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Production of negative ion plasmas using perfluoromethylcyclohexane (C_7F_{14})

Su-Hyun Kim, Robert Merlino, Vladimir Nosenko,
Ross Fisher, and Michael Miller

Department of Physics and Astronomy
The University of Iowa, Iowa City, IA

Negative ion plasmas are produced by electron attachment to neutral molecules when an electronegative gas is introduced into a plasma. One of the most widely used gases is sulfur hexafluoride, SF_6 which has a relatively high electron attachment cross section for low energy (<0.05 eV) electrons, making it particularly attractive for use in Q machines, where T_e ~ 0.2 eV. However, in discharge plasmas having T_e ~ several eV, multiple negative ion species are also formed, including F^-, which can be corrosive to vacuum system components. As an alternative, we have investigated the use of C_7F_{14} to produce negative ion plasmas, both in a Q machine and in a hot-filament, multidipole device. The maximum attachment cross-section is ~ 6 times higher than that of SF_6, and occurs at a higher energy, 0.15 eV, so that the attachment efficiency should be enhanced both in the Q machine and in the discharge plasma. Details of the experimental setup and Langmuir probe characteristics obtained in the plasma with C_7F_{14} will be presented.

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NEGATIVE ION PLASMAS

- **Negative ions are present in a number of different plasmas**
  - plasma processing devices which utilize reactive gases such as silane (SiH_4) or methane (CH_4)
  - In the earth's ionosphere (O^-, O_2^-, NO_2^-)
  - combustion plasmas
  - gaseous lasers
  - neutral beam sources for fusion (H^-)
  - stellar atmospheres (H^-)

- **Interest in negative ion plasmas**
  - plasmas with $m_+ \approx m_-$
  - shielding of low frequency fields by electrons is reduced
  - new wave modes appear
  - similar to dusty plasmas

- **Formation of negative ion plasmas**

  - *von Goeler, Ohe and D'Angelo* (J. Appl. Phys. 37, 2519, 1966), bombarded the hot tungsten plate of a Q machine with an atomic beam of CsCl to form a plasma containing Cs^+ and Cl^- ions.

  - *Douchet* (Phys. Lett. 33A, 283, 1970) introduced Iodine gas into a gas discharge to produce a plasma with I^- ions by dissociative attachment $I_2 + e^- \rightarrow I + I^-$

  - *Wong, Mamas and Arnush* (Phys. Fluids 18, 1489, 1975) introduced SF_6 into a multidipole plasma to produce a plasma with a significant fraction of negative ions produced by the reaction $SF_6 + e^- \rightarrow SF_6^-$

  - *Sato* (Proc. 1989 ICPP, p 79; Plasma Sources Sci. Technol. 3, 395, 1994) introduced SF_6 into a potassium Q machine to produce SF_6^- negative ions by electron attachment

  - *Song, Suszcynsky, D'Angelo and Merlino* (Phys. Fluids B, 1, 2316, 1989) also introduced SF_6 into a K machine to produce a negative ion plasma. The presence of negative ions was observed directly using an ion mass spectrometer (Suszcynsky, D'Angelo and Merlino, Rev. Sci. Instrum. 59, 1376, 1988)

  - *Sheehan and Rynn* (Rev. Sci. Instrum. 59, 1369, 1988) discussed a variety of methods to produce negative ion plasmas with low residual electron densities.

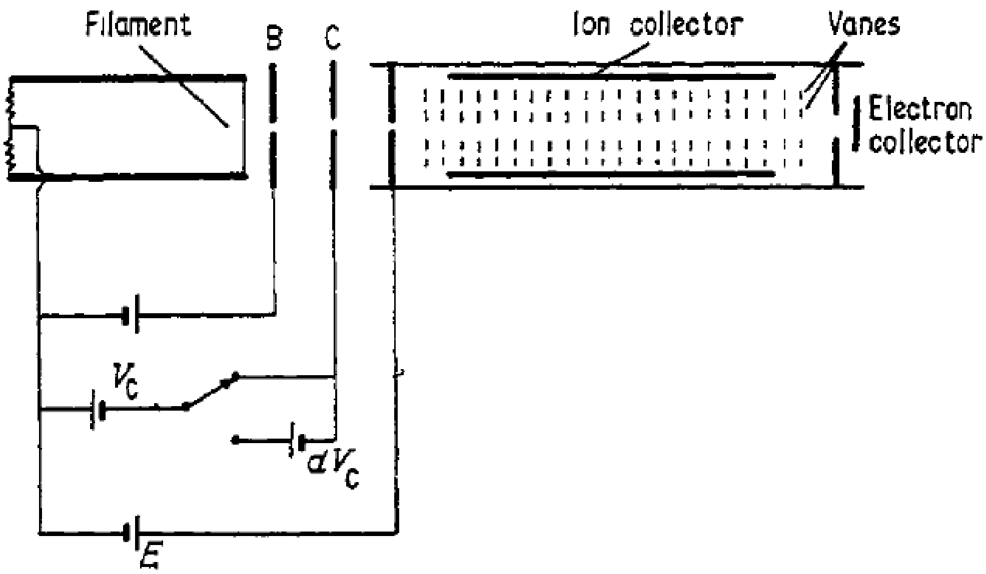
  - *Hiroshi Amemiya* (J. Phys. D: Appl. Phys. 23, 999, 1990) provided an excellent review article discussing the use of Langmuir probes in negative ion plasmas

- *Sato, Mieno, Hirata, Yagi, Hatakeyama and Iizuka* (Phys. Plasmas 1, 3480, 1994) produced a C_{60} plasma consisting of K^+ positive ions and C_{60}^- negative ions by introducing Buckminsterfullerene particles into a Q machine plasma

