Mass Spectroscopy of Metastable Atomic Species in Gas Analysis and Processing Plasmas at High Spectrometer Source Pressures

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Abstract

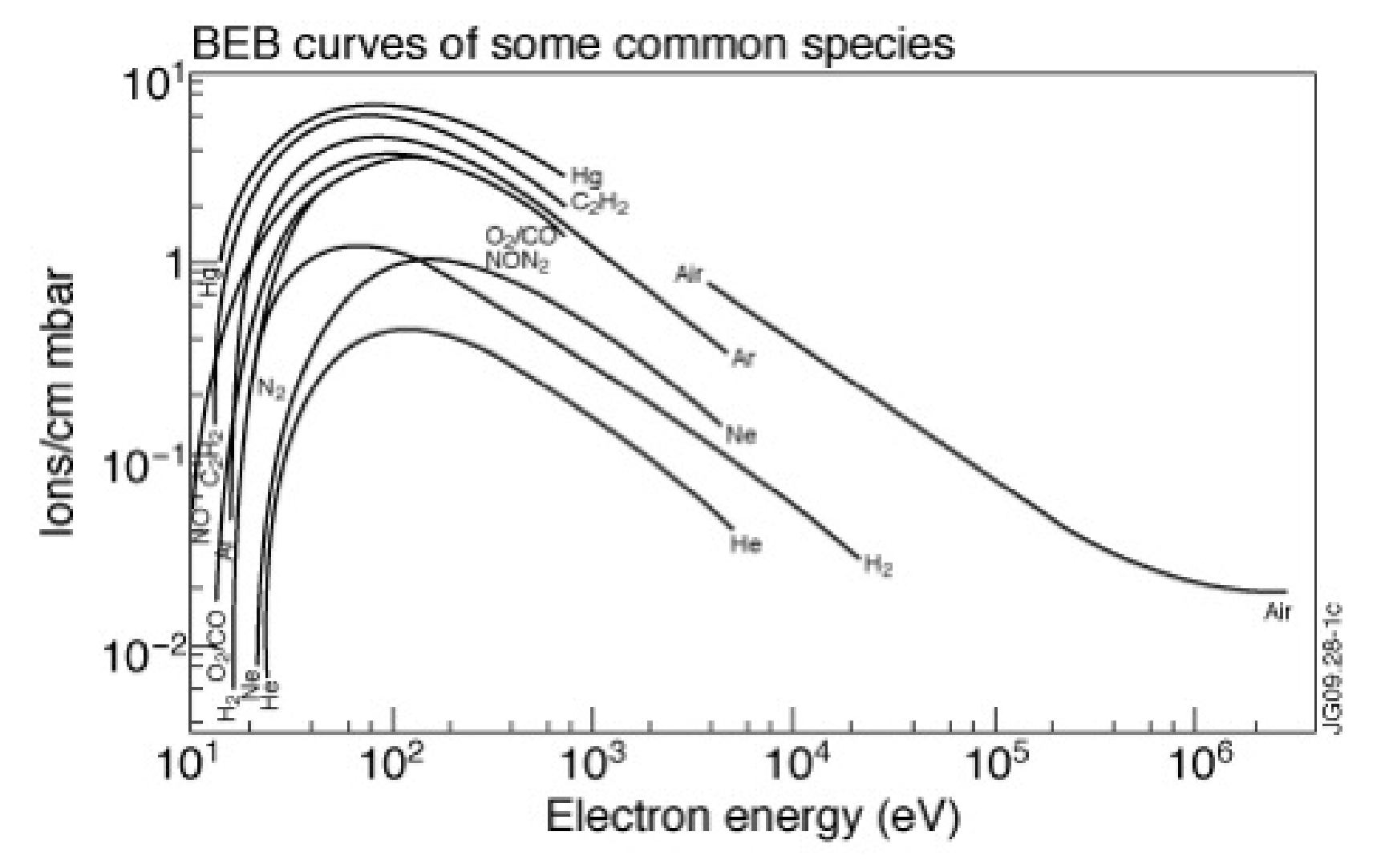
The availability of particle counters which may be operated at ambient pressures of up to $2x10^{-4}$ Torr is highly desirable in many current research applications. In one field in particular, it allows mass spectroscopy of gas analysis and processing plasmas to be performed using pressures of this order in the quadrupole mass spectrometer (QMS). These pressures are much closer to those of many processing plasmas so that the sampling of neutral species, in particular, from the plasma is improved. The sampling of ion and neutral species from magnetron plasmas is a good example. The particle counter used in the present investigation, could be mounted axially so as to have a direct line-of-sight view of the sampling orifice of the QMS. Consequently, energetic neutral species such as metastable atoms of helium, which are produced in helium plasmas and have long lifetimes against spontaneous de-excitation, may travel to the detector and have sufficient energy to be counted there. The detection of metastable helium may be of importance in the study of reaction processes during hydrogen (H/HD)-Deuterium (D_2) plasma fusion, of which the residual fusion byproduct is helium ash. Furthermore, collision processes in the ionisation source of the QMS, (including Penning ionisation), which are insignificant at the more usual source pressures of below $1x10^{-5}$ Torr, generate product ion species whose study helps the interpretation of the processes occurring in the plasma reactor. Typical data from neutral gases and plasmas in a range of gas mixtures which include helium, krypton or argon are shown. The majority of the data presented consist of electron impact threshold ionization efficiency curves obtained by scanning the energy of the electrons in the QMS source. The results presented are discussed in terms of processes which include collisions between metastable species such as He (2^1S and 2^3S) at 20.61eV and 19.82eV respectively [1] having radiative lifetime states of around 3000s and also other plasma constituents.

