



Abstract

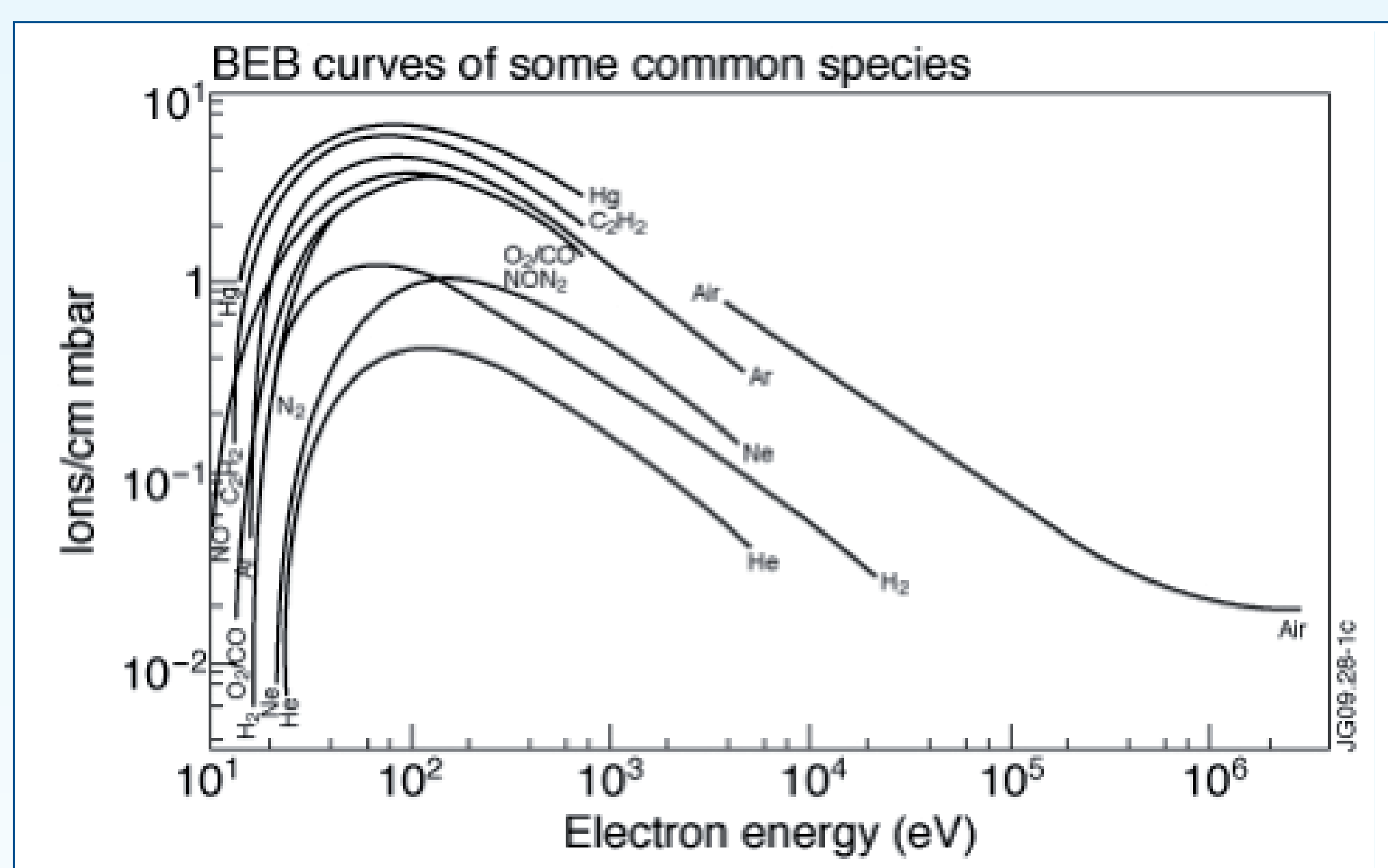
Among the techniques in common use for mass spectrometric studies of processing plasmas, the so-called "threshold ionisation" (TI) method for examining the neutral species generated in a plasma has been particularly useful. In the past, the technique has been applied using source pressures in the mass spectrometer of about 10^{-6} Torr. With the current availability of particle detectors which can be operated at much higher pressures, it is of interest to examine possible extensions of the TI technique. The present data for mass spectrometer pressures of up to $4 \cdot 10^{-4}$ Torr,

using gas mixtures which include rare gases, show clearly the generation of long-lived metastable atoms of the inert gases in both the source of the mass spectrometer and in the plasmas. For gases such as oxygen, generation of metastable species in the mass spectrometer source is also observed. The interpretation of the experimental threshold ionisation data is discussed. The measurements suggest new avenues of research for both gas analysis and plasma diagnostics for gases having long-lived, metastable states.

