

PRODUCTION OF NEGATIVE ION PLASMAS USING PERFLUOROMETHYLCYCLOHEXANE (C₇F₁₄)

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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 (SiH₄) or methane (CH₄)
 - In the earth's ionosphere (O⁻, O₂⁻, NO₂⁻)
 - combustion plasmas
 - gaseous lasers
 - neutral beam sources for fusion (H⁻)
 - stellar atmospheres (H⁻)

- Interest in negative ion plasmas
 - plasmas with m_e ≈ m_i
 - shielding of low frequency fields by electrons is reduced
 - new wave modes appear
 - similar to dusty plasmas

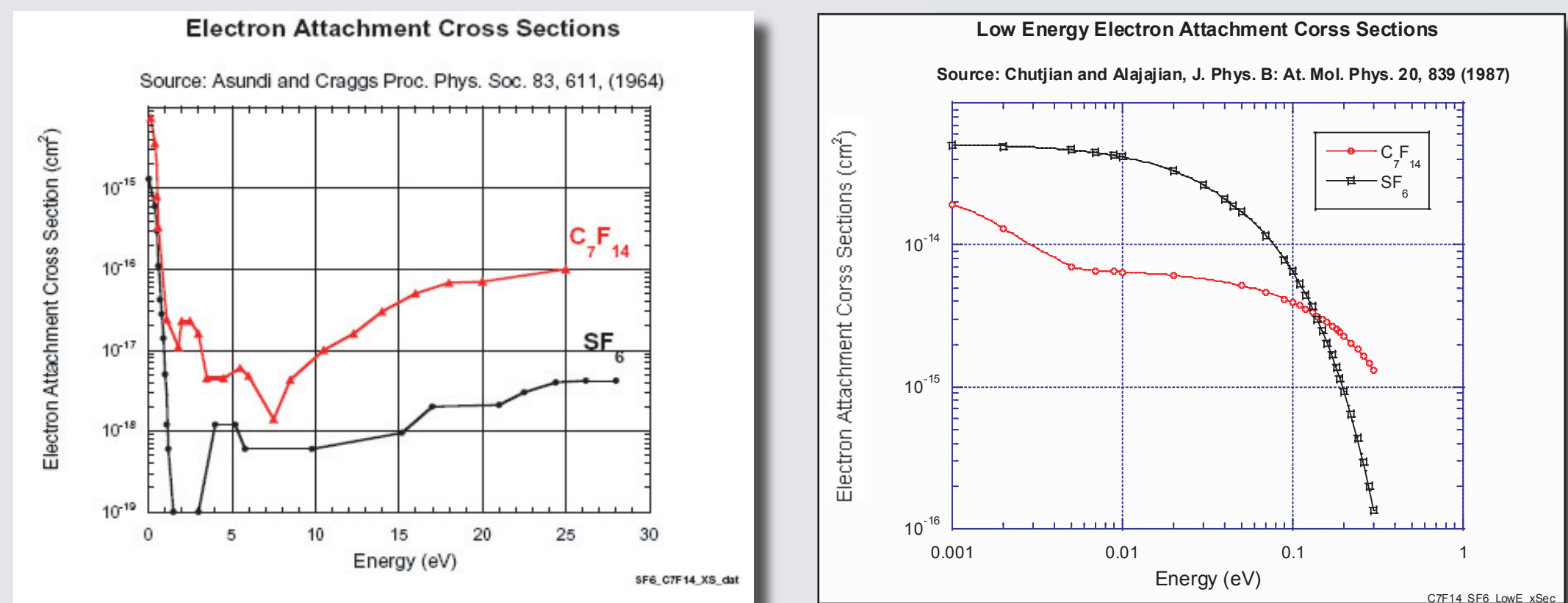
Attachment cross sections for SF₆

- In the energy range of 0 – 30 eV, mass-spectroscopic studies show that SF₆⁻, SF₅⁻, F⁻ are formed.
- The peak at energies near zero are due to the resonant capture of electrons by the process
$$\text{SF}_6 + e \rightarrow \text{SF}_6^{-*} \rightarrow \text{SF}_6^{-}$$
- In the range of 4 – 14 eV, the predominant negative ion is F⁻, while at an energy of 17.3 eV, the negative ion SF₅⁻ appears.
- The maximum cross section of $1.3 \times 10^{-15} \text{ cm}^2$ is obtained at an electron energy of 0.03 eV.

Attachment cross sections for C₇F₁₄

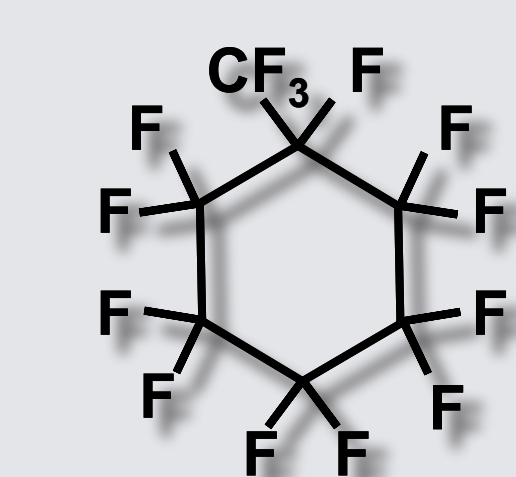
- In the energy range of 0 – 30 eV, mass spectrometric studies show that seven negative ions are formed, with the most abundant being the parent negative ion C₇F₁₄⁻.
- The resonant peak appearing at 0.15 eV is attributed to C₇F₁₄⁻ in the process
$$\text{C}_7\text{F}_{14} + e \rightarrow \text{C}_7\text{F}_{14}^{-*} \rightarrow \text{C}_7\text{F}_{14}^{-}$$
- The maximum cross section is $7.5 \times 10^{-15} \text{ cm}^2$, occurring at 0.15 eV.