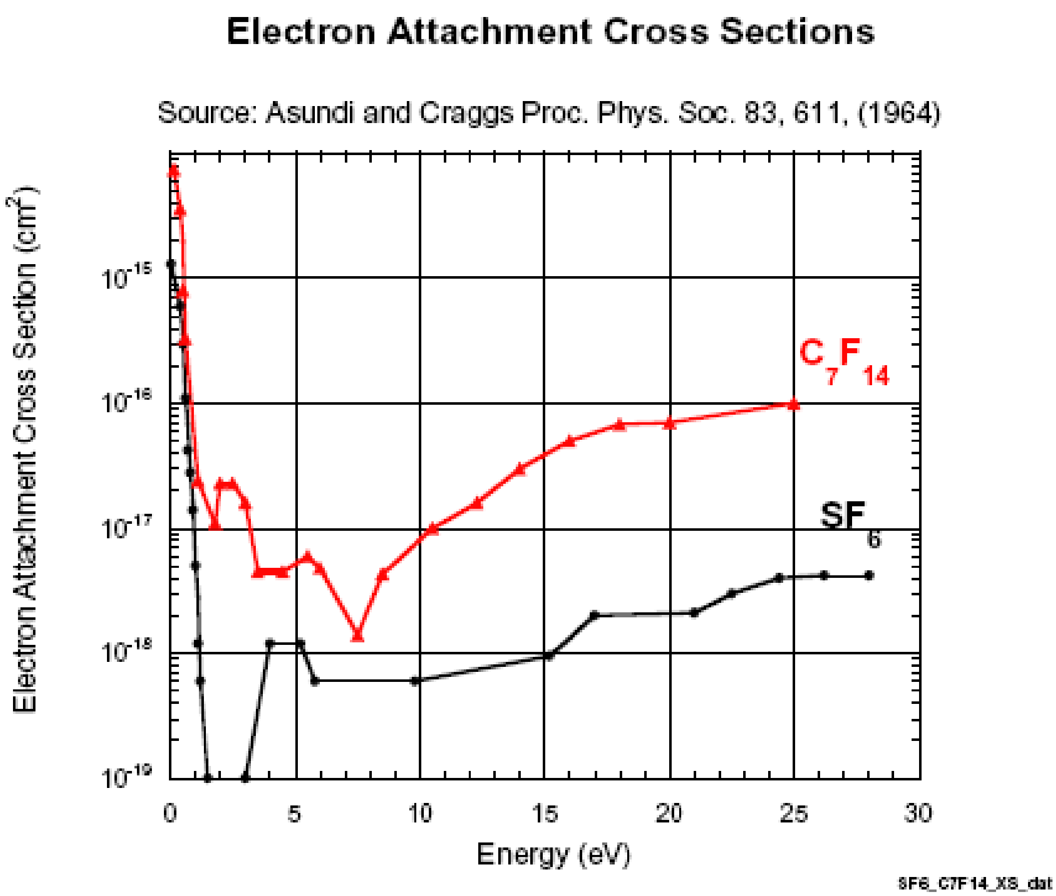
- *Oohara and Hatakeyama* (Phys. Rev Lett. 91, 205005, 2003) generated a pure plasma consisting of C_{60}^+ and C_{60}^- by electron beam impact ionization

Electron Attachment Cross Sections

R. K. Asundi and J. D. Craggs in their paper "Electron capture and ionization phenomena in SF_6 and C_7F_{14}" *Proc. Phys. Soc. 83, 611, (1964),* measured the cross sections for electron capture for both molecules using the retarded potential difference technique.



This method provides an electron beam at a well defined energy and with an energy spread ~ 0.05 eV. The resulting cross sections are shown below.



Attachment cross sections for SF_6

- In the energy range of 0 – 30 eV, mass-spectroscopic studies show that SF_6^-, SF_5^-, *and* F^- are formed.

- The peak at energies near zero are due to the resonant capture of electrons by the process

$$SF_6 + e \rightarrow SF_6^{-*} \rightarrow SF_6^-$$

- In the range of 4 – 14 eV, the predominant negative ion is F^-, while at an energy of 17.3 eV, the negative ion SF_5^- appears.

- The maximum cross section of 1.3×10^{-15} cm^2 is obtained at an electron energy of 0.03 eV.

Attachment cross sections for C_7F_{14}

- In the energy range of 0 – 30 eV, mass spectrometric studies show that seven negative ions are formed, with the most abundant being the parent negative ion $C_7F_{14}^-$.
- The resonant peak appearing at 0.15 eV is attributed to $C_7F_{14}^-$ in the process

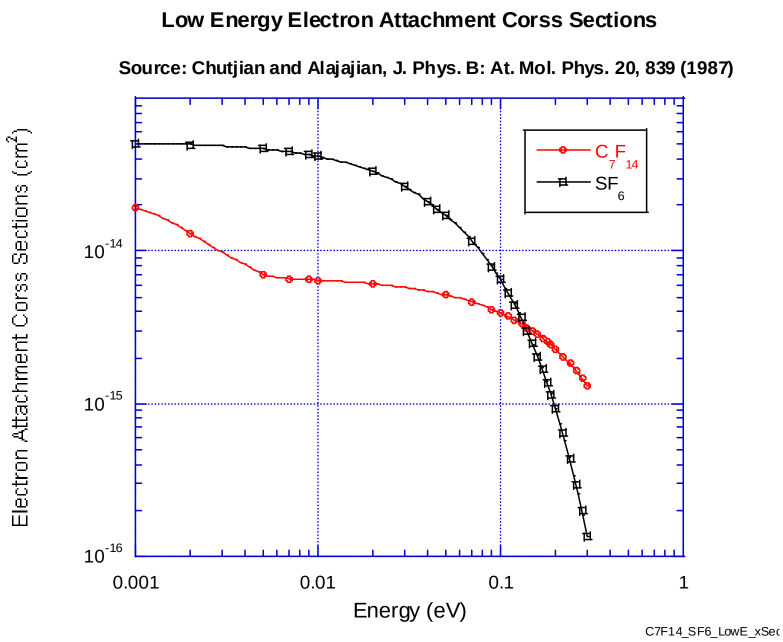
$$C_7F_{14} + e \rightarrow C_7F_{14}^{-*} \rightarrow C_7F_{14}^-$$

- The maximum cross section is 7.5×10^{-15} cm^2, occurring at 0.15 eV.

