{lt}$ , for a species X is approximately equal to the sum of continuum and molecular long tube conductances<sup>26</sup>

$$C_{lt}(X) = C_c + C_m(X) = \frac{\pi d^4}{256\eta l} (P_u + P_d) + \frac{d^3}{3l} \sqrt{\frac{\pi R T_g}{2m_X}}, \quad (5)$$

where d (= 3.6 cm) and l (which cancels out when taking the ratio below) are the tube inside diameter and length,  $P_u$  and  $P_d$  are the pressures at the upstream and downstream ends of the tube,  $\eta$  is the viscosity of the gas, and  $m_X$  the mass of species, X. As long as the gas is less than ~70% (H + H<sub>2</sub>), a rather safe assumption, the viscosity will be governed by heavier species that have similar values (e.g., CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CH<sub>4</sub> have viscosities of 1.4, 0.9, 2.0, and  $1.1 \times 10^{-4}$  g cm<sup>-1</sup> s<sup>-1</sup>),<sup>26</sup> hence  $\eta$  will only be weakly dependent on gas composition as power increases. ( $\eta$  does increase mildly with temperature and hence power, but that has not been taken into account.) For a given H-to-Ar flow ratio,  $n_H/n_{Ar}$  will be reduced by a factor  $C_{lt}(Ar)/C_{lt}(H)$ . For a typical gas viscosity of  $1.5 \times 10^{-4}$  g cm<sup>-1</sup> s<sup>-1</sup> and an approximate

average temperature across the tube of 600 K at 400 W and 10 mTorr, where  $P_u + P_d \approx 17.1$  mTorr (see above),  $C_{lt}(Ar)/C_{lt}(H) = 0.216$ . If the gas were completely dissociated, then the maximum possible  $n_{H}/n_{Ar}$  value would be about  $600 \times 0.216 = 130$ , close to the observed  $n_{H}/n_{Ar} = 99$  to 103 at 400 W. Therefore, the CH<sub>3</sub>F feed gas and other fragments are largely dissociated at the highest powers investigated.

If CH<sub>3</sub>F were completely dissociated then  $n_F/n_{Ar}$  could reach 200 (in the limit of no pumping speed differences under continuum flow conditions) for the feed gas ratio. Figure 8 shows that  $n_F/n_{Ar}$  is much lower (e.g., 16 at 400 W). The most likely explanation is that HF is a sink for fluorine.  $I_{HF}/I_{Xe}$  and  $I_{HF+}/I_{Xe}$  increase only slightly between 100 and 300 W, and then begin to fall between 300 and 400 W (Figure 9), while  $n_H/n_{Ar}$  and  $n_F/n_{Ar}$  increase by factors of 2.5 and 8 over this power range. This can be explained by the fact that HF is dissociated by electron impact at high power, causing its number density to reach a broad maximum before beginning to fall slightly at the highest power. The very different power dependences for the  $I_F/I_{Ar}$ , compared to  $I_{HF}/I_{Xe}$ and  $I_{HF+}/I_{Xe}$ , and  $I_{CF}/I_{Xe}$ , and the near-zero value of  $I_F/I_{Ar}$ extrapolated to zero power, also support the conclusion that F emission is mainly excited by electron impact on F.

The power dependence of  $n_O/n_{Ar}$  in Figure 8 indicates that O emission is mainly via dissociative excitation (from  $O_2$ ) at low powers. This is commonly observed<sup>25,27</sup> and must be corrected for, to obtain accurate number densities. Dissociative excitation of O from CO is not likely, since the CO bond strength is 11.1 eV. Dissociative excitation from  $CO_2$  is possible, since the O-CO bond strength is 5.5 eV, similar to  $O_2$  (5.16 eV). If this were the case, then O emission would be expected to track  $CO_2^+$  (and maybe CO) emission as a function of power, when to the contrary, O/Ar emission increases by a factor of 3 between 75 and 400 W (Figure 8), while  $CO_2^+/Xe$  and CO/Xe emission increases by only 20% over this power range (Figure 9). Despite the uncertainty caused by dissociative excitation of O<sub>2</sub>,  $n_O/n_{Ar}$ = 9 to 11 at 400 W is much lower than the maximum possible values of 253 (=  $400 \times [16/40]^{1/2}$  for molecular-flowdetermined pumping speed disparity) to 400 (in the limit of no pumping speed differences under continuum flow conditions) for the feed gas ratio. The percent conversion of  $O_2$  is likely much higher than the  $\sim 3\%$  suggested by these numbers. It is expected that a substantial amount of oxygen is contained in CO, CO<sub>2</sub>, and OH, reflected in their strong emissions (Figures 6 and 9), as well as in  $H_2O$  and perhaps other species that do not possess optical emission bands of their own.