Electron attachment cross sections



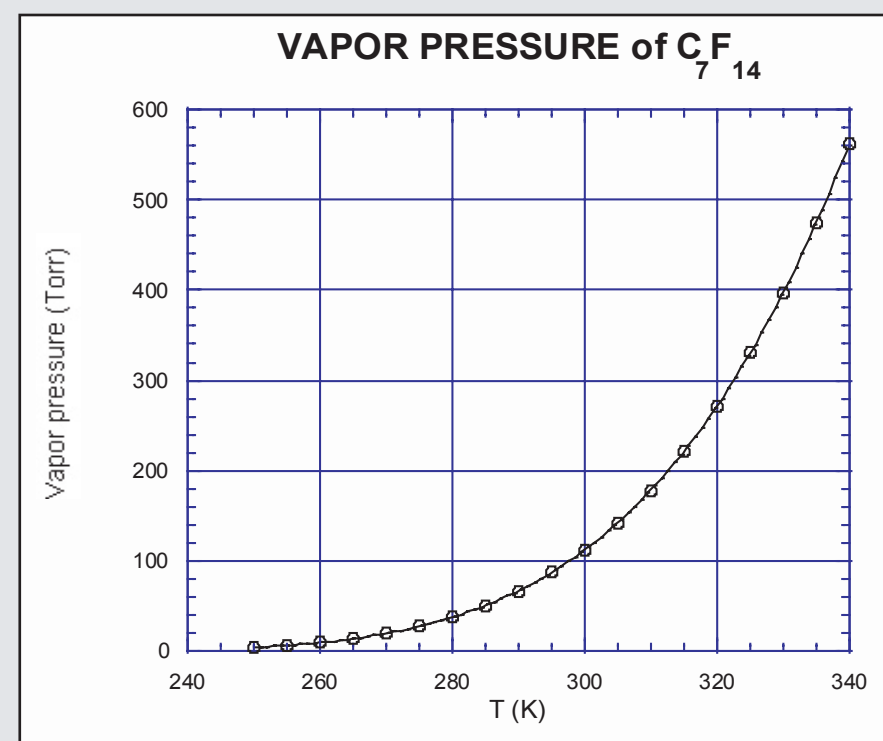
- These low energy results show that the cross section for attachment to SF₆ is larger than that of C₇F₁₄ for energies below ~ 0.1 eV. For energies slightly above ~ 0.1 eV, the cross section for attachment to C₇F₁₄ is larger by almost an order of magnitude.

Perfluoromethylcyclohexane C₇F₁₄



PROPERTIES

Physical : clear, colorless, odorless, stable liquid
Molecular mass : 350 amu
Density : 1.78 g/cm³
Boiling point : 76 °C
Vapor pressure : 107 Torr @ 25 °C



- C₇F₁₄ 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 SF₆.

Measurement of the pressure of C₇F₁₄

- For pressures above ~ 10⁻⁴ Torr, a capacitance manometer can be used to measure the absolute pressure of C₇F₁₄ 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 C₇F₁₄ 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.

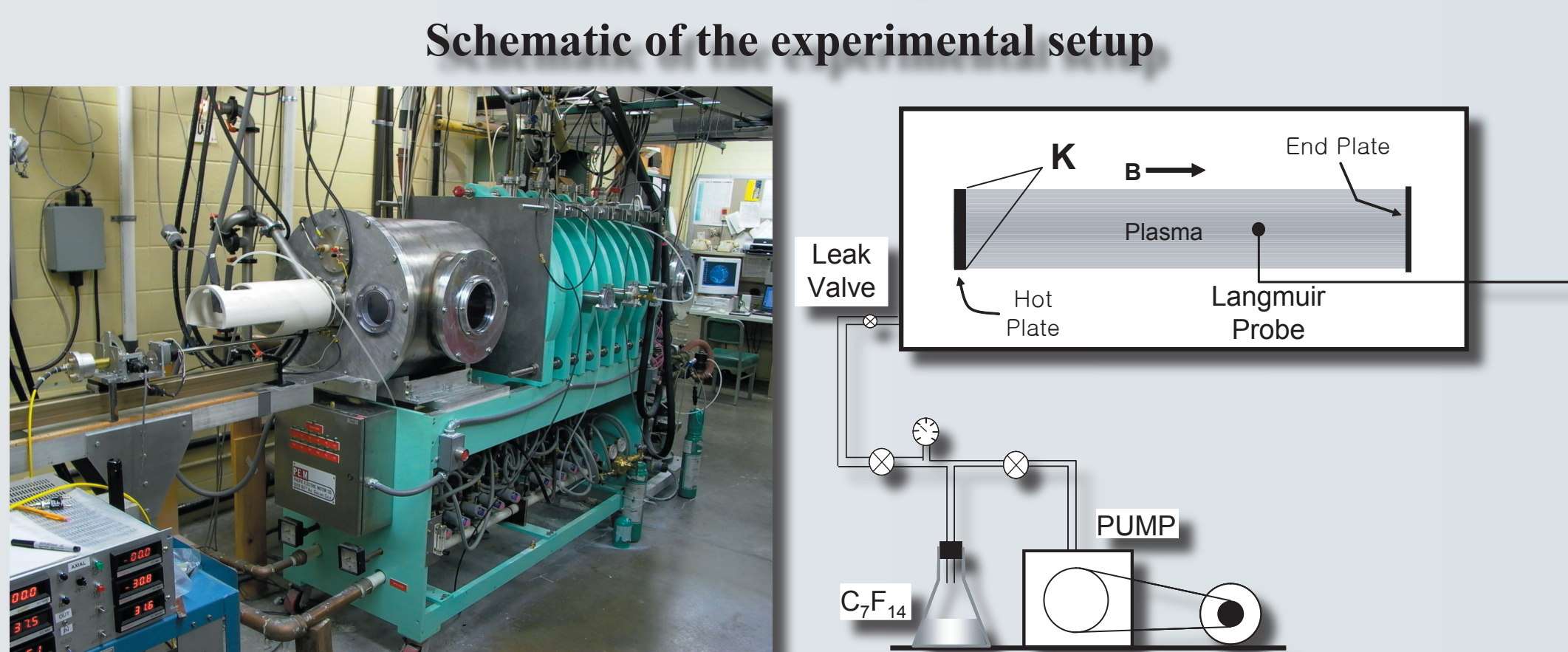
- Using this method, the relative gas sensitivity factors for SF₆ and C₇F₁₄ are found to be

$$\text{SF}_6: \quad S_{\text{SF}_6}/S_{\text{N}_2} = \frac{\sigma_{\text{ions}}^{\text{SF}_6}(80 \text{ eV})}{\sigma_{\text{ions}}^{\text{N}_2}(80 \text{ eV})} = 2.3$$

$$\text{C}_7\text{F}_{14}: \quad S_{\text{C}_7\text{F}_{14}}/S_{\text{N}_2} = \frac{\sigma_{\text{ions}}^{\text{C}_7\text{F}_{14}}(80 \text{ eV})}{\sigma_{\text{ions}}^{\text{N}_2}(80 \text{ eV})} = 2.3$$

The estimated value for SF6 agrees with the published values.