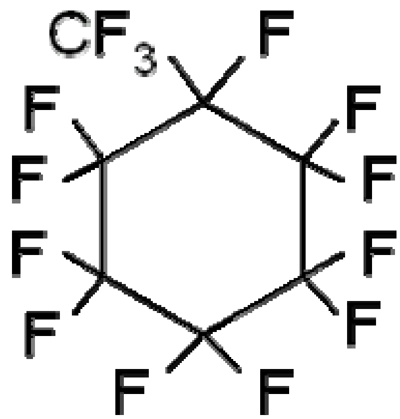
Low energy electron attachment cross sections

- A considerable amount of experimental work has been done to measure the attachment cross sections at ultra low electron energies (0-160 meV) and with energy resolutions ~ few meV.A good deal of this work is due to Chutjian (e.g., Chutjian and Alajajian, J. Phys. B: At. Mol. Phys. 20, 839, 1987). The photoionization method was used, in which krypton gas is photoionized at threshold, generating low energy electrons with an energy width determined by the slit width of the vacuum ultraviolet monochromator. The result are shown below.

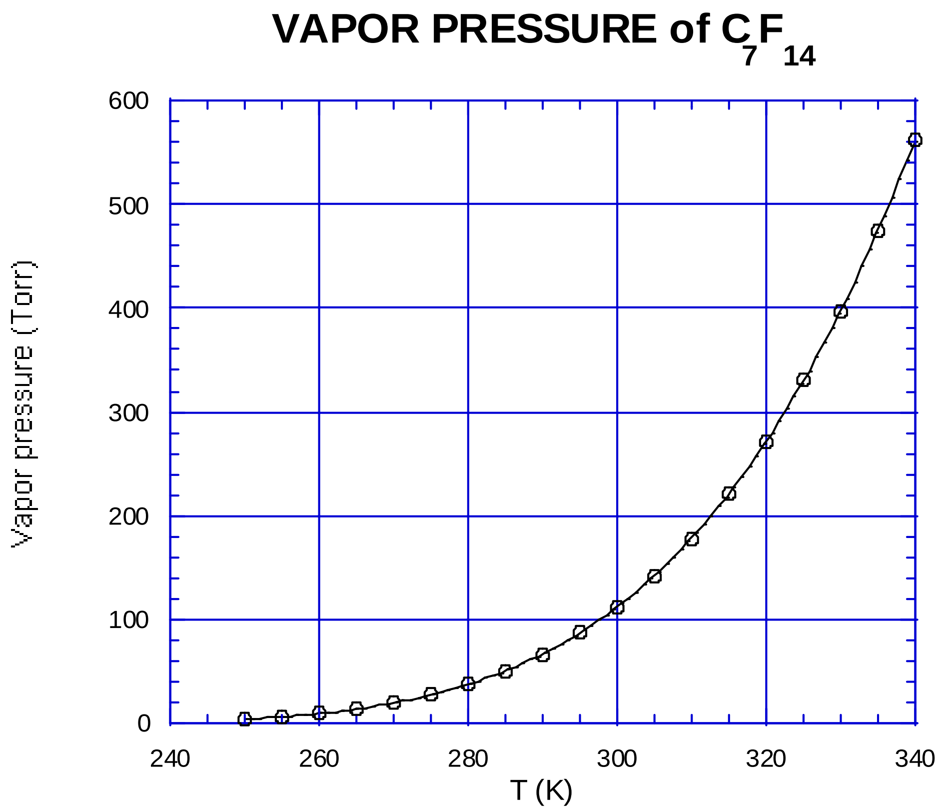
- These low energy results show that the cross section for attachment to SF_6 is larger than that of C_7F_{14} for energies below ~ 0.1 eV. For energies slightly above ~ 0.1 eV, the cross section for attachment to C_7F_{14} is larger by almost an order of magnitude.



Perfluoromethylcyclohexane C_7F_{14}



PROPERTIES	
Physical	clear, colorless, odorless, stable liquid
Molecular mass	350 amu
Density	1.78 g/cm^3
Boiling point	76 C
Vapor pressure	107 Torr @ 25 C



- C_7F_{14} is a liquid at room temperature, but has a relatively high vapor pressure of ~ 100 Torr.
- The vapor can be leaked into a vacuum vessel in the same way as the gas SF_6.

Measurement of the pressure of C_7F_{14}

- For pressures above ~ 10^{-4} Torr, a capacitance manometer can be used to measure the absolute pressure of C_7F_{14} present in the vacuum chamber.

- For the lower pressures used in these experiments, the only available pressure measurement device was the Bayard-Alpert ionization gauge.

- However, the gas sensitivity factor for C_7F_{14} was not available.

- An estimate of the gas sensitivity factor was obtained following the suggestion by Holanda (J. Vac. Sci. Technol. 10, 1133, 1973) who showed that the relative gas sensitivity factors correlate best with the ionization cross sections of the gas in question compared to that of nitrogen, using an energy corresponding to 2/3 of the accelerating voltage of the BA tube.
- Using this method, the relative gas sensitivity factors for SF_6 and C_7F_{14} are found to be

SF_6: $$S_{SF_6} / S_{N_2} = \frac{\sigma_{ionz}^{SF_6}(80eV)}{\sigma_{ionz}^{N_2}(80(eV)} = 2.3$$

C_7F_{14}: $$S_{C_7F_{14}} / S_{N_2} = \frac{\sigma_{ionz}^{C_7F_{14}}(80eV)}{\sigma_{ionz}^{N_2}(80(eV)} = 6.3$$

- The estimated value for SF_6 agrees with the published values.

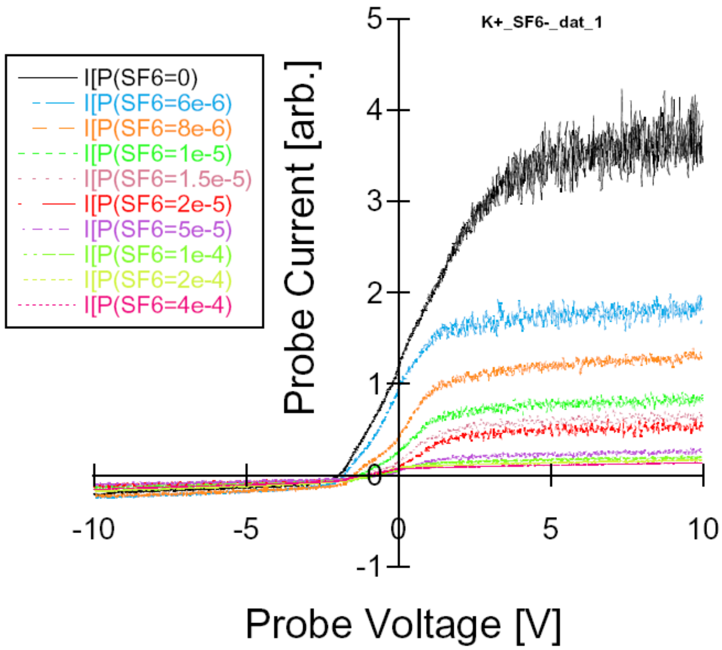
Admitting C_7F_{14} into the vacuum system