The normalized emission intensity ratios of molecular species in Figure 9 behave differently than the atomic constituents in Figure 8 as a function of power. In the low power, capacitively coupled regime, molecular species rise linearly or superlinearly with power, and extrapolate to zero at zero power. The zero-power extrapolation is to be expected, since unlike H and O, none of these emissions can be produced by dissociative excitation of the feed gas. (Excited HF<sup>+</sup> emission is unlikely to occur by dissociative excitation of CH<sub>3</sub>F, and indeed the low power behavior supports this supposition.)

In the higher power inductive mode, the emission ratios in Figure 9 rise somewhat (factor of ~2) between ~70 and ~300 W for some species (CF, CH), while others (CO,  $CO_2^+$ , OH, HF, HF<sup>+</sup>) increase by <30% over this power range. Normalized emission intensity ratios either do not change, or exhibit a shallow maximum between 300 and 400 W. (Note that the Ar and Xe emission intensities in Figure 7 increase with power between 200 and 400 W, showing no sign of saturation at high power.)

It is reasonable to assume that the predominant mode of excitation of HF emission is through electron impact excitation of the stable species, HF. There are no stable molecules that contain an HF group and would be easily fragmented into excited electronic states of HF and HF<sup>+</sup>. As discussed above, excitation of HF or HF<sup>+</sup> emission by electron-impact dissociative excitation on CH<sub>3</sub>F is not important, so by inference, neither is dissociative excitation from any CH<sub>x</sub>F<sub>y</sub> species. Therefore,  $n_{HF}/n_{Xe}$  is expected to be proportional to  $I_{HF}/I_{Xe}$  and  $I_{HF+}/I_{Xe}$ .

CO is also a stable species and electron impact excitation from its ground state is expected to give rise to strong CO emission. While contributions to CO emission from dissociative excitation of CO<sub>2</sub> cannot be ruled out, the different pressure dependences for CO emission relative to  $CO_2^+$ (Figure 11) and the peaking of  $I_{CO2+}/I_{Xe}$  at 65% O<sub>2</sub> addition vs. the peaking of  $I_{CO}/I_{Xe}$  at 50% O<sub>2</sub> found in a previous study<sup>7</sup> suggest that CO and  $CO_2^+$  emissions arise from different species, i.e., CO, and either CO<sub>2</sub> or  $CO_2^+$ , respectively. Since  $CO_2^+$  number density would be expected to be proportional to CO<sub>2</sub> number density,  $CO_2^+$  emission should track the number density of both CO<sub>2</sub> and  $CO_2^+$ .

The origin of OH emission is less certain. While OH would be expected in the plasma, many stable OH-containing species are possible, most importantly H<sub>2</sub>O. In fact, OH emission did not track very well with OH concentration measured as a function of power and  $%O_2$  in preliminary experiments using ultraviolet absorption spectroscopy. Hence  $I_{OH}/I_{Xe}$  should be interpreted as a qualitative indicator of the behavior of the sum of all OH-containing species.

Similarly, it is questionable to what extent emission from CF, CH, and C reflects the relative number densities of these species. Because of the strong dependence of  $I_{CF}/I_{Xe}$ ,  $I_{CH}/I_{Xe}$ , and  $I_C/I_{Xe}$  on power between 20 and 40 W, and the large energy required, it is unlikely that any of these emissions are a result of dissociative excitation of CH<sub>3</sub>F. CF, CH, and C emission therefore arises from electron impact on an undetermined distribution of smaller fragments. The superlinear power dependence for  $I_C/I_{Xe}$  in the inductive mode suggests that a high degree of fragmentation is required to produce this emission, so it could be from electron impact on C or perhaps CH, but less likely from CH<sub>2</sub>, CH<sub>3</sub>, or CH<sub>2</sub>F.