Introduction

With the availability of particle detectors that can be used at pressures up to $4x10^{-4}$ Torr, it has become possible to operate mass spectrometers at pressures that are much closer to those used in many plasma processing systems. This enables the improved sampling of both neutral and ionised species from plasma reactors. Additionally, the Hiden Analytical quadrupole mass spectrometer (QMS) can operated in a mode where the energy of the electrons emitted within the ionization source is variable. This mode is called TIMS (Threshold Ionization Mass Spectrometry). Different elements have defined ionization energies required to remove an orbiting electron. This energy is dependent on the electron orbital, i.e. outer shell electrons generally have weaker ionization energies due to the greater distance and lower electrostatic forces from the nucleus.

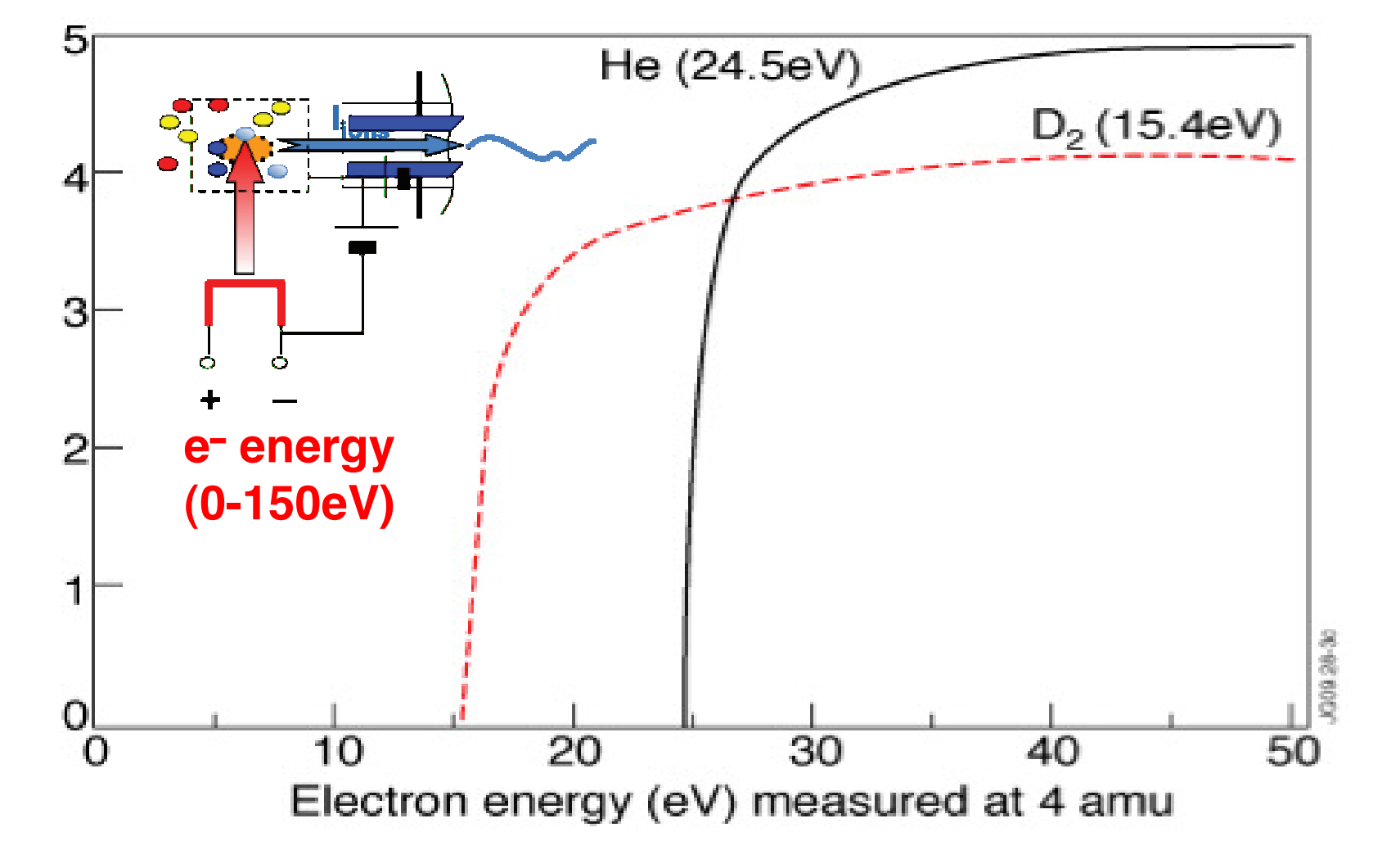
This gives rise to the electron impact "threshold ionization energy" curve shown in figure 1