- The procedure for leaking C_7F_{14} into the vacuum system is shown schematically Fig. 1. A glass flask is used as the liquid reservoir and sealed with a rubber stopper fitted with a 0.25” polyethylene tube. This tube is then connected to the main vacuum chamber first through a coarse valve then through a needle leak valve. A connection through an additional valve to a mechanical pump is provided to initially remove any ambient air in the vacuum lines and liquid reservoir. At room temperature, the vapor pressure is sufficient to provide a constant pressure supply of C_7F_{14} molecules to the vacuum chamber. The maximum pressure of C_7F_{14} used in the system was 1 mTorr.

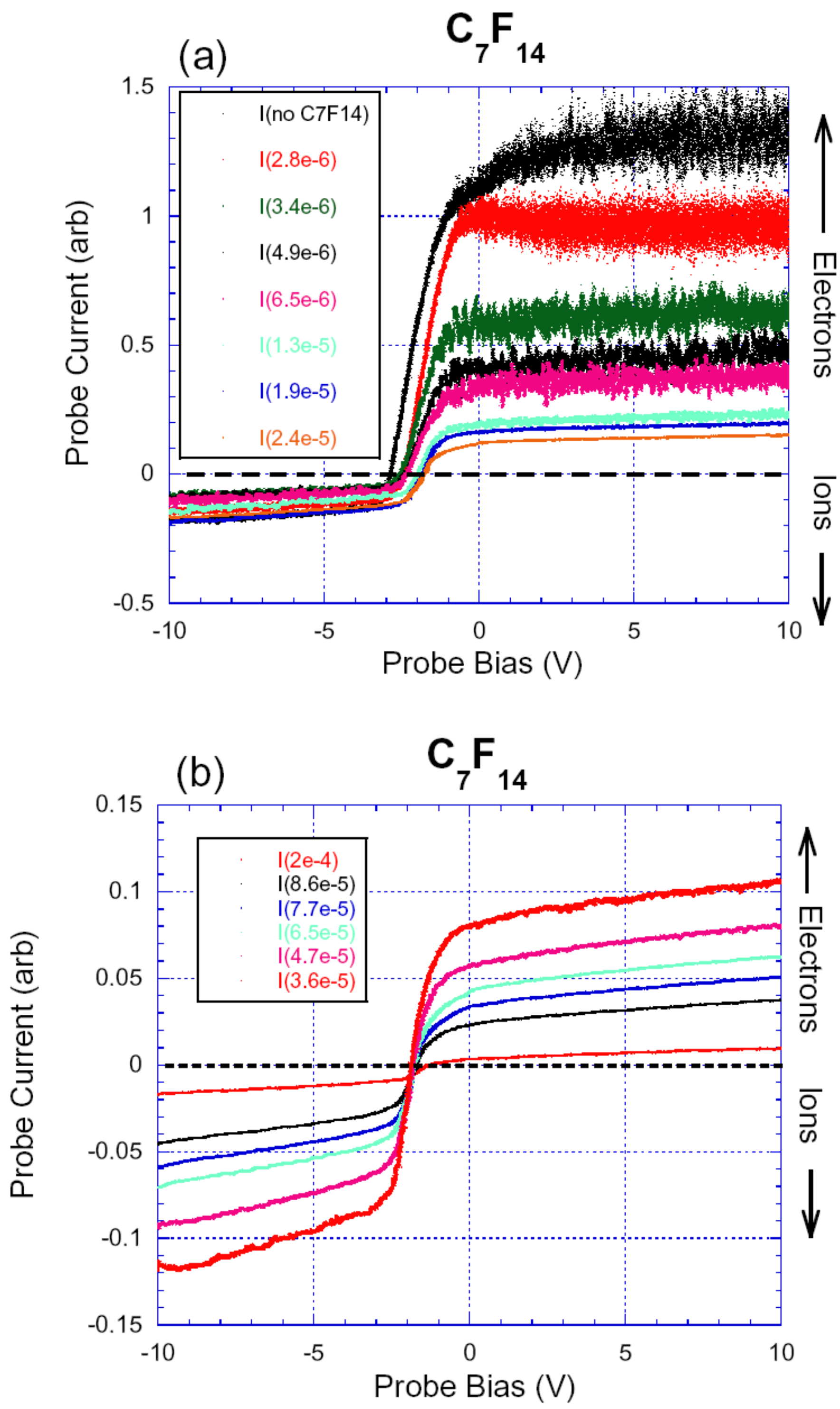
- *Effect of C_7F_{14} on the vacuum vessel.* — We have not observed any corrosive effects on the vacuum components of the Q machine. Also, when the input of C_7F_{14} is closed, we observe that the system returns relatively quickly to the initial base pressure. This was generally no the case when C_7F_{14} was used in a hot filament discharge plasma. In that case, the energetic ionizing electrons would give rise to additional species of negative ions as well as dissociation of the molecule, resulting in the formation of corrosive fluorine compounds.