Plasma Source: Q Machine



- The plasma in a Q machine is produced by surface ionization of alkali metal atoms (K or Cs) on a hot tungsten or tantalum plate (hot plate). In our case, potassium atoms are surface ionized on a tantalum plate.

- Neutral K atoms are emitted from the nozzle of an atomic beam oven, in which a combination of KCl and Ca undergo a chemical reaction at 400 °C.

- The emerging K atoms impinge on a 6 cm diameter (electrically grounded) tantalum plate that is heated by electron bombardment from behind to ~ 2200 °K.

- Upon contact with the hot plate, the neutral K gives up its electron, forming K⁺ ions. The K⁺ ions, along with thermionically emitted electrons from the hot plate, for a roughly 6 cm diameter plasma column. The plasma is very nearly fully ionized, with any un-ionized K atoms condensed on the wall of the vessel which is maintained at ~30 °C.

- The 1 m long plasma is confined radially by a uniform axial magnetic field of variable strength up to 0.4 T.

- Plasma parameters
 - plasma density: $n_e \approx 10^{15} - 10^{16} \text{ m}^{-3}$
 - temperatures: $T_e \approx T_i \approx 0.2 \text{ eV}$

- The relatively low value of the electron temperature (0.2 eV) ensures that the electron attachment process (with either SF₆ or C₇F₁₄) results in the formation of the parent negative ions, SF₆⁻, C₇F₁₄⁻.

ABSTRACT

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, SF₆, 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 C₇F₁₄ to produce negative ion plasmas in a Q machine. The maximum attachment cross-section is ~ 6 times higher than that of SF₆, and occurs at a higher energy, 0.15 eV, so that the attachment efficiency should be enhanced in the Q machine. Details of the experimental setup and Langmuir probe characteristics obtained in the plasma with C₇F₁₄ will be presented.

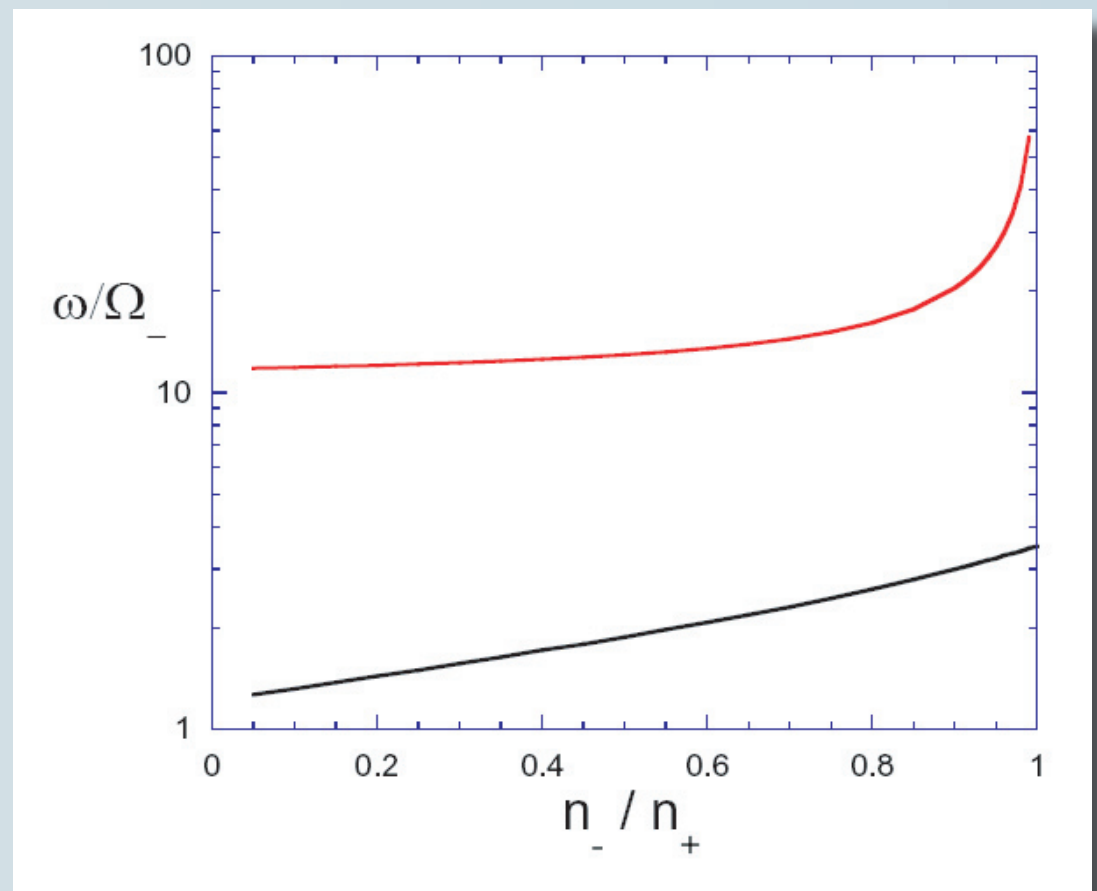
Admitting C₇F₁₄ into the vacuum system

- 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 C₇F₁₄ molecules to the vacuum chamber. The maximum pressure of C₇F₁₄ used in the system was 1 mTorr.