Figure 1



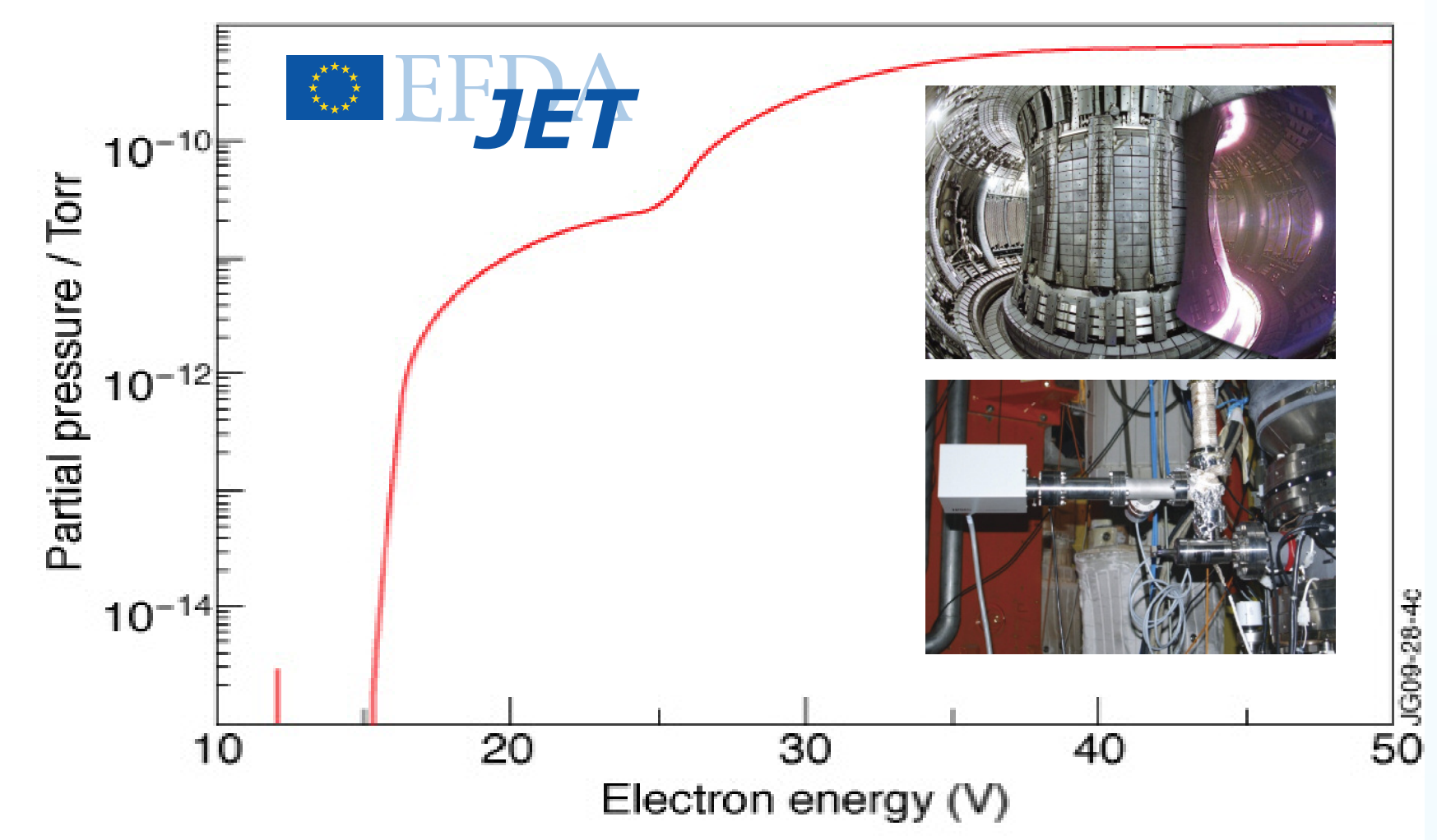
The ionization process of neutral particles commences at a minimum (threshold) energy of the impacting electrons. This minimum energy is dependent and unique to any species present in the gas matrix, resulting in a spectral "identifier" or fingerprint for all atomic or molecular species. For neutral species, for example, a particular application of the TIMS technique has been to accurately quantify the determination of helium/deuterium ratios during plasma fusion, where helium ash is the by-product. Normally, this quantification is precluded when using a QMS in conventional mass spectral mode due to the overlapping convoluted mass spectral signatures of both D_2 and He at 4amu (the actual mass separation is just 0.02amu). When operating the Hiden Analytical QMS in TIMS mode figure 2 shows the electron energy spectra for Deuterium (D_2) and Helium (He) with ionization onsets at 15.4eV and 24.5eV respectively [1].

Figure 2



When these two gases are present simultaneously, the resulting electron energy spectrum is shown in figure 2a. It can be seen that there is a clear deconvolution of the two species in the TIMS spectra such that the presence of D_2 can be accurately detected in Helium down to parts per million (ppm) detection levels [2]. Hiden Analytical TIMS equipped mass spectrometers are now routinely used and in current operation at JET the Joint European Torus experimental nuclear fusion facility, Oxford, UK.

Figure 2a



If it is the helium which is the minor constituent the determination is less tractable than for the reverse situation. However, experiments with a system of the form shown in figure 3 showed an alternative procedure to be effective.