RESULTS

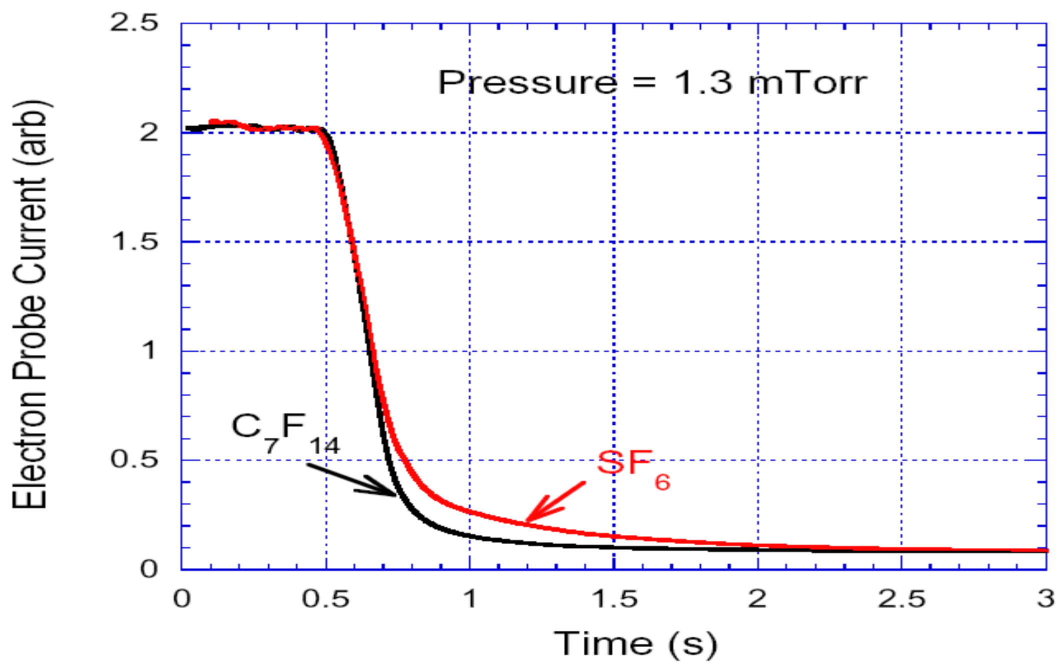
Langmuir probe I-V traces for increasing amounts of SF_6



Langmuir probe I-V traces showing the reduction in the electron saturation current with increasing amounts of C_7F_{14}



Electron probe current vs time for SF_6 and C_7F_{14}



Determination of n_e/n_+ from Langmuir probe I-V traces

The densities of the positive ions, electrons and negative ions are related through the quasineutrality condition:

$$n_+ = n_e + n_- \qquad [1]$$

Probe saturation currents:

$$I_+ = en_+ v_{+,T} A \qquad [2]$$

$$I_- = en_e v_{e,T} A + en_- v_{-,T} A \qquad [3]$$

where, $v_{j,T} = \left(\frac{kT_j}{m_j}\right)^{\frac{1}{2}}$ is the thermal speed of species j, with T_j and m_j are respectively, the temperature and mass of species j. A is the probe collection area.

Define, $\varepsilon = n_e / n_+$, then from [1], $n_- = (1-\varepsilon)n_+$. and using these in [2] and [3] we obtain:

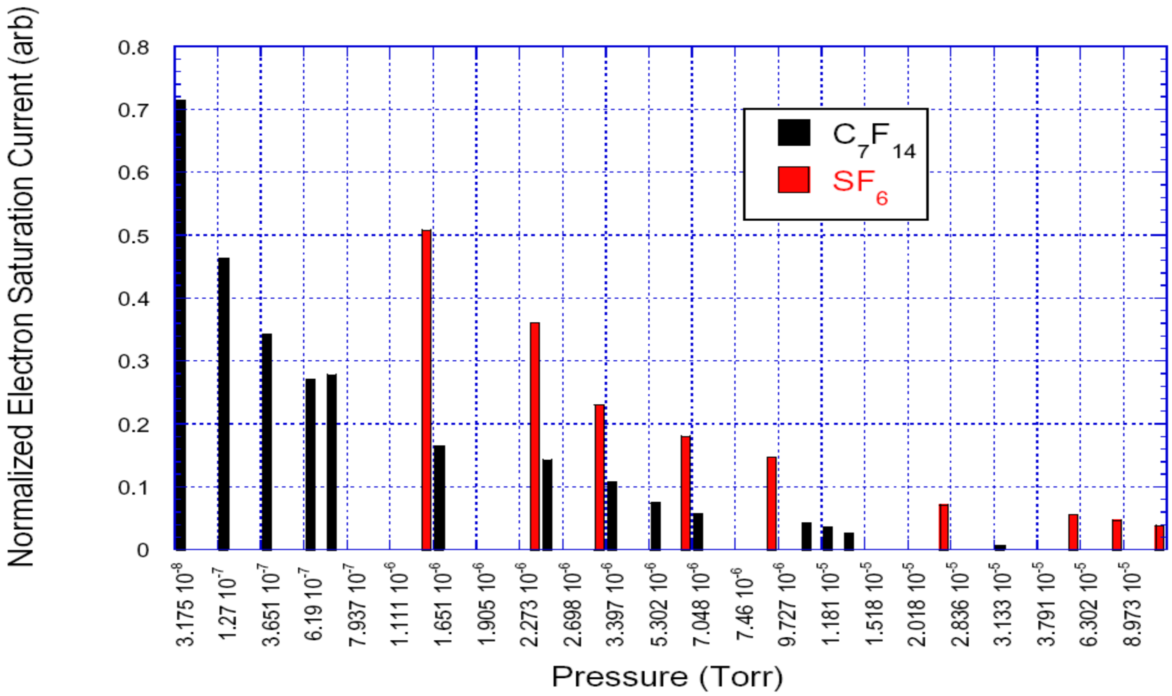
$$\varepsilon = n_e / n_+ = \frac{I_- / I_+ - \left(T_- / T_+\right)^{1/2} \left(m_+ / m_-\right)^{1/2}}{\left(T_e / T_+\right)^{1/2} \left(m_+ / m_e\right)^{1/2} - \left(T_- / T_+\right)^{1/2} \left(m_+ / m_-\right)^{1/2}} \qquad [4]$$

- Expression [4] provides a method of estimating ε, from a measurement of the ratio of the negative to positive probe saturation currents I_- / I_+

- To apply [4], the known positive and negative ion masses are required:
    - SF_6: $m_+/m_- = 0.27$
    - C_7F_{14}: $m_+/m_- = 0.11$