Introduction

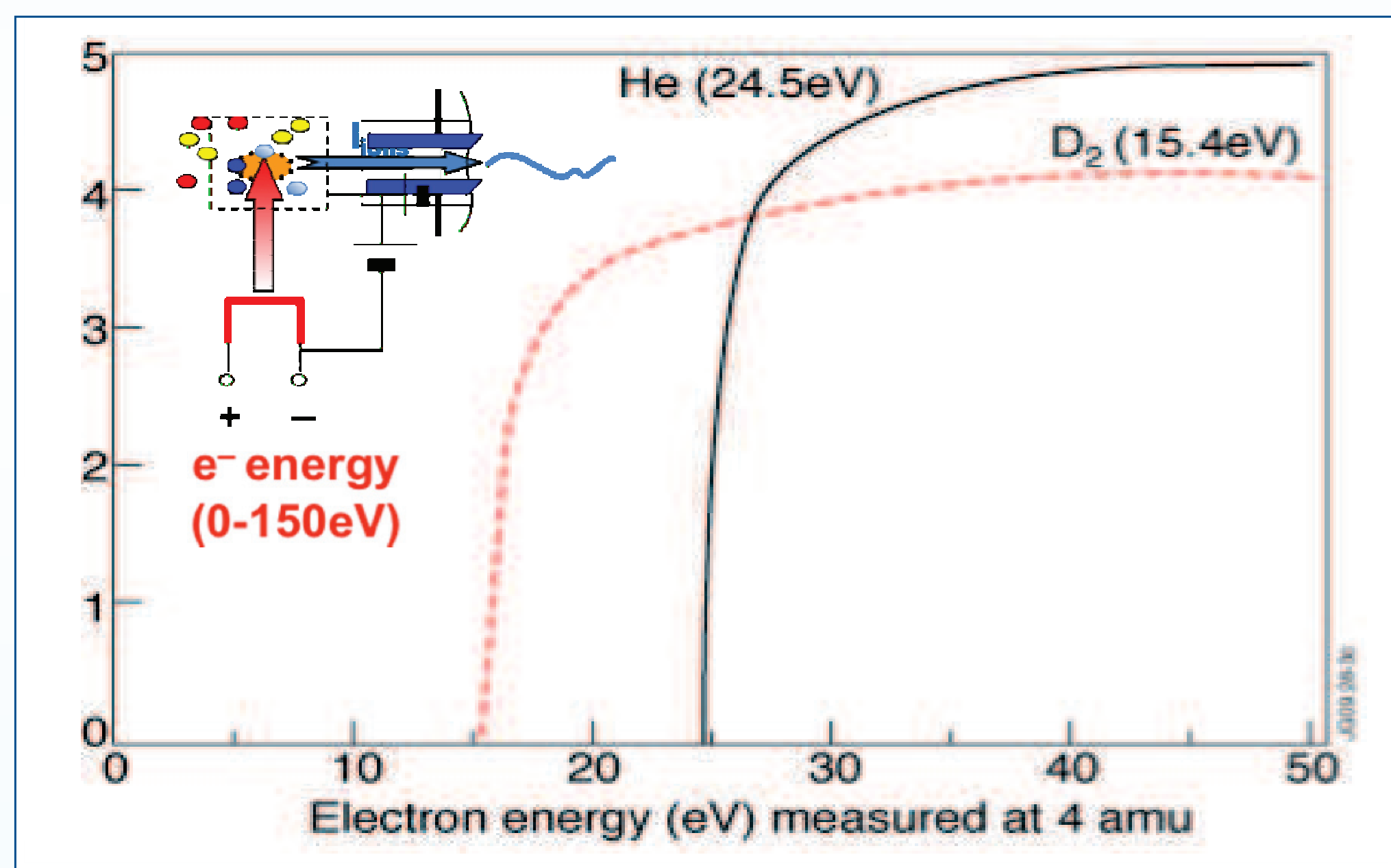
With the availability of particle detectors that can be used at pressures up to $4 \cdot 10^{-4}$ Torr, it has become possible to operate mass spectrometers at pressures that are much closer to those used in many plasma processing systems. This enables the improved sampling of both neutral and ionised species from plasma reactors. Additionally, the Hidden Analytical quadrupole mass spectrometer (QMS) can be operated in a mode where the energy of the electrons emitted within the ionisation source is variable. This mode is called TIMS (Threshold Ionisation Mass Spectrometry). Different elements have defined ionisation energies required to remove an orbiting electron. This energy is dependent on the electron orbital, i.e. outer shell electrons generally have weaker ionisation energies due to the greater distance and lower electrostatic forces from the nucleus. This gives rise to the electron impact ionisation efficiency curves shown in Figure 1.