Absolute number density ratios,  $n_H/n_{Ar}$ ,  $n_F/n_{Ar}$ , and  $n_O/n_{Ar}$ , were also obtained as a function of pressure at 300 W (Figure 10).  $n_H/n_{Ar}$  increased 1.5-fold between 9 and 30 mTorr, while  $n_F/n_{Ar}$  decreased by half and  $n_O/n_{Ar}$  was nearly independent of pressure. Relative  $I_{HF+}/I_{Xe}$  increased by a small amount (~30%) between 9 and 30 mTorr, while  $I_{HF}/I_{Xe}$  increased slightly (perhaps ~5%) over this pressure range. As discussed above,  $I_{HF}/I_{Xe}$  and  $I_{HF+}/I_{Xe}$  are believed to scale with relative  $n_{HF}/n_{Xe}$ . The similar pressure

dependence of the neutral and ion emission ratios supports this claim.  $I_{CO}/I_{Xe}$  increased by 1.74, while  $I_{CO2+}/I_{Xe}$ decreased by almost half between 9 and 30 mTorr. This is consistent with the supposition that CO and CO<sub>2</sub><sup>+</sup> emissions have different parentage, i.e., CO and CO<sub>2</sub>, respectively, so that  $I_{CO}/I_{Xe}$  and  $I_{CO2+}/I_{Xe}$  are proportional to relative  $n_{CO}/$  $n_{Xe}$  and  $n_{CO2}/n_{Xe}$ . Relative  $I_{OH}/I_{Xe}$ ,  $I_{CH}/I_{Xe}$ ,  $I_{CF}/I_{Xe}$ , and  $I_{C}/$  $I_{Xe}$  emission intensity ratios increased by a factor of 2.7, 1.69, 1.6, and 3.3, respectively, from 9 to 30 mTorr.

#### F. Reaction mechanism

While the chemistry of  $CH_3F/O_2$  plasmas is very rich, some general trends can be predicted and compared to observations. Electron impact of  $CH_3F$  forms F, H,  $CH_3$ , and  $CH_2F$  in approximately a statistical ratio, with apparently no  $HF.^{28}$  A simple subset of reactions may be used to demonstrate the power and pressure dependence expected for F and HF number densities. F is formed by electron impact dissociation of  $CH_xF$  (x = 3, 2, 1, or 0, i.e.,  $CH_3F$  and its fragments)

$$e + CH_x F \xrightarrow{\kappa_{1,x}} CH_x + F + e,$$
 (R1)

with rate coefficients  $k_{I,x}$ . F is lost in the gas phase by H abstraction reactions with  $CH_xF_y$  that form HF (x = 3, 2, or 1 and y = 1 or 0) with rate coefficients  $k_{2,x,y}$  ( $k_{2,3,I} = 3 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>)<sup>29,30</sup>

$$F + CH_x F_y \xrightarrow{k_{2,x,y}} HF + CH_{x-1}F_y, \qquad (R2)$$

as well as with H<sub>2</sub>O ( $k_3 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )<sup>31</sup>

$$F + H_2O \xrightarrow{k_3} HF + OH$$
 (R3)

and H<sub>2</sub> 
$$(k_4 = 2.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})^{31}$$
  
F + H<sub>2</sub> $\xrightarrow{k_4}$  HF + H. (R4)

(Because these reactions are so fast, they have weak temperature dependences, hence room temperature rate constants were used in (R2)–(R4).) F is also lost on the walls through abstraction of H from adsorbed species,  $YH_x$  (hydrocarbons, H<sub>2</sub>O, and perhaps even weakly bound H)

$$F + YH_x$$
-wall  $\xrightarrow{k_5}$  HF + YH<sub>x-1</sub>-wall, (R5)

F is also formed and HF is destroyed by the electron impact reaction

$$HF + e \xrightarrow{k6} H + F + e.$$
 (R6)

The steady-state number density of F under these simplifying conditions is

$$n_F = \frac{\left(\sum_{x=0}^{3} k_{1,x} n_{CHxF} + k_6 n_{HF}\right)}{\sum_{x=1}^{3} \sum_{y=0}^{1} k_{2,x,y} n_{CHxFy} + k_3 n_{H2O} + k_4 n_{H2} + k_5 n_{YHx-wall} + k_{pump}} n_e,$$
(6)