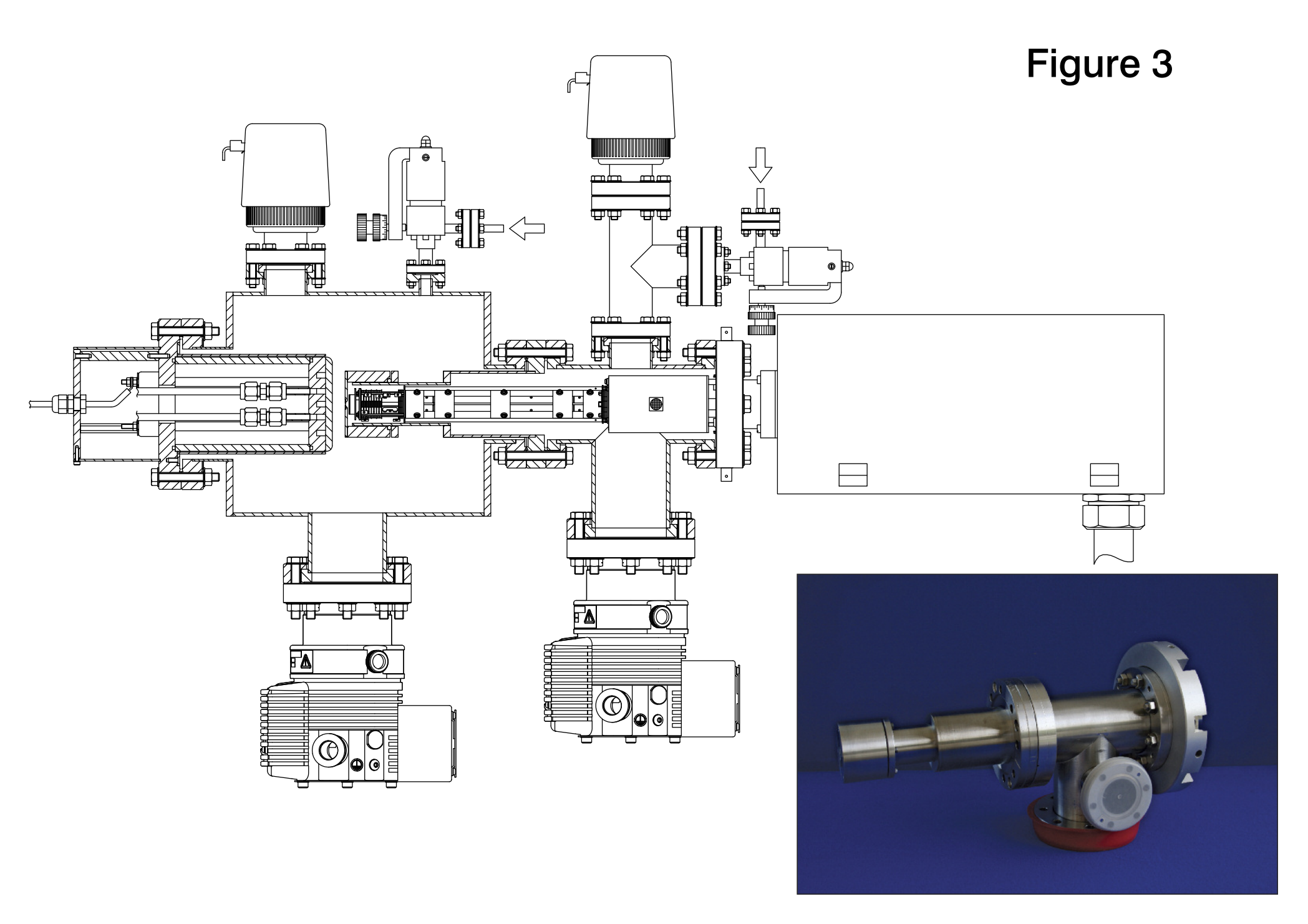


Figure 3

Results

Flowing a gas mixture combining Helium (He) and Deuterium (D_2) at various test gas mixture ratios, at a source pressure of $1x10^{-4}$Torr, there are significant numbers of ions formed with a mass to charge ratio m/e = 8. These are much less abundant even at the more usual maximum source pressures that quadrupole mass spectrometers typically operate at ($\leq 1x10^{-5}$ Torr). This suggests the increased pressure in the source leads to a collision enhanced environment resulting in greater probability of Helium atoms and ions combining to form molecular Helium (He_2) with He.He$^+$ ions. Figure 4 shows the mass spectral scans of these He.He$^+$ ions. An additional pathway as suggested by Van Dyck et al [3] for production of He$^+$.He ions is

$$He^*(2^3S) + He^*(2^3S) \rightarrow He_2^+ + e^-$$

The mass peak at m/e=6 is for D_3^+ ions and/or D$^+$. He ions. Figure 4a shows the variation in the count rates for m/e=8 and 6 at an electron energy of 30eV as a function of the helium content of the helium/deuterium mixture.