Figure 1



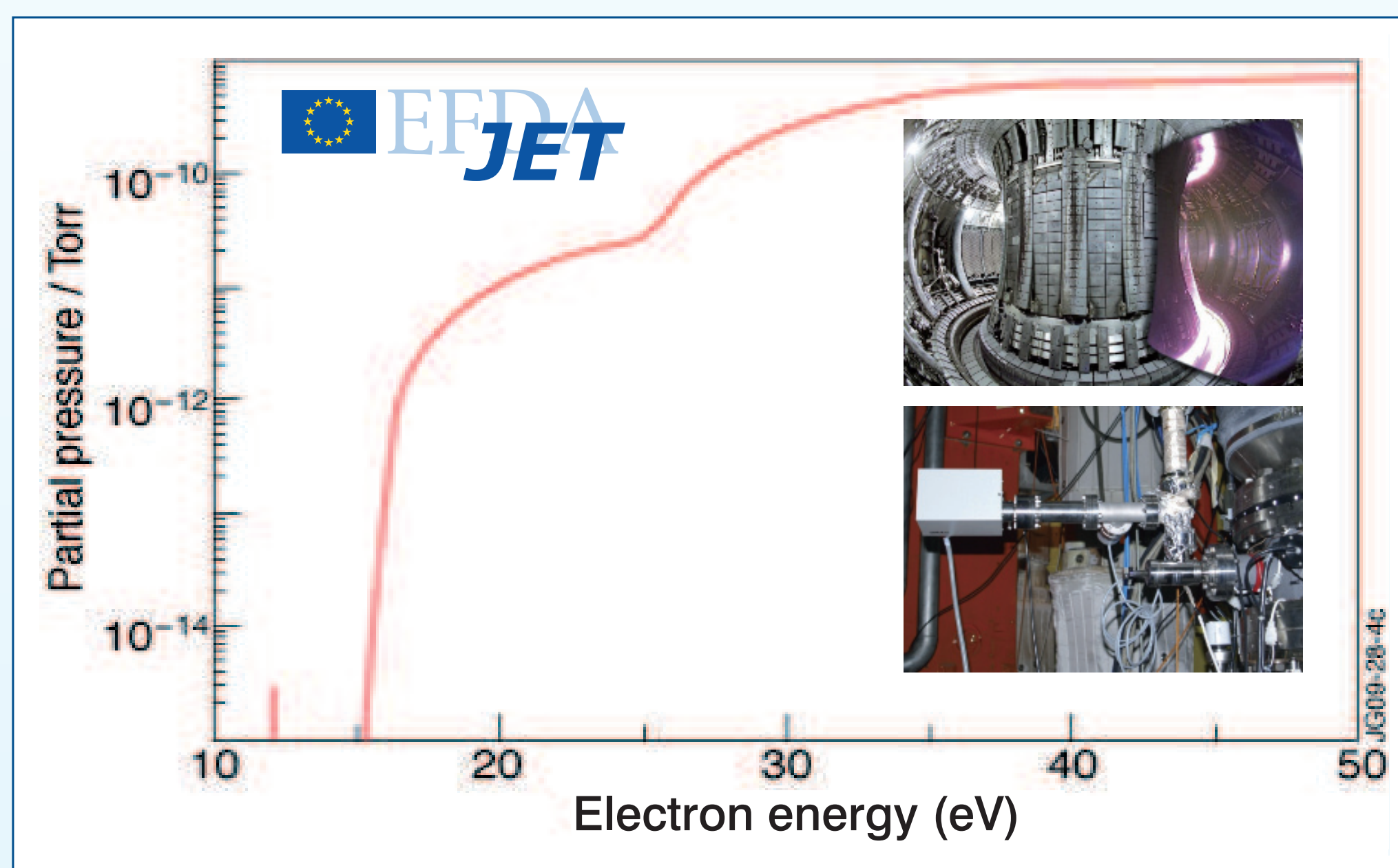
The ionisation process of neutral particles commences at a minimum (threshold) energy of the impacting electrons. This minimum energy is dependent and unique to any species present in the gas matrix, resulting in a spectral "identifier" or fingerprint for all atomic or molecular species. For neutral 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 [1]. Normally, this quantification is precluded when using a QMS in conventional mass spectral mode due to the overlapping convoluted mass spectral signatures of both D2 and He at 4amu (the actual mass separation is just 0.02amu). When operating the Hidden Analytical QMS in TIMS mode figure 2 shows the electron energy spectra for Deuterium (D2) and Helium (He) with ionisation onsets at 15.4eV and 24.5eV respectively.