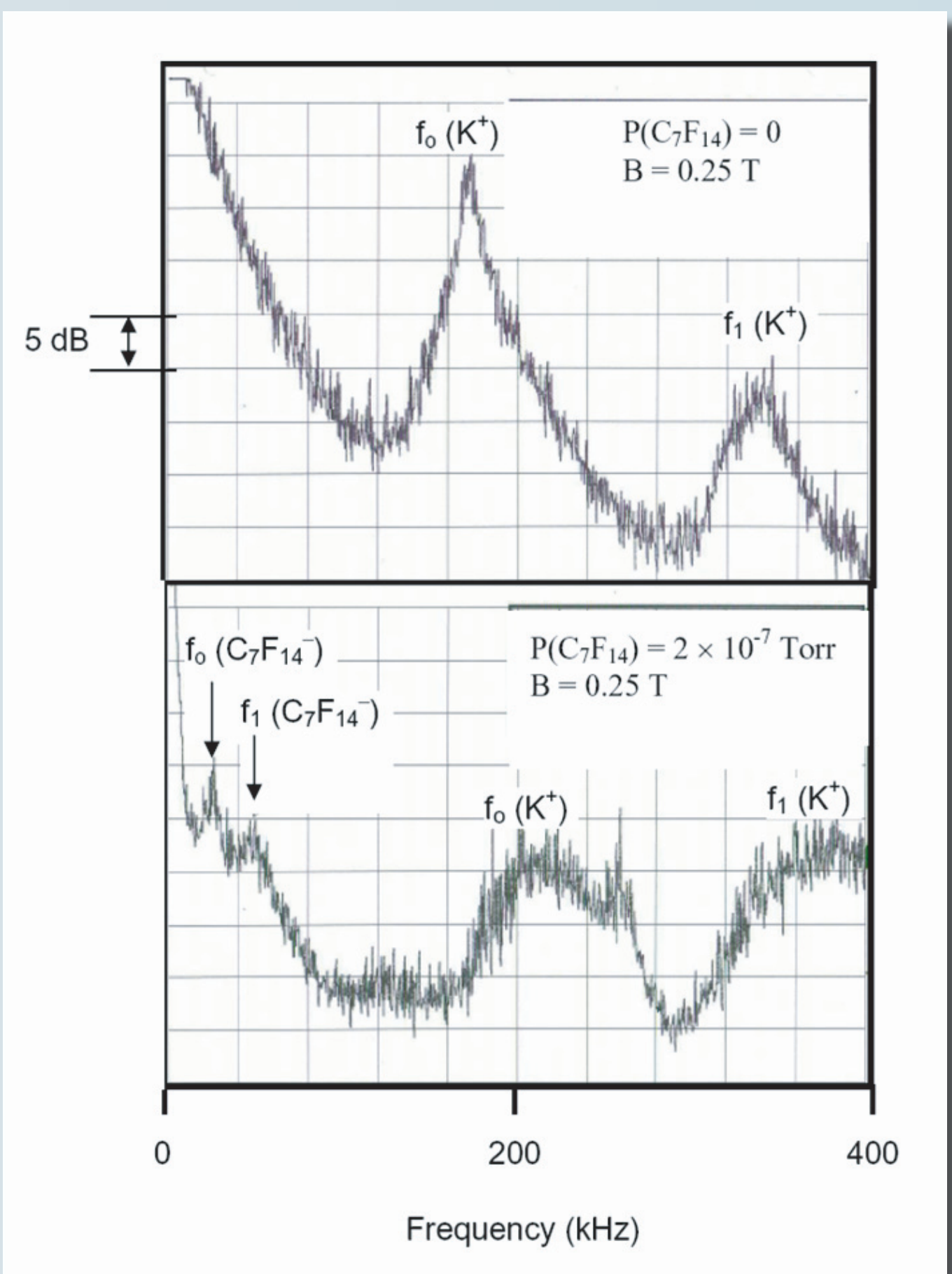
- Effect of C₇F₁₄ on the vacuum vessel. — We have not observed any corrosive effects on the vacuum components of the Q machine. Also, when the input of C₇F₁₄ is closed, we observe that the system returns relatively quickly to the initial base pressure. This was generally not the case when C₇F₁₄ was used 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.

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

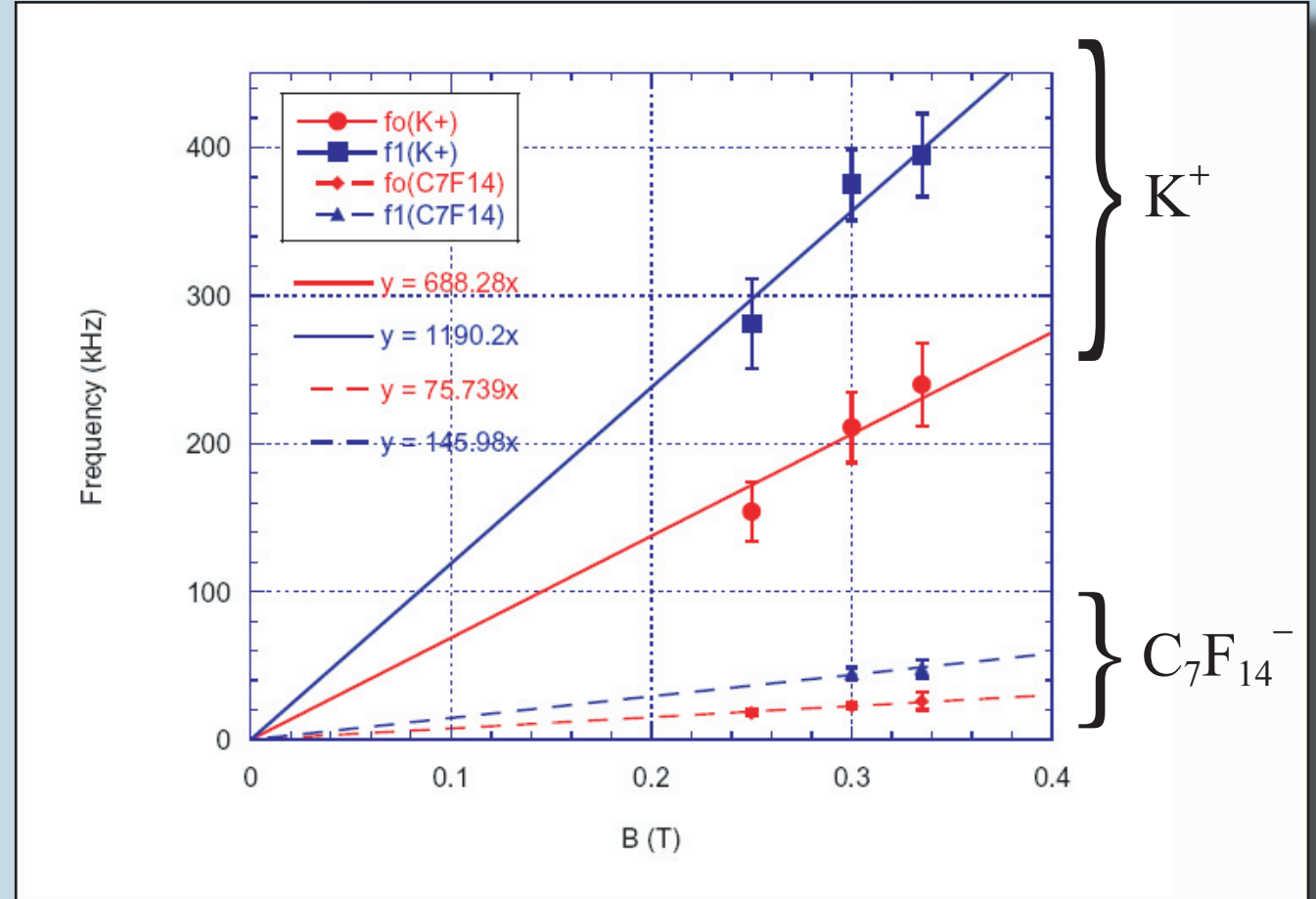
- Observation of current-driven EIC waves can be used as a diagnostic for the presence of the negative ion C₇F₁₄⁻.
- EIC waves can be driven unstable by providing an electron current along the magnetic field in the plasma
- In a plasma composed of electrons, positive ions and negative ions, two wave modes are excited, one associated with the positive ions and one associated with the negative ion.
$$\Omega = eB/m_j$$
- The EIC modes occur at frequencies above the cyclotron frequency associated with the particular ion,
- The mode frequencies, ω, increase with the relative negative ion concentration, n_- / n_+ , as shown in the theoretical plot shown below.