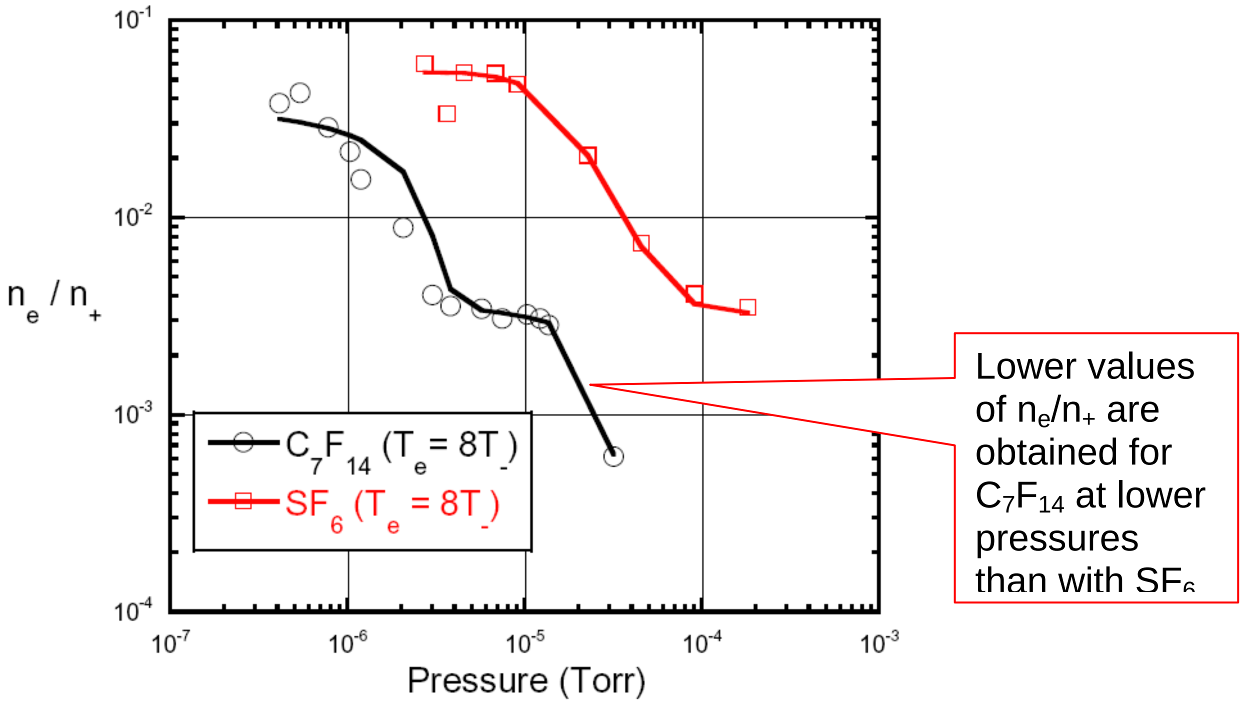
- T_e, T_+, and T_- are also required in applying [4]
    - for the Q machine plasma $T_e \approx T_+ \approx 0.2$ eV
    - The negative ions are formed by electron attachment to gas molecules at room temperature. It is expected that the negative ions will be relatively close to room temperature, or perhaps not more than a factor of (2-4) higher than room temperature, $T_- \approx (0.025 – 0.1)$ eV.

Comparison of the reduction in electron saturation currents with SF_6 and C_7F_{14}

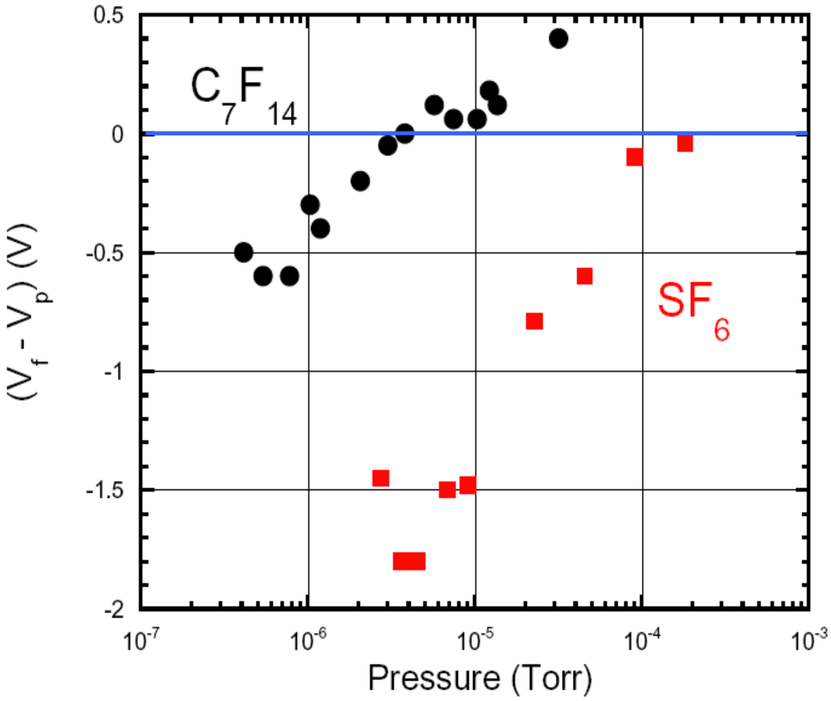


The saturation currents are normalized to the electron saturation currents before SF_6 or C_7F_{14} are introduced

n_e/n_+ vs. pressure for SF_6 and C_7F_{14}



Difference between probe floating potential, V_f and plasma potential, V_p vs. pressure in SF_6 and C_7F_{14}