Figure 2



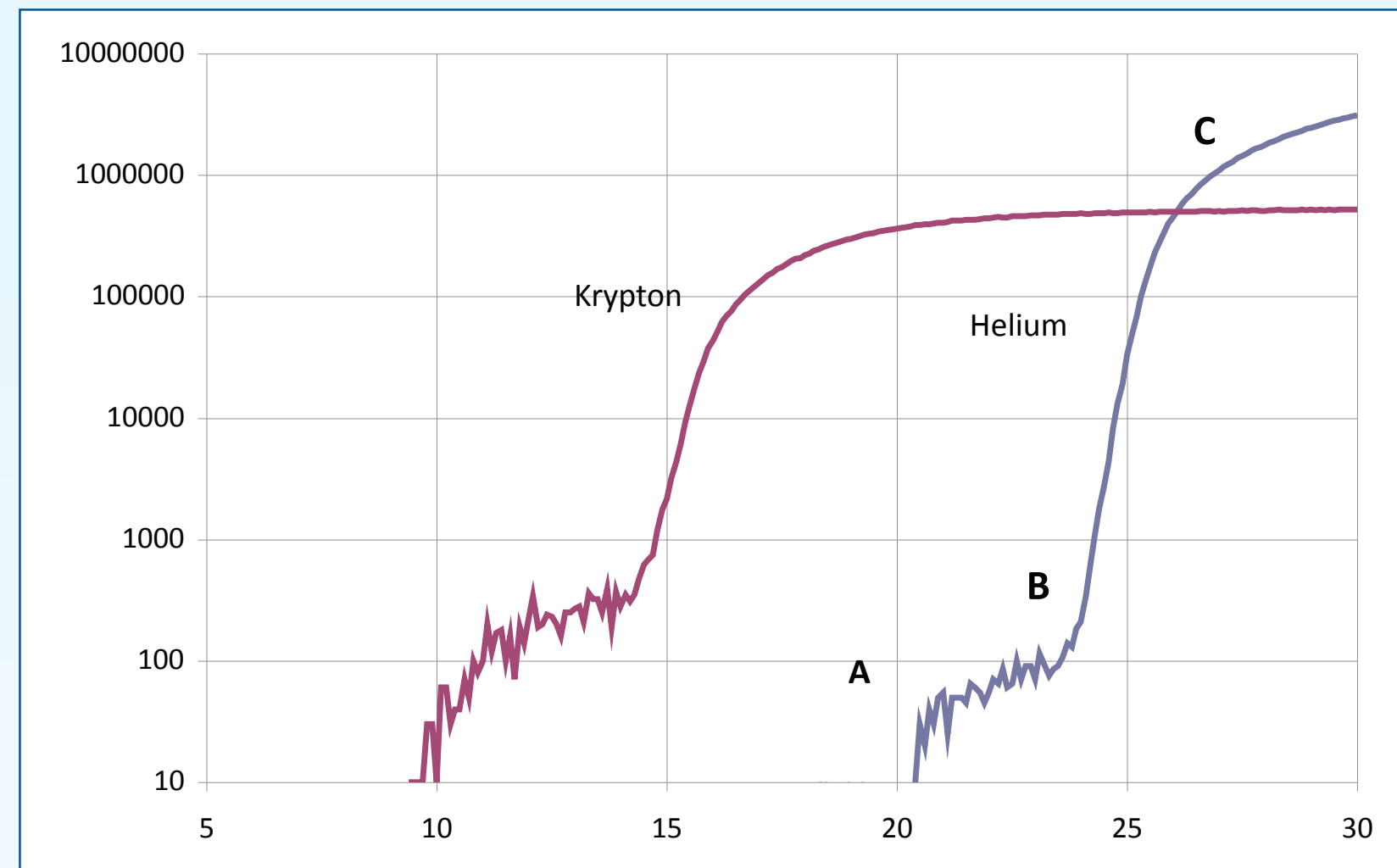
When these two gases are present simultaneously, the resulting electron energy spectrum is shown in figure 2a. It can be seen that there is a clear deconvolution of the two species in the TIMS spectra such that the presence of D2 can be accurately detected in Helium down to parts per million (ppm) detection levels [1]. Hidden 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



Results

Figure 3



The ionisation potential of helium is 24.6 eV. The section AB of the curve is attributed to the formation of metastable He^*_m atoms, which have a long lifetime against spontaneous decay. They have sufficient energy to generate pulse counts when impacting on the detector. For electron energies above 24.6 eV the section BC of the curve includes both metastable and ionised helium contributions. Similar data were obtained in other experiments for neon, krypton and argon. Data for krypton are included in figure 3. The form of the curves shown in figure 3 may be understood by reference to figure 4.