where  $k_{pump}$  represents loss of F through pumping at the reactor exit. In a prior study,<sup>7</sup> it was found that heterogeneous H abstraction was four times faster than homogeneous abstraction for O<sub>2</sub> percentages <48%, but became slower than the gas phase abstraction for O<sub>2</sub> percentages >48% in the feed gas (due to the presence or absence of a hydrocarbon film on the walls for O<sub>2</sub> percentages of <48% or >48%, respectively). Since in the present case the O<sub>2</sub> percentage is 50%,  $k_{3}n_{CHx-wall}$  can be ignored in Eq. (6). Assuming (a) similar electron impact rate coefficients,  $k_d$ , for destruction of HF and CH<sub>x</sub>F for all values of *x*, (b) that the gaseous abstraction reactions (R3) and (R4) proceed with the same rate coefficient,  $k_a$ , (c) that reaction (R2) also proceeds with rate coefficient  $k_a$  for all values of *x* and *y*, and (d)  $k_{pump}$  is small compared to the sum of the other terms in the denominator of Eq. (6) yields

$$n_F \approx \left(\frac{k_d n_e}{k_a}\right) \frac{\sum_{x=0}^{3} n_{CHxF} + n_{HF}}{\sum_{x=1}^{3} \sum_{y=0}^{1} n_{CHxFy} + n_{H2O} + n_{H2}}.$$
 (7)

Ignoring pumping speed differences for the fluorinecontaining fragments, and assuming that  $n_F \ll \sum_{x=0}^{3} n_{CHxF}$  $+ n_{HF}$ , as was found (see Figure 8 and discussion above), the F-atom balance is

$$\sum_{x=0}^{3} n_{CHxF} + n_{HF} = \frac{T^0}{\bar{T}_g} n_{CH3F}^0,$$
(8)

where superscript 0 indicates feed gas number density with the plasma off, and  $\overline{T}_g$  represents the mean gas temperature in the discharge tube, taken as the average of  $T_g$  (the measured temperature at the center of the tube) and the wall temperature of  $T^0 = 300$  K. Similarly, the H-atom balance is given by

$$\sum_{x=1}^{3} \sum_{y=0}^{1} x n_{CHxFy} + 2n_{H2O} + 2S_{H2}n_{H2} + S_{H}n_{H} + n_{HF} + n_{OH} = \frac{3T^{0}}{\bar{T}_{g}} n_{CH3F}^{0}.$$
 (9)

In Eq. (9),  $S_{H2}$  and  $S_H$  are the conductance of H<sub>2</sub> and H, respectively, both divided by the average gas conductance. Even if all the fluorine is present as HF, the amount of hydrogen in HF cannot exceed 1/3 of the total hydrogen. It is likely less than 1/3 and hence a relatively small error is made in ignoring it. Similarly the OH number density is likely much less than the total H-containing species number densities. Neglecting  $n_{HF}$  and  $n_{OH}$ , noting that the weighted average for x is roughly 2, and rearranging Eq. (9) gives

$$\sum_{x=1}^{3} \sum_{y=0}^{1} n_{CHxFy} + n_{H2O} + S_{H2}n_{H2} \approx \frac{3T^{0}}{2\bar{T}_{g}} n_{CH3F}^{0} - \left(\frac{S_{H}n_{H}}{2}\right).$$
(10)

Using Eq. (5), and assuming an average mass of ~20 for all species excluding H and H<sub>2</sub>, yields  $S_H = 3.61$  and  $S_{H2} = 3.36$ . As long as  $\sum_{x=1}^{3} \sum_{y=0}^{1} n_{CHxFy} + n_{H2O} > S_{H2}n_{H2}$ , a relatively small error is introduced in substituting  $\frac{3T^0}{2T_g} n_{CH3F}^0 - \left(\frac{S_H n_H}{2}\right)$  for  $\sum_{x=1}^{3} \sum_{y=0}^{1} n_{CHxFy} + n_{H2O} + n_{H2}$  in Eq. (7). Then substituting Eq. (8) into Eq. (7) yields the fluorine number density

$$n_F \approx \left(\frac{k_d n_e}{k_a}\right) \left(\frac{T^0}{\bar{T}_g}\right) \frac{2n_{CH3F}^0}{3n_{CH3F}^0 \left(\frac{T^0}{\bar{T}_g}\right) - S_H n_H}$$
(11)

and a F-to-Ar number density ratio of

$$\frac{n_F}{n_{Ar}} \approx \left(\frac{k_d n_e}{k_a}\right) \left(\frac{n_{CH3F}^0}{n_{Ar}^0}\right) \left\{\frac{2}{3n_{CH3F}^0 \left(\frac{T^0}{\bar{T}_g}\right) - S_H\left(\frac{n_H}{n_{Ar}}\right)}\right\}.$$
 (12)