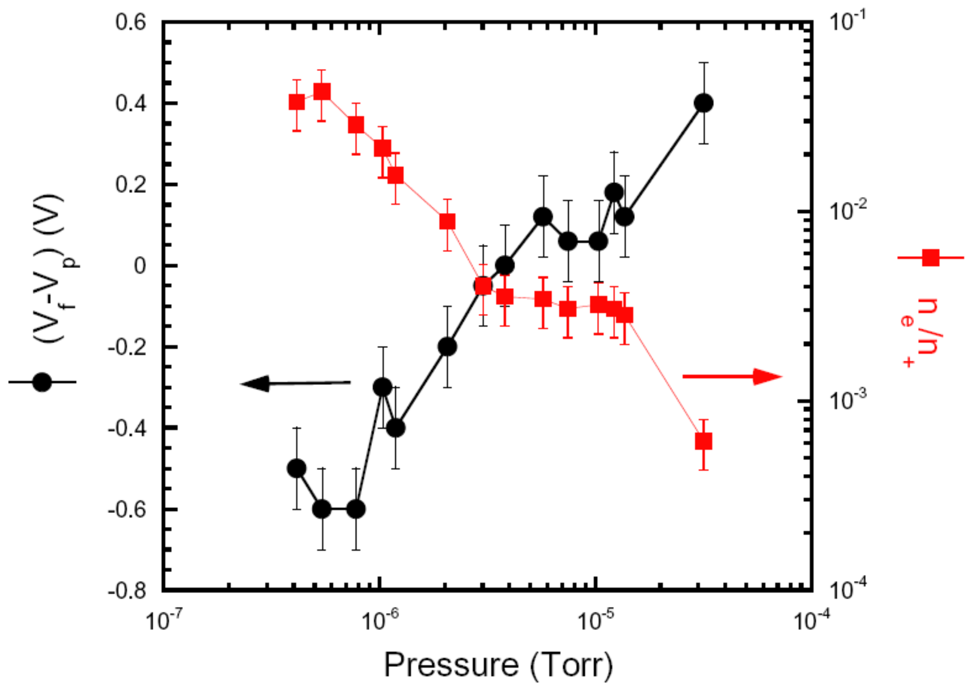


- As the amount of C_7F_{14} increases, the difference between V_f and V_p also decreases.

- At some point the floating potential actually is greater than the plasma potential, $V_f - V_p > 0$.

- This occurs because the plasma is composed of light positive ions and heavy negative ions.

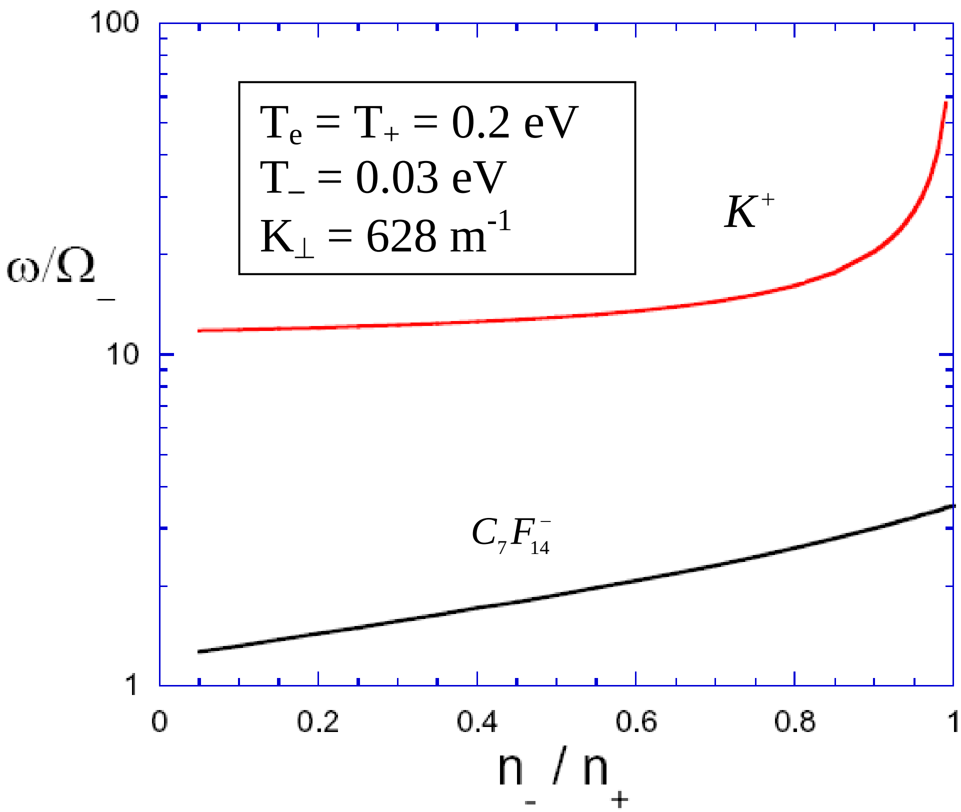
Summary of results for C_7F_{14}



As $n_e/n_+ \rightarrow 0$, the plasma is basically a positive ion/negative ion plasma, with the positive ions as the lighter species.

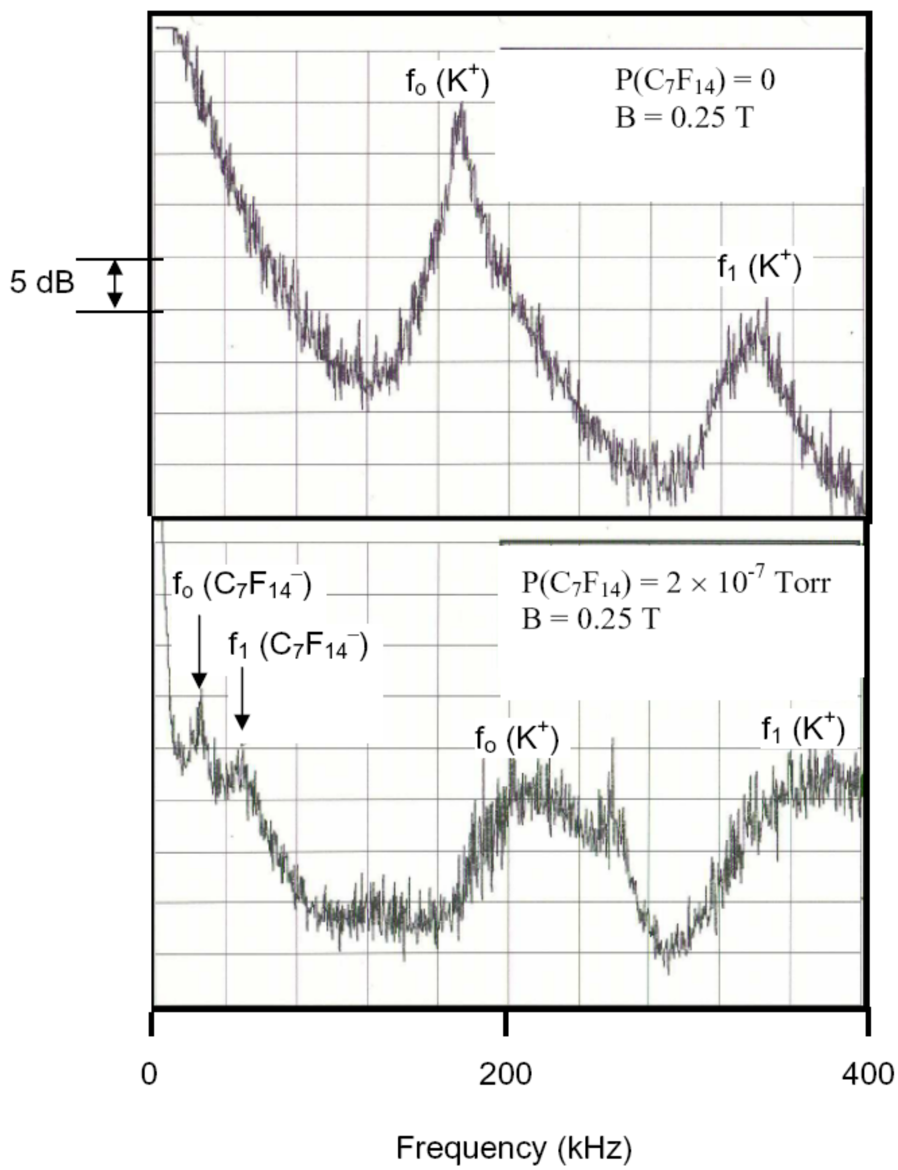
Current-Driven Electrostatic Ion Cyclotron Waves (EIC) in a Plasma with Negative Ions