Figure 4

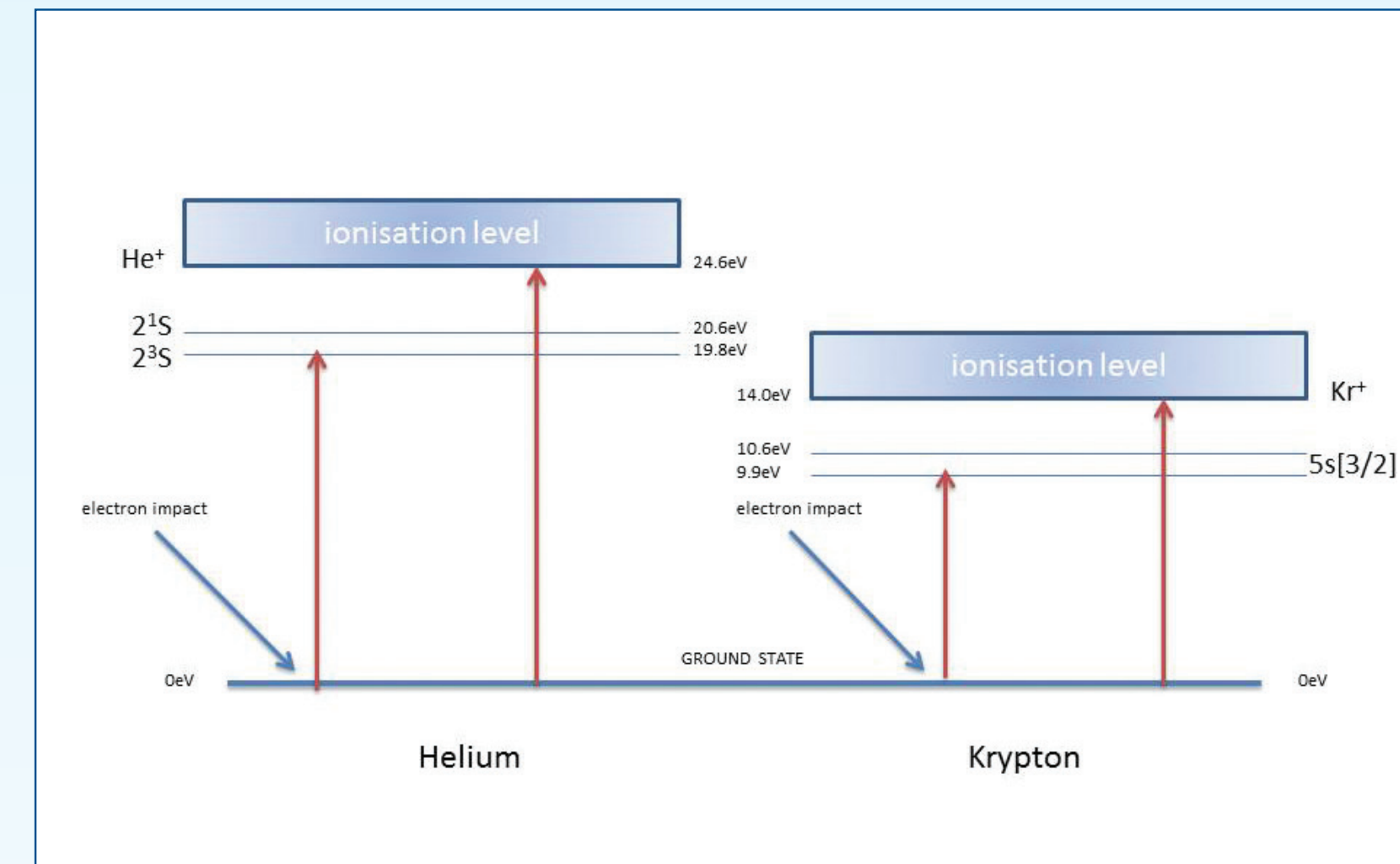