Power Spectra of Electrostatic Ion Cyclotron Waves

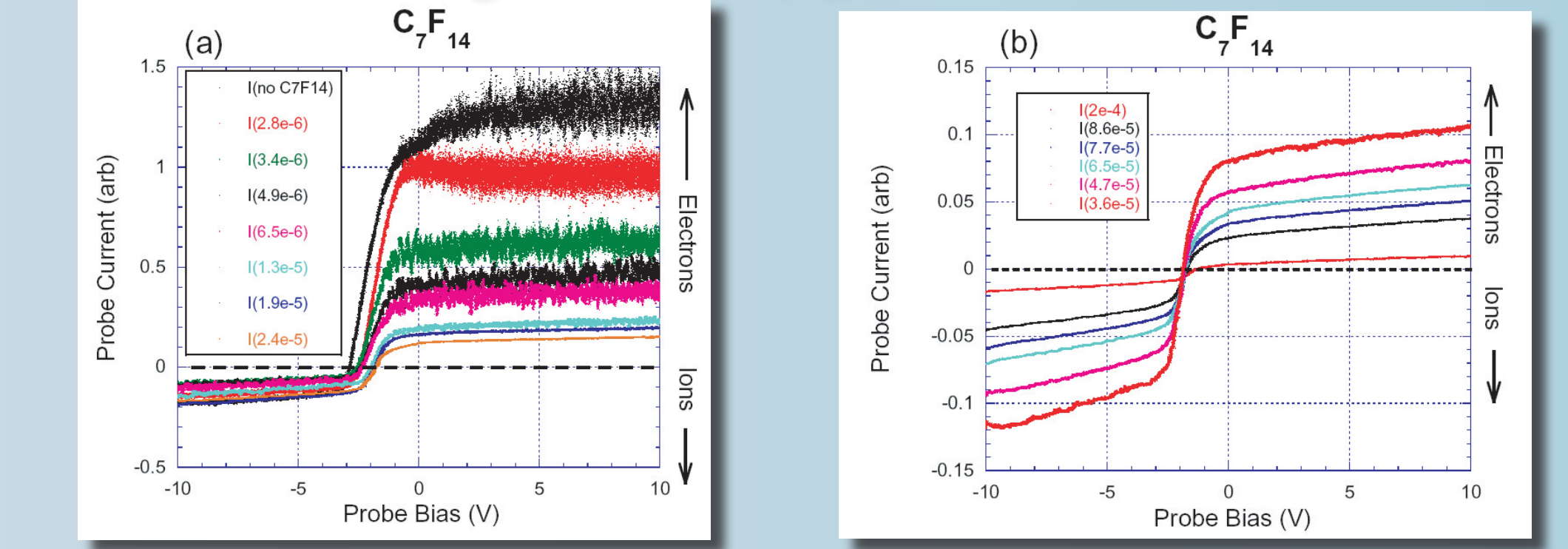


EIC mode frequencies vs. magnetic field strength

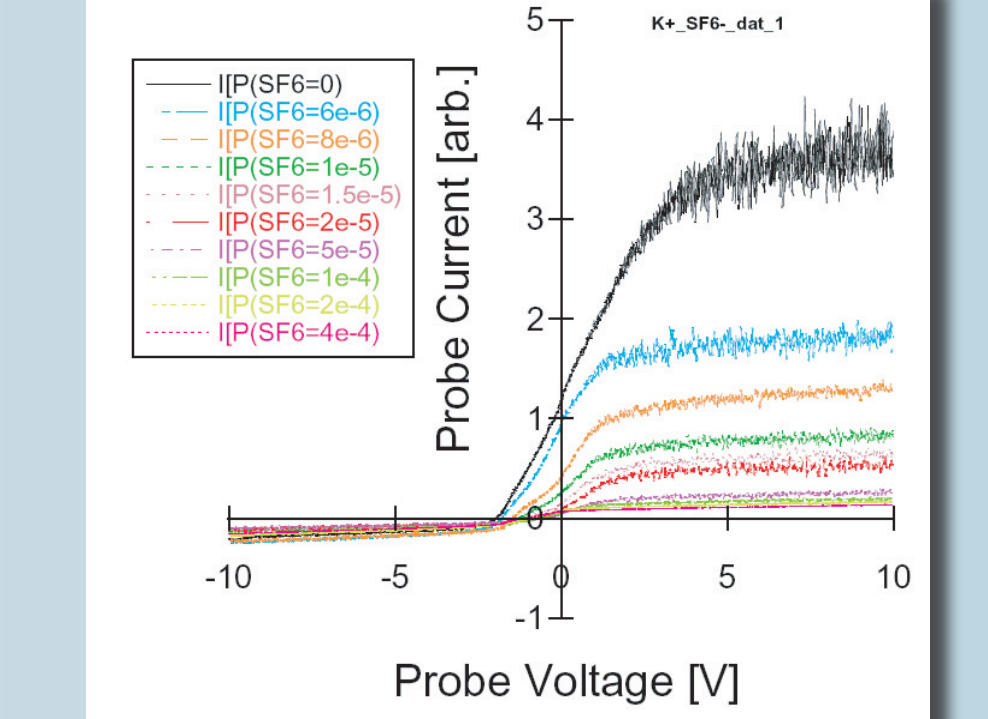


⇒ The ratios of the slopes of the f vs B lines are consistent with the proper mass ratios for K⁺ and C₇F₁₄⁻ ions.

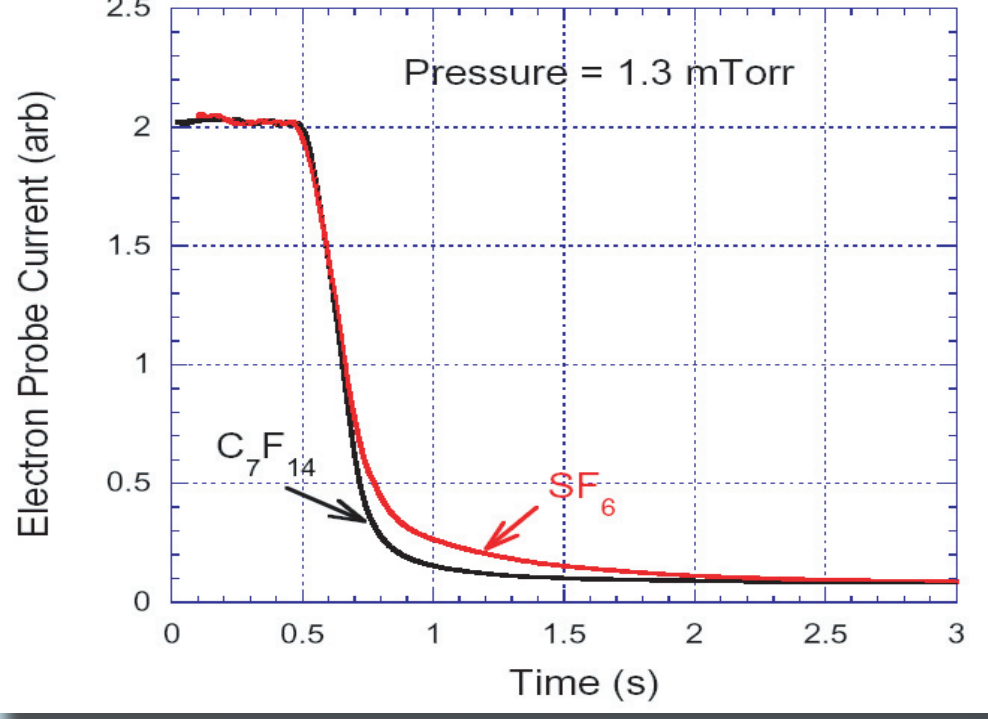
Langmuir probe I-V traces showing the reduction in the electron saturation current with increasing amounts of C₇F₁₄



Langmuir probe I-V traces for increasing amounts of SF₆



Electron probe current vs time for SF₆ and C₇F₁₄