Figure 4

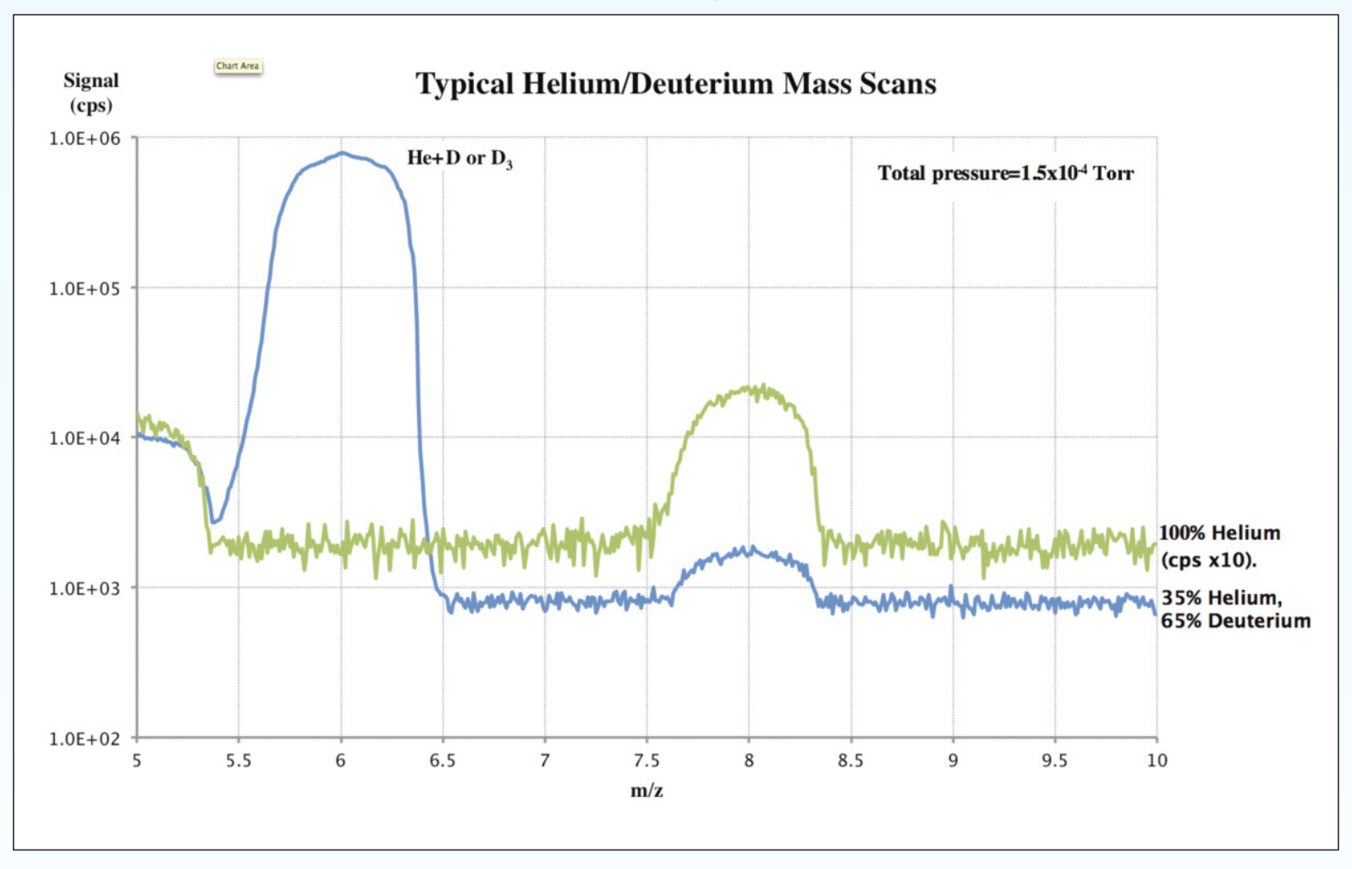
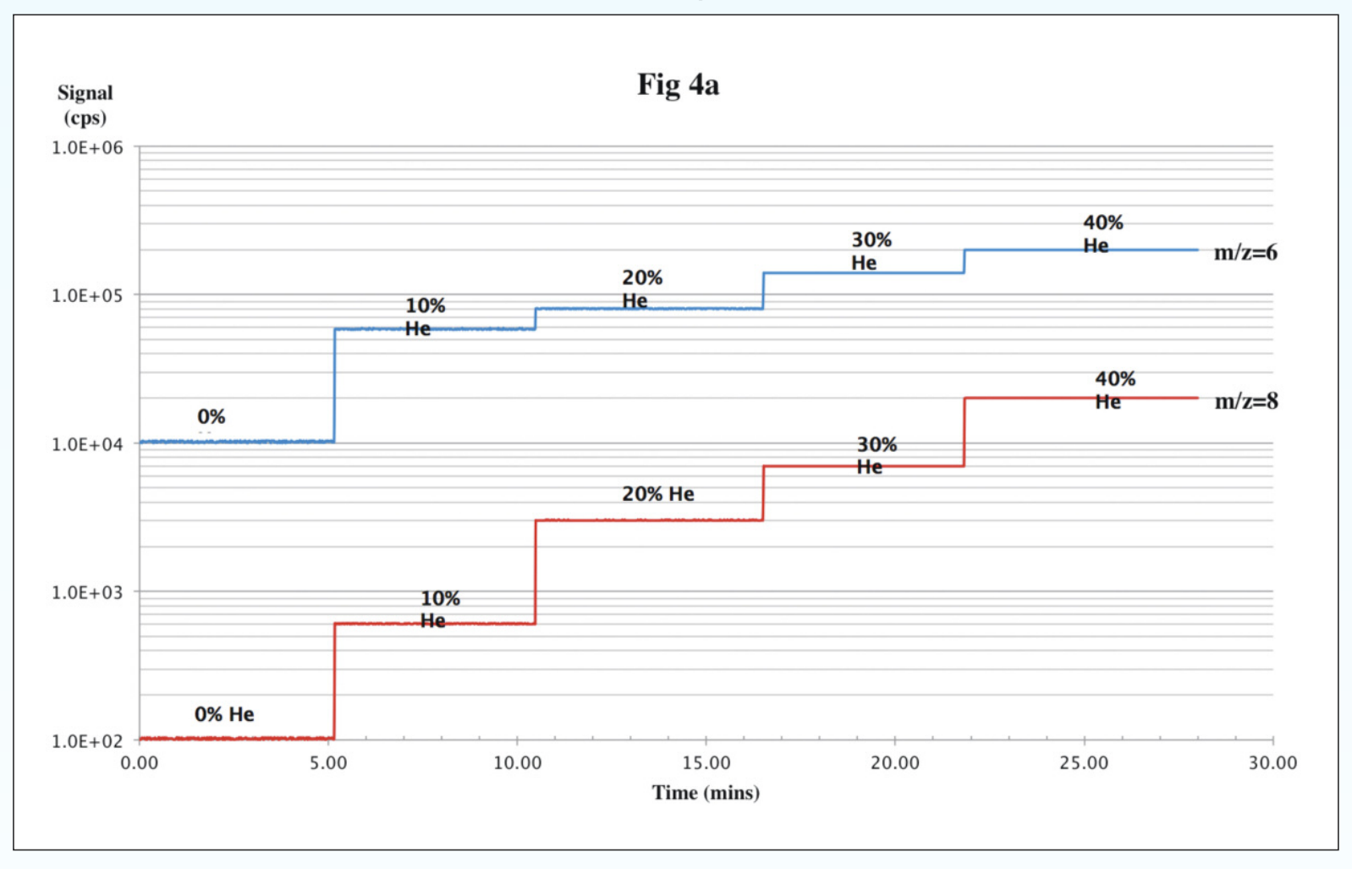