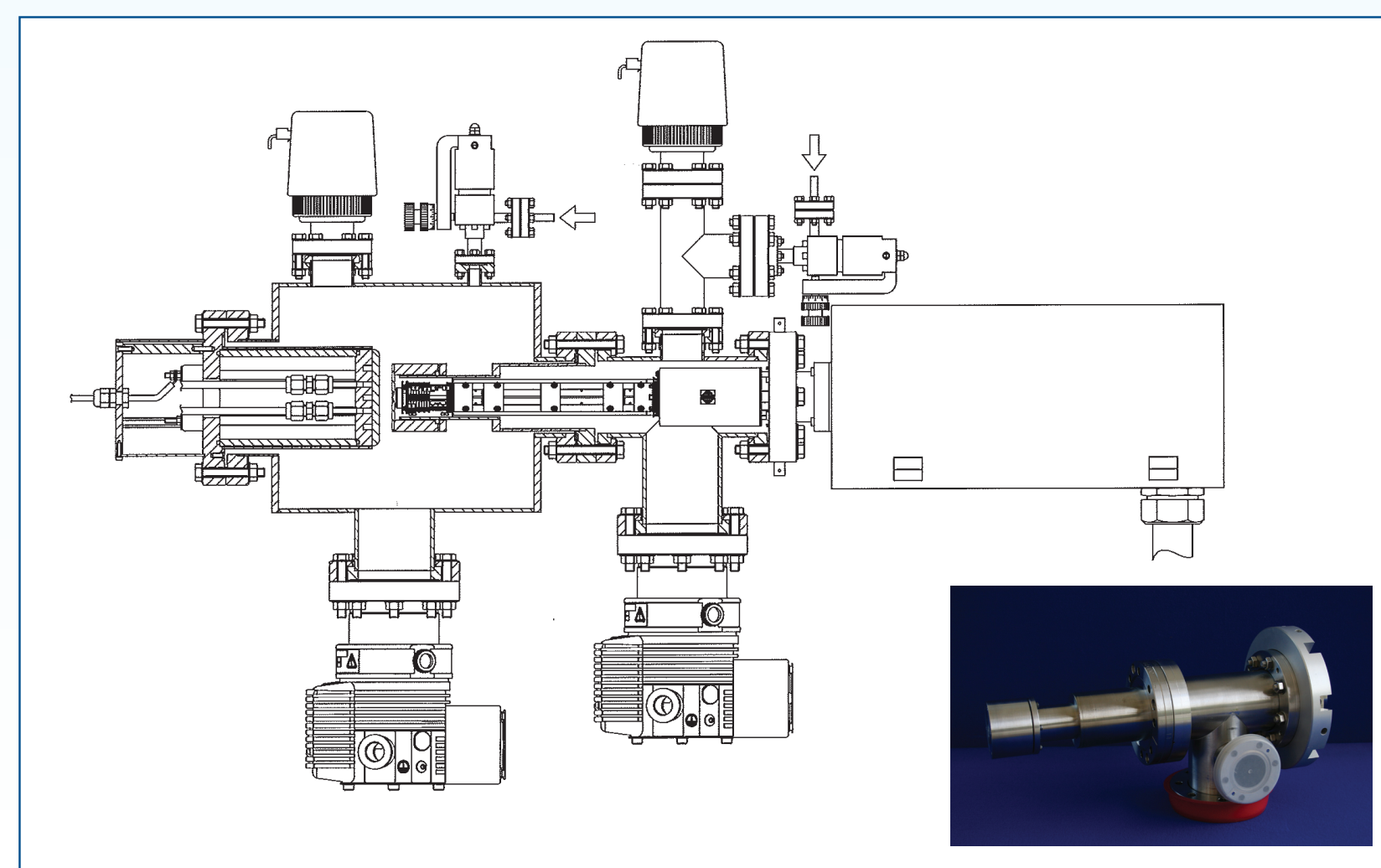
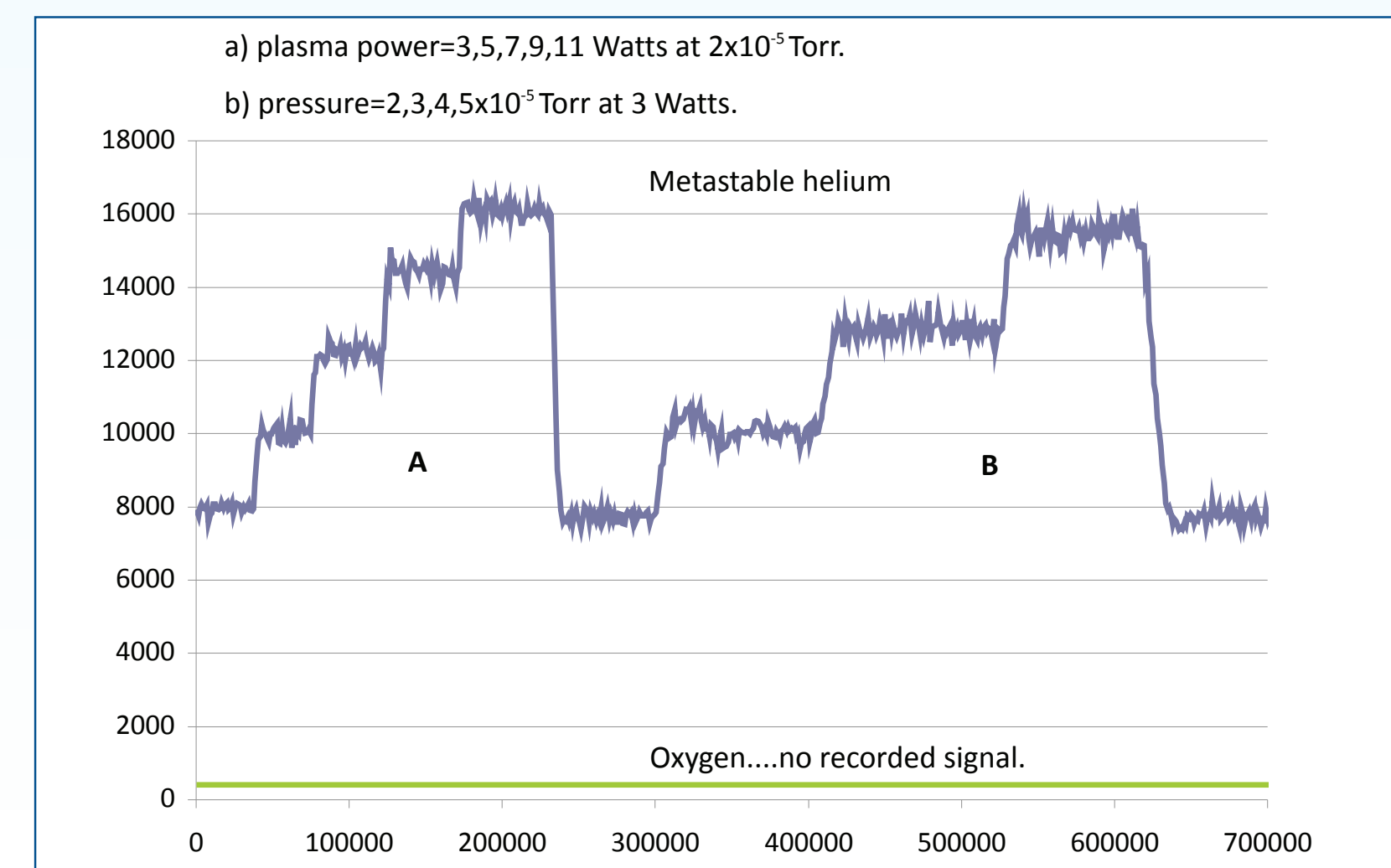