Determination of n₋/n₊ from Langmuir probe I-V traces

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

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

Probe saturation currents:

$$I_+ = e n_+ v_{e,T} A \quad [2]$$

$$I_- = e n_- v_{e,T} A + e n_+ v_{-T} A \quad [3]$$

where, $v_{e,T} = (kT_e/m_e)^{1/2}$ 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.

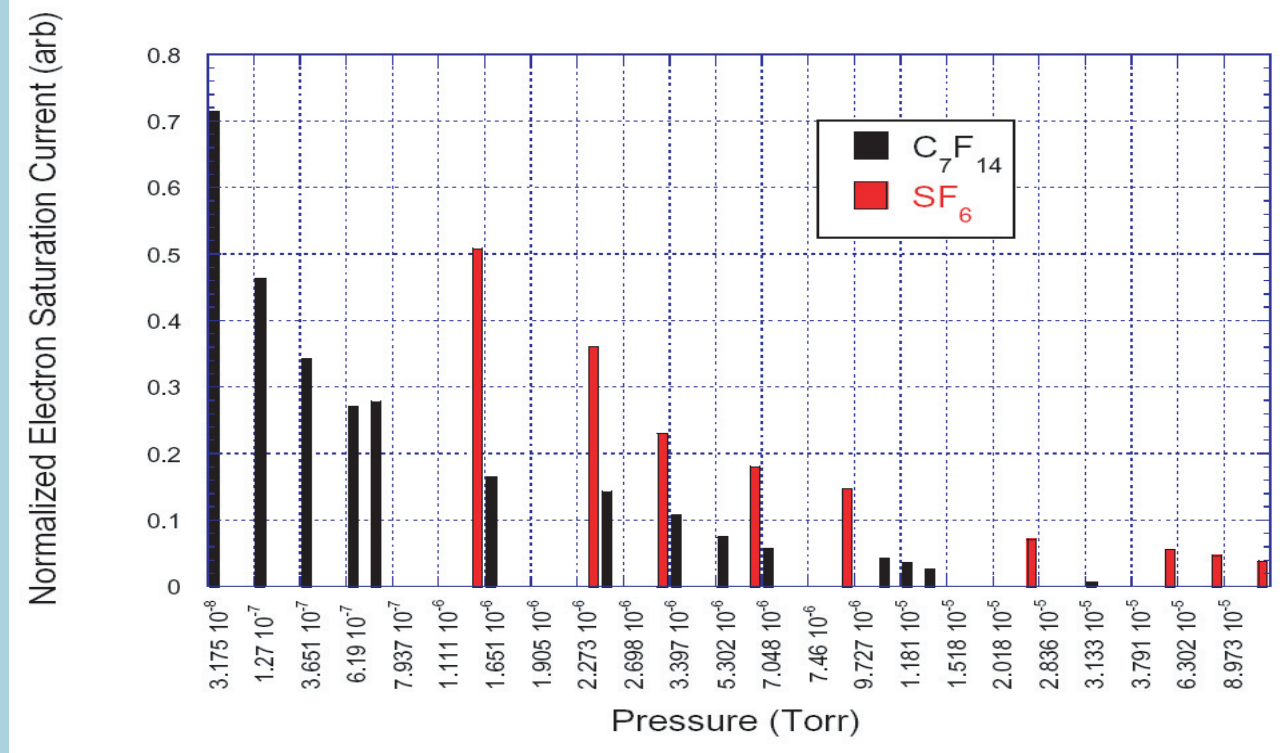
Define, $\epsilon = n_- / n_+$, then from [1], $n_- = (1 - \epsilon)n_+$, and using these in [2] and [3] we obtain:

$$\epsilon = n_- / n_+ = \frac{I_- / I_+ - (T_e / T_+)^{1/2} (m_+ / m_-)^{1/2}}{(T_e / T_+)^{1/2} (m_+ / m_-)^{1/2} - (T_- / T_+)^{1/2} (m_+ / m_-)^{1/2}} \quad [4]$$

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

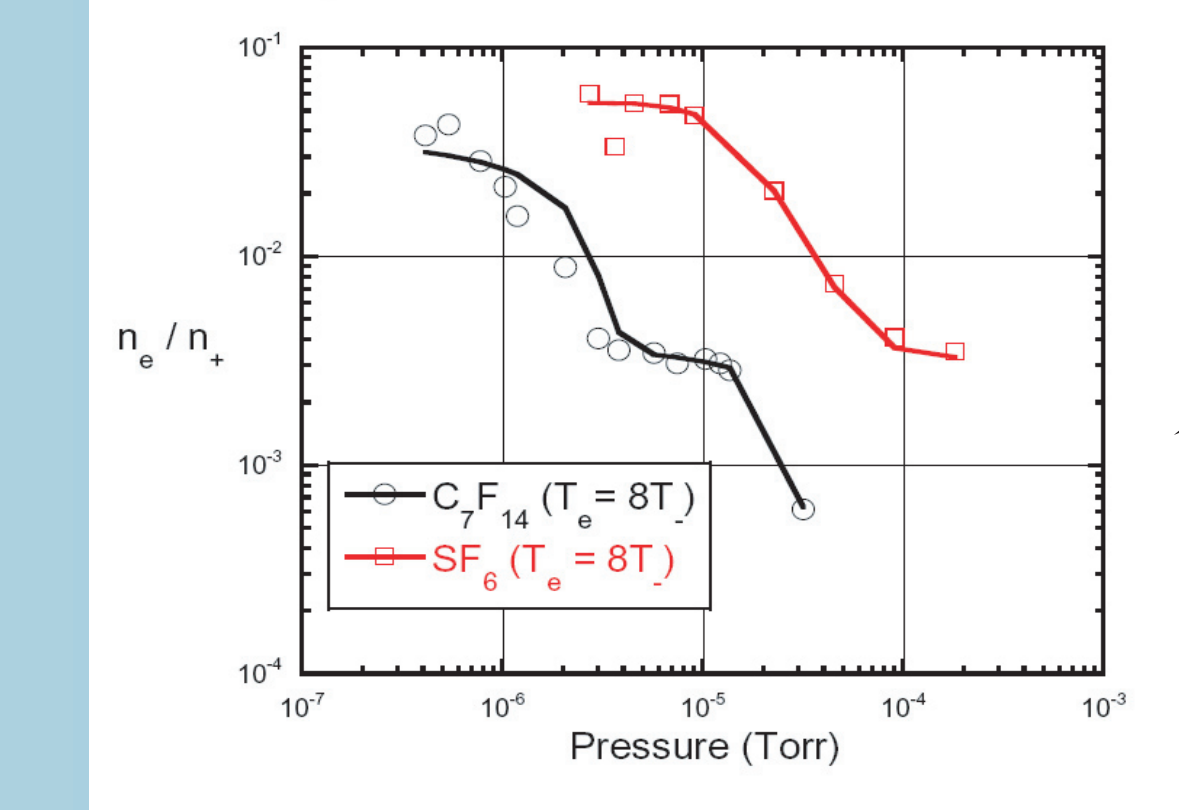
- To apply [4], the known positive and negative ion masses are required:
 - SF₆: $m_- / m_+ = 0.27$
 - C₇F₁₄: $m_- / m_+ = 0.11$
- T_e, T₊, and T₋ are also required in applying [4]
 - For the Q machine plasma T_e ≈ T₊ ≈ 0.2 eV
 - The negative ions are formed by electron attachment to gas molecules at 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₋ ≈ (0.025 – 0.1) eV.

Comparison of the reduction in electron saturation currents with SF₆ and C₇F₁₄



The saturation currents are normalized to the electron saturation currents before SF₆ or C₇F₁₄ are introduced