Using the cross section measurements of Motlagh and Moore<sup>28</sup> for CH<sub>3</sub>F dissociation as the average for dissociation of all CH<sub>x</sub>F species (as well as HF) and a nearly constant  $T_e \approx 5.5 \text{ eV}$  (see Figure 3), the rate coefficient  $k_d$  is computed to be  $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The rate coefficient  $k_a = 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (the average of (R2)–(R4)) for the average for all gas-phase abstraction processes. Using the measured  $n_e$  and  $T_g$  as a function of power at 10 mTorr (Figures 3 and 5),  $n_F/n_{Ar}$  computed from Eq. (12) is represented by the thick red line in Figure 8. The predicted values from this simple reaction model are in excellent agreement with the measurements as a function of power, without using any adjustable parameters.

For HF, the steady-state number density is given by

$$n_{HF} = \frac{\sum_{x=1}^{3} \sum_{y=0}^{1} k_{2,x,y} n_{CHxFy} + k_3 n_{H2O} + k_4 n_{H2} + k_5 n_{YHx-wall}}{k_6 n_e + k_{pump}} n_F.$$
(13)

It is reasonable to assume that  $k_6 n_e \gg k_{pump}$ . Ignoring the  $k_5 n_{CHx-wall}$  term in Eq. (13), making the other assumptions as before, and substituting for  $n_F$  from Eq. (11), yields

$$n_{HF} = \frac{T^0}{\bar{T}_g} \frac{k_d}{k_6} n_{CH3F}^0.$$
 (14)

Dividing by  $n_{Ar} = \frac{T^0}{T_g} n_{Ar}^0$ ,

$$\frac{n_{HF}}{n_{Ar}} = \frac{k_d}{k_6} \frac{n_{CH3F}^0}{n_{Ar}^0}.$$
 (15)

Consequently, the HF number density should be independent of electron density and hence discharge power, as observed experimentally (Figure 9). Furthermore,  $n_{HF}$  should be a major fluorine species at higher powers, since  $k_d/k_4$  is of the order of unity. In the capacitively coupled low power regime below 75 W,  $n_{HF}/n_{Xe}$  falls abruptly with decreasing power. From Eq. (13), as  $n_e \rightarrow 0$ ,  $k_{pump} \gg k_6 n_e$  and  $n_{HF}$  becomes proportional to  $n_F$  and hence to  $n_e$ . (Note from Eq. (11) that  $n_F$  will remain proportional to  $n_e$  as  $n_e \rightarrow 0$ .)

The H atom number densities are very large (Figure 8) because there are no efficient mechanisms that destroy H atoms. Gas-phase abstraction of F from fluorocarbon species is slow. For example, very small rate coefficients of  $4 \times 10^{-15}$  and  $1.6 \times 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup> have been reported for  $H + CH_3F \rightarrow HF + CH_3$ .<sup>32,33</sup> H is also not expected to recombine efficiently to form H<sub>2</sub> on a CH<sub>x</sub> surface. Formation of HF takes at most 1/3 of the H from the feed gas, hence the observed high levels of H are expected.

The mechanism discussed above can also be used to predict the dependence of the F and HF relative densities on pressure.  $n_F/n_{Ar}$  is given by Eq. (12). A third-order polynomial was fit to the measured  $T_e^{eff}$  values in Figure 4 and used to obtain  $T_e^{eff}$  as a function of pressure. Equating  $T_e^{eff}$  with a Maxwellian  $T_e$ , the cross section measurements of Motlagh and Moore<sup>28</sup> for CH<sub>3</sub>F dissociation were then used to compute  $k_d$ . Assuming a constant gas temperature, and using the  $n_H/n_{Ar}$  values in Figure 10, the  $n_F/n_{Ar}$  values were computed from Eq. (12), and are shown in Figure 10 (thick red line). The computed  $n_F/n_{Ar}$  values are in excellent agreement with the measurements at low pressures, even predicting the rapid falloff between 9 and 12 mTorr and the slower fall off between 15 and 30 mTorr. Again, there were no adjustable parameters. Small discrepancies between predictions and observations could easily be explained by the assumptions used to compute  $n_F/n_{Ar}$ , as well as in the errors inherent in the actinometry measurements. Since even the small pressure dependence of  $T_e$  will largely cancel out in the ratio of rate coefficients,  $n_{HF}/n_{Ar}$  as given by Eq. (15) is predicted to be pressure independent, as was found experimentally (Figure 11).