- Observation of current-driven EIC waves can be used as a diagnostic for the presence of the negative ion $C_7F_4^-$
- EIC waves can be driven unstable by providing an electron current along the magnetic field in the plasma
- In a plasma composed of electrons, positive ions and negative ions, two wave modes are excited, one associated with the positive ions and one associated with the negative ion.
- The EIC modes occur at frequencies above the cyclotron frequency associated with the particular ion, $\Omega_j = eB/m_j$
- The mode frequencies, ω_j increase with the relative negative ion concentration, n_-/n_+, as shown in the theoretical plot shown below.

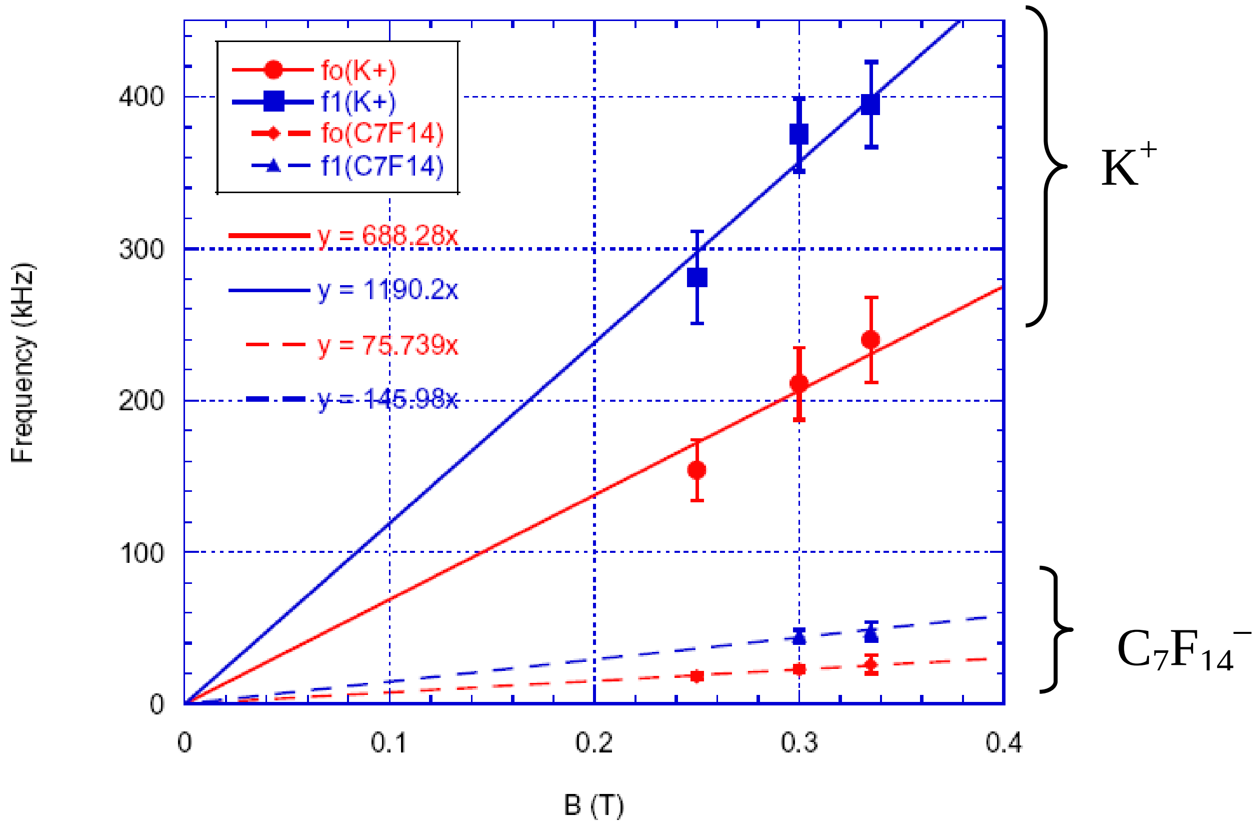


EXPERIMENTAL RESULTS

(1) Power Spectra of Electrostatic Ion Cyclotron Waves



(2) EIC mode frequencies vs. magnetic field strength



⟹ The ratios of the slopes of the *f vs B* lines are consistent with the proper mass rations for K^+ and $C_7F_{14}^-$ ions.

SUMMARY AND CONCLUSIONS

(1) Negative ion plasmas in C_7F_{14} have been formed in a K^+ Q machine plasma

(2) Electron attachment to C_7F_{14} results in significant reductions in the electron density with relative concentrations $n_e / n_+ \sim 0.1$ obtained at C_7F_{14} pressures $< 10^{-6}$ Torr.

(3) For C_7F_{14} pressures $\sim 10^{-5}$, $n_e / n_+ < 0.001$.

(4) For C_7F_{14} pressures $> 10^{-5}$, $(V_f - V_p) > 0$, indicating that the plasma is dominated by light positive ions and heavy negative ions

(5) The presence of $C_7F_{14}^-$ ions has been verified by observation of the negative ion EIC wave mode that is produced when an electron current is present along the magnetic field.