Figure 4a



With the prototype QMS arrangement of figure 3, it is seen that a unique combination of system design, geometry and operational mode of Threshold Ionization Mass Spectrometry (TIMS) allows the detection and clear identification of metastable neutral atoms. Typically, the metastable states of rare gas atoms have internal energies between 12 to 20 eV, and the first excited states have lifetimes in the order of milliseconds to thousands of seconds. Since the interaction time during collisions is in the order of nanoseconds, the lowest metastable state level may be viewed as an effective ground state. These metastable species are not identified in conventional mass spectrometer designs and significantly are mass independent of the resulting ion that is produced by increased electron impact stimulus. Of all metastable systems, the helium collision system is particularly interesting because of its small mass and because of the prototype character of its electronic system containing only four electrons.

Figure 5

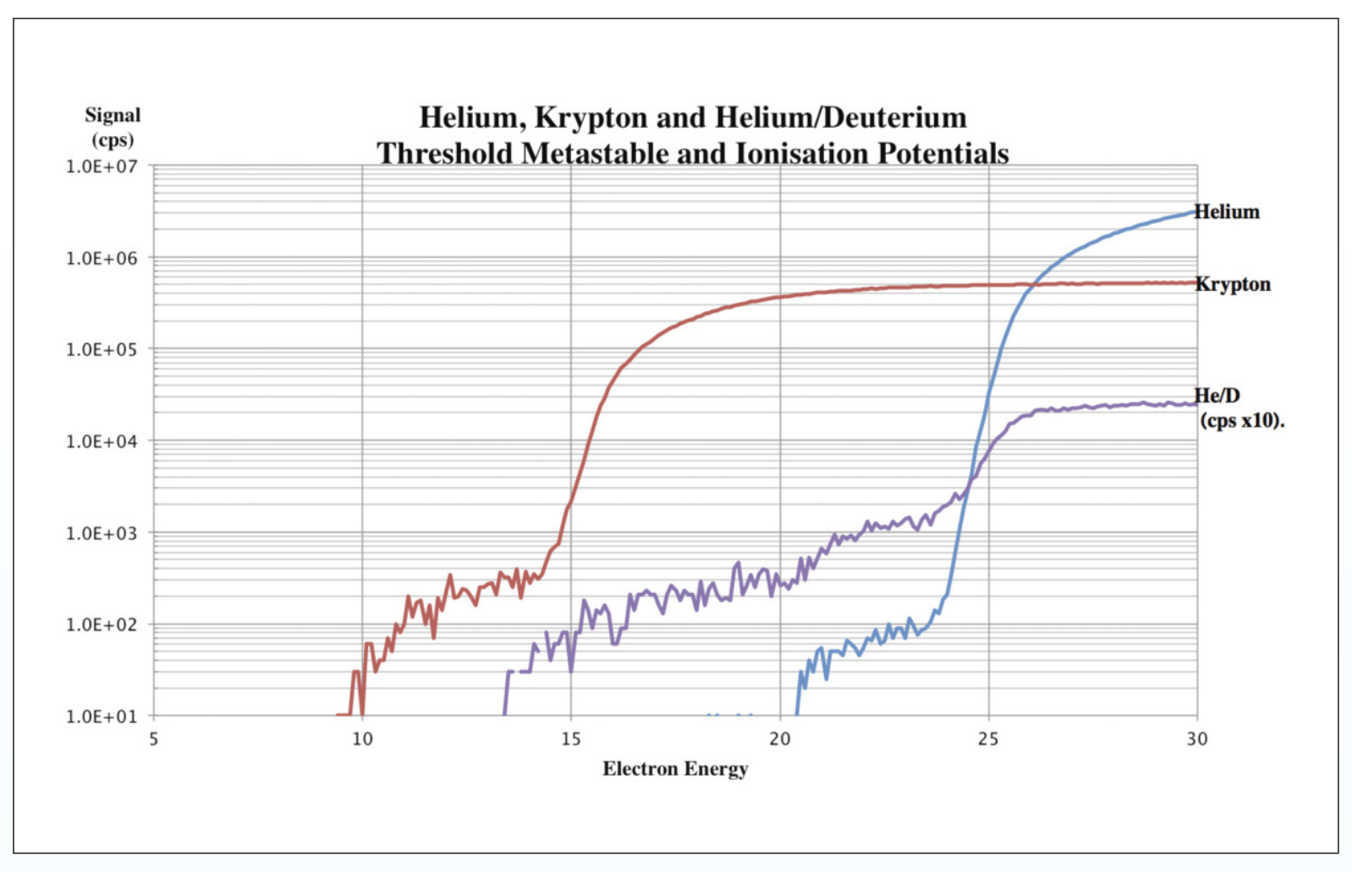
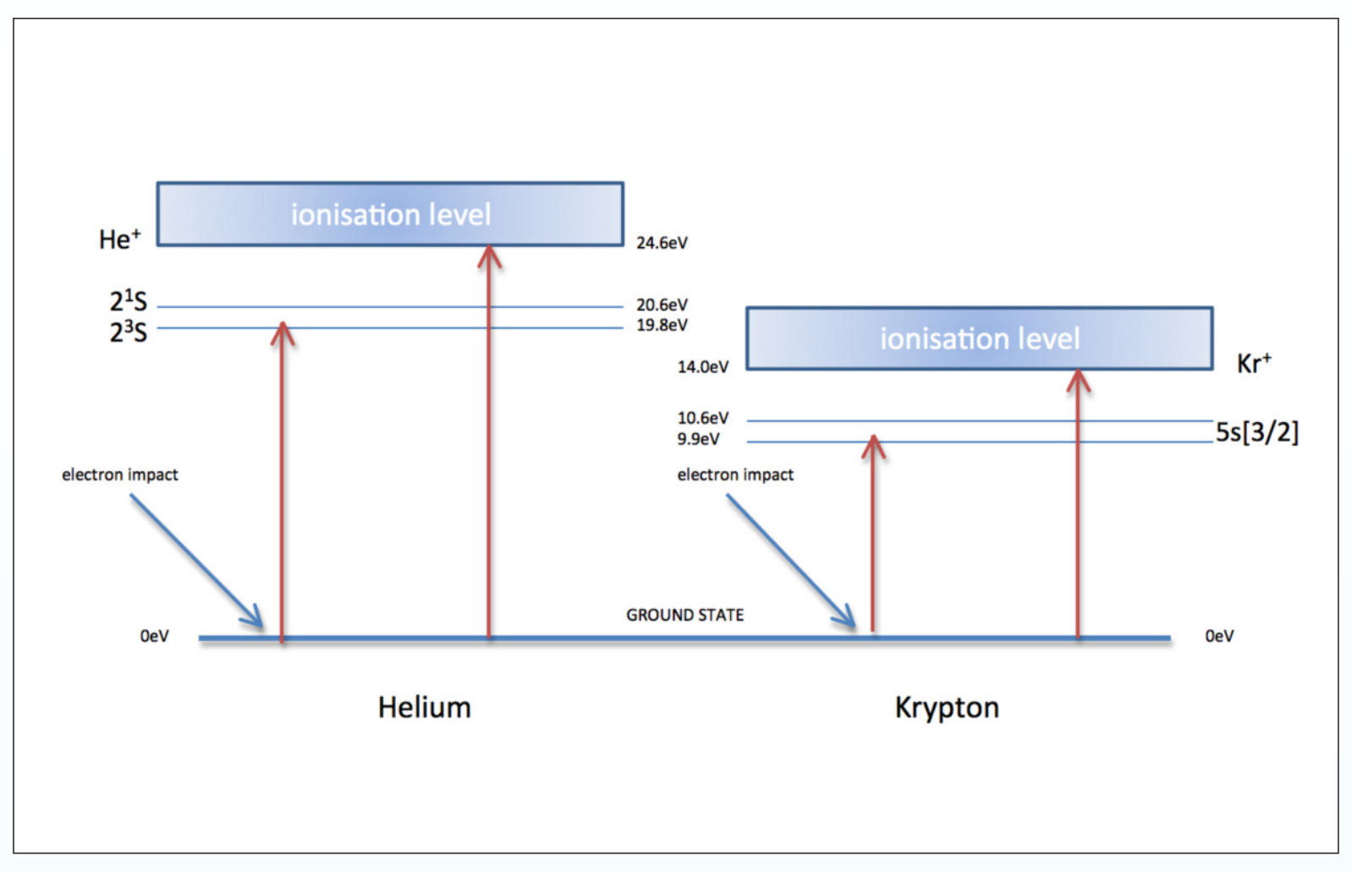


Figure 5a



In this current presentation, metastable neutral atomic species of helium and deuterium *formed in the source* are also counted by the particle detector. This is readily seen in electron energy scans such as those shown in figure 5. The figure shows typical scans at a source pressure of $1x10^{-4}$ Torr for pure helium, pure krypton and a helium/deuterium mixture. To better understand the form of the scans they can be understood by particular reference to the energy-level diagrams of figure 5a. Figure 5 shows the electron impact induced metastable He*(2^1S or 2^3S states) from the Helium ground 1^1S state. The He(2^3S) atoms are produced by electron impact excitation on He(1^1S) ground state atoms. Radiative decay from the He(2^3S) level back to the He(1^1S) ground state is forbidden by quantum spin selection rules. It is seen that the energy states of the metastable He* atoms are 20.6eV and 19.8eV respectively with lifetimes of the order of 3000 seconds, essentially acting as pseudo ground state levels.

The form of the TIMS electron energy spectra in figure 5 for Helium evolves as the electron energy is increased. For electron energies beyond 20.6eV, He*(2^3S) is produced and detected, contributing to the detected signal. For energies beyond 24.5eV He$^+$ ions are produced by ionization of the ground state He(1^2S), and the combined He$^+$ and He*(2^3S) signal increases as shown.