It is also informative to compare the measured number densities with thermodynamic equilibrium values. For a mole ratio of C:O:H:F = 1:2:3:1 (corresponding to the 50%CH<sub>3</sub>F/50%O<sub>2</sub> feed gas), at 10 mTorr, HF is predicted to be the sole fluorine species between room temperature and 2000 K. HF will of course be dissociated in the plasma, but since there are so many fast reactions that form HF and no other stable F-containing species exists at equilibrium, once the CH<sub>3</sub>F feed gas is initially dissociated, the formation of HF is the most likely outcome. This is consistent with our findings. Oxygen is mainly present as CO<sub>2</sub> and H<sub>2</sub>O at

equilibrium, with the former maximizing and the latter minimizing near 500 K. The plasma will dissociate  $H_2O$  and  $CO_2$ to form OH and CO, with the latter also being expected to form at equilibrium above 500 K.  $O_2$  is not predicted to be present at equilibrium for the gas temperatures reached in this study. Hence, once the  $O_2$  feed gas is dissociated, it will not reform by recombination. It is therefore expected that nearly all of the oxygen is present as CO, CO<sub>2</sub>, H<sub>2</sub>O, and OH radicals.

## **IV. CONCLUSIONS**

CH<sub>3</sub>F/O<sub>2</sub> (50%/50%) inductively coupled plasmas, sustained in a compact reactor, were investigated by optical emission spectroscopy and Langmuir probe measurements. Electron energy probability functions exhibited a bi-Maxwellian character. The electron density was of the order  $10^{11}$ /cm<sup>3</sup>, and increased linearly with power (in the inductive mode of operation), but only weakly with pressure in the range of 9–30 mTorr. The effective electron temperature  $(T_e^{eff})$  was 5.2 eV at 9 mTorr, decreased to 4.3 eV at 20 mTorr, and had a weak dependence on pressure at higher pressures.  $T_e^{eff}$  was also nearly independent of power. The gas temperature, measured using the rovibronic bands of the second positive system of  $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ , increased from 400 K at 75 W to 900 K at 400 W.

Optical emission actinometry was employed to estimate the absolute number density of H, F, and O atoms. All three atom number densities increased almost linearly with power in the inductive mode of reactor operation. The H-atom number density was estimated to be  $5.4 \times 10^{13}$  cm<sup>-3</sup> at 400 W and 10 mTorr. F and O atom number densities were estimated to be  $8.3 \times 10^{12} \text{ cm}^{-3}$  and  $5.9 \times 10^{12} \text{ cm}^{-3}$ , respectively. Most of F was in the form of HF. Given the total gas number density of  $1.13 \times 10^{14} \text{ cm}^{-3}$  at 10 mTorr and 400 W (the corresponding gas temperature is 900 K), one concludes from the high H atom number densities (and high H pumping speeds) that the CH<sub>3</sub>F feed gas was highly dissociated. The number density of H atoms was relatively high because there were no efficient Hatom loss pathways. The absolute number density ratios,  $n_X/$  $n_{Ar}$  (X = H, F, or O), were also measured as a function of pressure. The H/Ar density ratio increased by 50%, while the F/Ar ratio decreased by half, and the O/Ar ratio remained almost constant as pressure increased between 9 and 30 mTorr.

Emission intensities of HF, HF<sup>+</sup>, C, CO, CO<sub>2</sub><sup>+</sup>, CF, CH, and OH divided by the emission intensity of the Xe 834.7 nm line for the particular condition, were also measured as a function of pressure and power. The emission intensity ratios suddenly increased during the transition from capacitive to inductive mode but they appeared to reach a plateau beyond 150 W. The emission intensity ratios of most molecules increased moderately with pressure. However, the  $I_{HF}/I_{Xe}$ emission ratio remained almost flat and the  $I_{CO2+}/I_{Xe}$  emission ratio decreased by half, as pressure was varied from 9 to 30 mTorr. Emission intensity ratios for HF and HF<sup>+</sup> are expected to scale approximately with the relative number density ratios for  $n_{HF}/n_{Xe}$ , while those for CO and CO<sub>2</sub><sup>+</sup> mainly scale with the relative number density ratios  $n_{CO}/n_{Xe}$  were proposed to predict the F and HF number densities as a function of power and pressure.

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