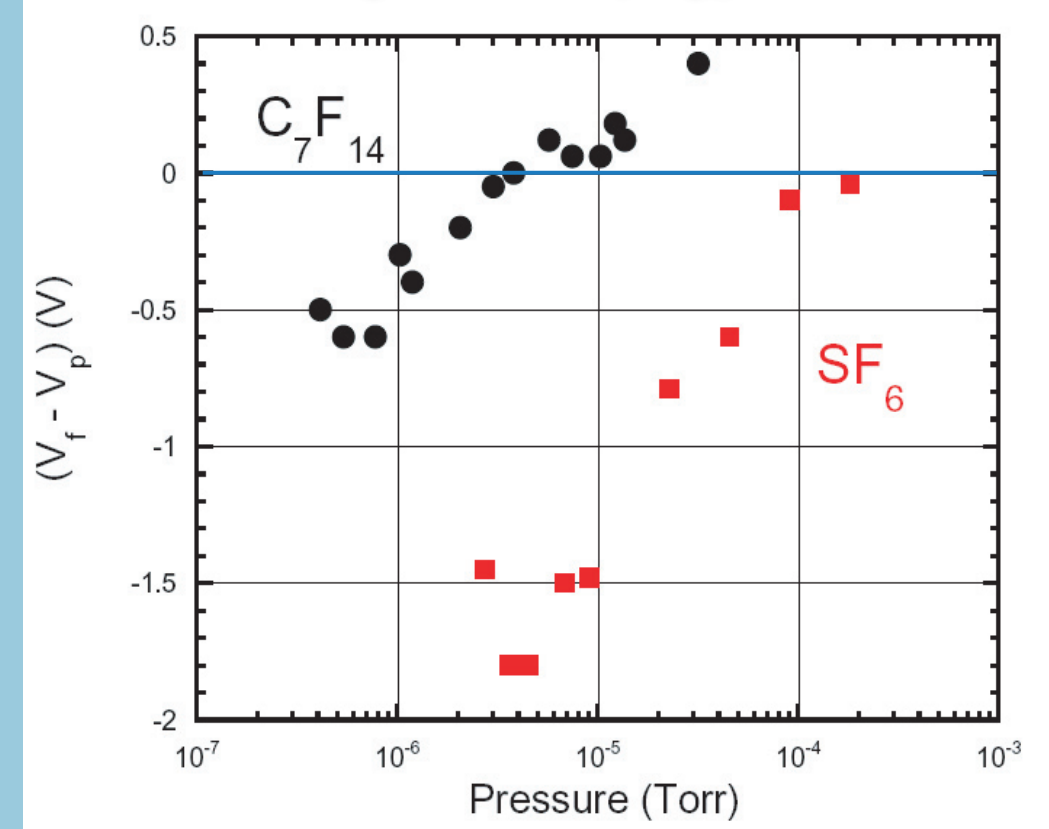
n_e/n₊ vs. pressure for SF₆ and C₇F₁₄



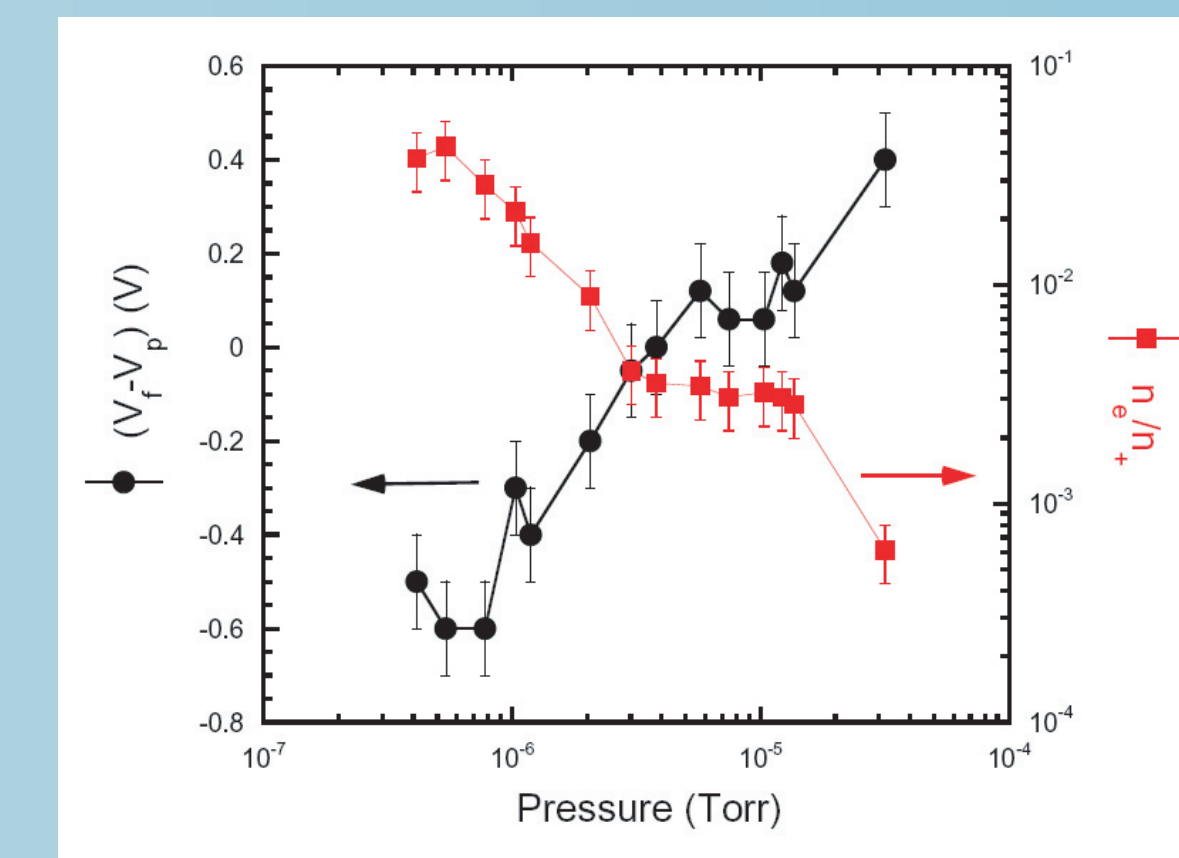
Lower values of n₋/n₊ are obtained for C₇F₁₄ at lower pressures than with SF₆

Difference between probe floating potential, V_f and plasma potential, V_p vs. pressure in SF₆ and C₇F₁₄

- As the amount of C₇F₁₄ 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 C₇F₁₄



As n₋/n₊ → 0, the plasma is basically a positive ion/negative ion plasma, with the positive ions as the lighter species.

SUMMARY AND CONCLUSIONS

- Negative ion plasmas in C₇F₁₄ have been formed in a K⁺ Q machine plasma
- Electron attachment to C₇F₁₄ results in significant reductions in the electron density with relative concentrations n₋/n₊ ~ 0.1 obtained at C₇F₁₄ pressures < 10⁻⁶ Torr.
- For C₇F₁₄ pressures ~ 10⁻⁵, n₋/n₊ < 0.001.
- For C₇F₁₄ pressures > 10⁻⁵, (V_f – V_p) > 0, indicating that the plasma is dominated by light positive ions and heavy negative ions.
- The presence of C₇F₁₄⁻ 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.

ACKNOWLEDGEMENT

This work was supported by U.S. Department of Energy.