With the arrangement of figure 3 long-lived metastable species, such as those of the inert gases, formed in the plasma reactor travel to the detector. They can be readily distinguished from ions of the same value of m/e by rejecting the latter by suitably tuning the mass spectrometer's sampling electrodes. Figure 6 shows a typical electron energy scan. The ions obtained for electron energies below 25eV are formed from metastable helium sampled from the plasma.

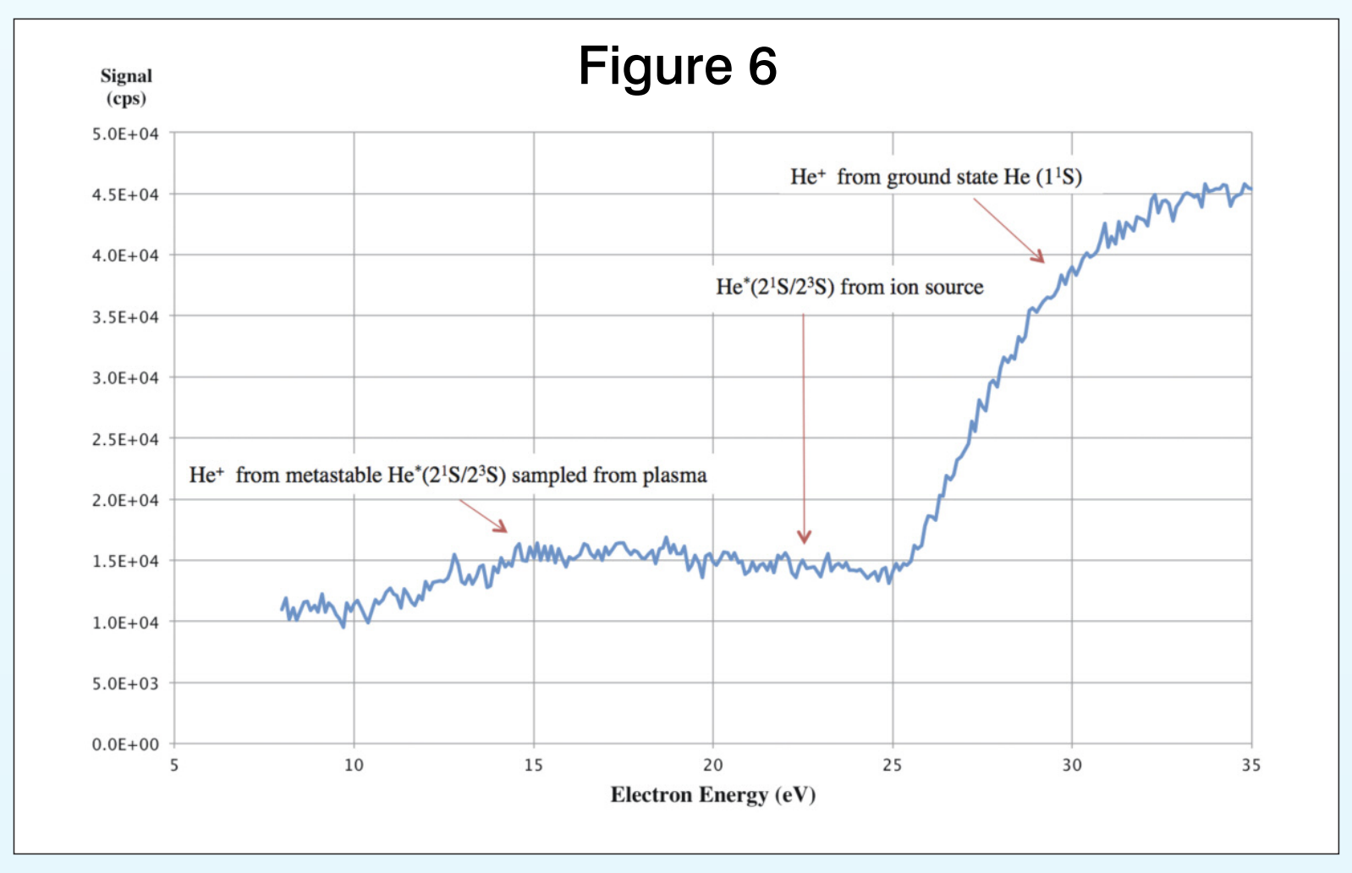


Figure 6

Conclusions

The availability of particle detectors that can be operated at high pressures opens up the possibility of directly observing long-lived, high energy, metastable species such as He_m^* when these are produced in a plasma or other reactor.The direct detection of He*($2^1S/2^3S$) may be of importance in applications when quantification of residual Helium in Deuterium is needed such as He ash by products in fusion processing This is possible due to the mass independence of He* detection in the QMS type shown in Figure 2. Indirect observation of other long-lived excited species, even when these are less energetic (for example metastable oxygen) is also possible using threshold ionisation techniques because of the reduced pressure differential between the reactor and mass spectrometer. Ion/molecule reactions, such as clustering, in the mass spectrometer source may also be studied,as shown here for He$^+$.He.

References

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[2]Coyne.T, Davies.S, et al, 36th International Conference on Plasma Science and Symposium on Fusion Engineering, 2009

[3] Van Dyck, Robert,S et al. Phys. Rev. A 4, 1327–1336 (1971)

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