Figure 5



The data of figure 3 were obtained using the system shown schematically in figure 5.

Figure 6



An RF plasma could be maintained in the reactor between an electrode and the sampling orifice of the mass spectrometer. Electrodes behind the orifice could be used to control the entrance of ions from the reactor into the Hidden mass spectrometer. The particle detector could be used to pressures of $4 \cdot 10^{-4}$ Torr. Gases were admitted into the reactor or directly into the source of the mass spectrometer.

With a plasma operating in helium, but with the internal ionisation source of the mass spectrometer off and its sampling system set to prevent all plasma ions from entering it the detector recorded the arrival of He^*_m produced in the plasma. The metastable signal was proportional to the plasma power and to the gas pressure in the reactor, as shown in figure 6. When the helium plasma was replaced by an oxygen plasma no energetic particles from the plasma were detected, since metastable oxygen species, although long-lived, have insufficient energy to be recorded by the detector.

Figure 7

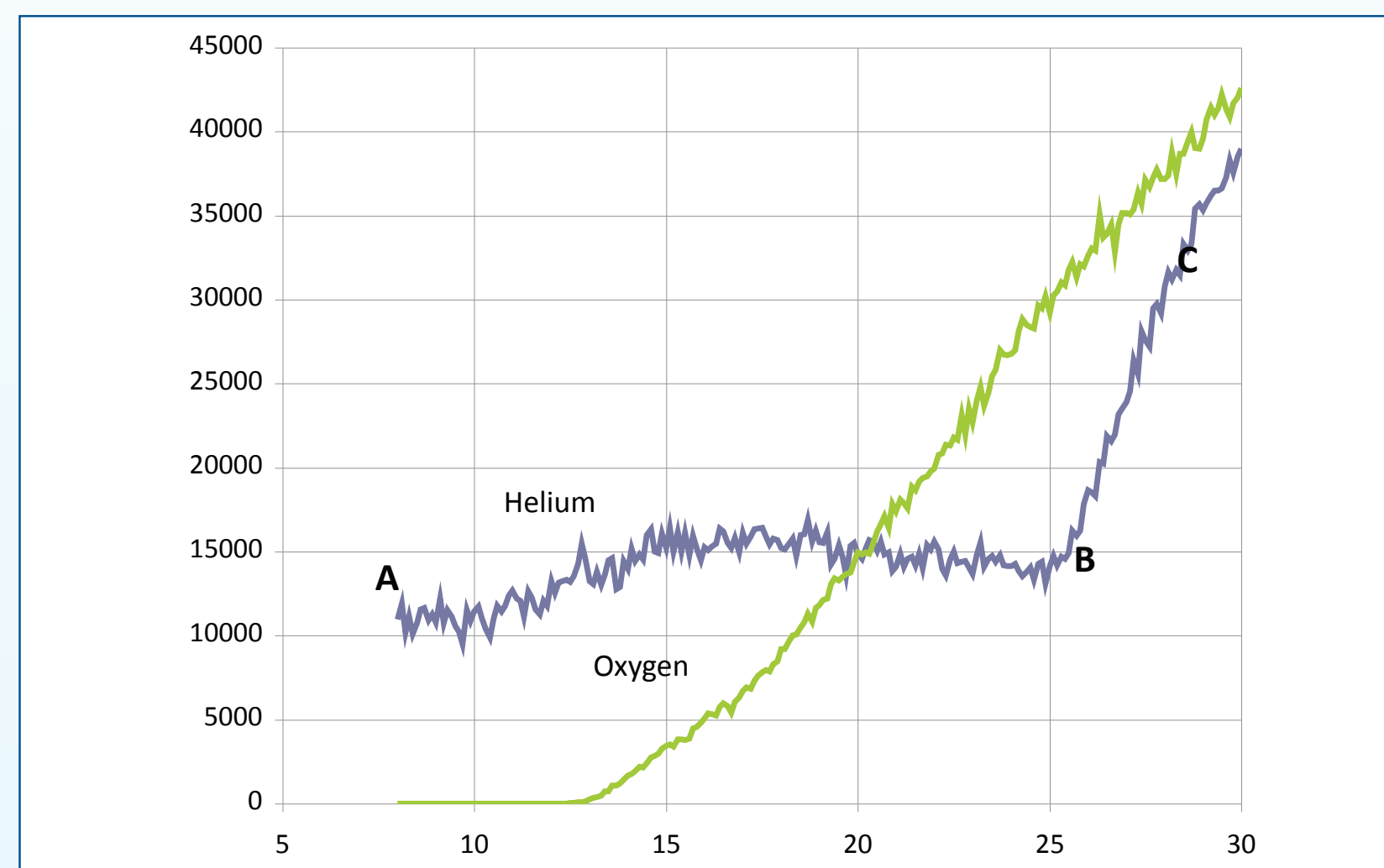
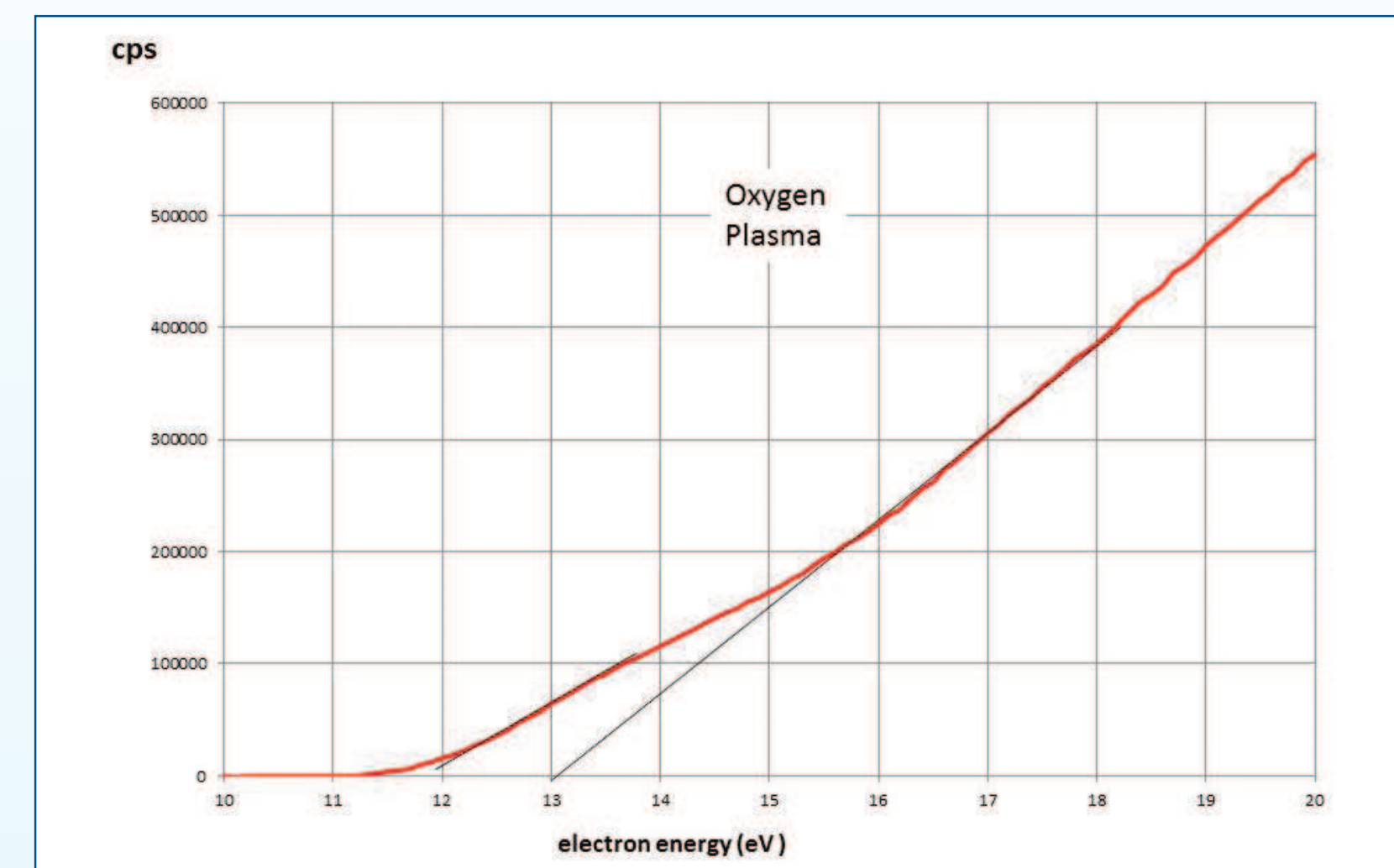


Figure 8



With both plasma and mass spectrometer source operating, and the sampling system again set to reject plasma ions, the recorded signals for a mixture of helium and oxygen were as shown in figure 7. For the helium curve, the section BC shows ions generated from ground-state helium sampled from the reactor, while section AB shows ions generated from sampled metastable helium. There will be a small contribution due to metastable helium atoms generated in the source between 20 and 25 eV. The threshold energy (not shown) is expected to be around 5eV (see figure 4). For oxygen, there was no evidence of Penning ionisation in the internal source.

For pure oxygen, a 15 Watt plasma at 30mTorr and a mass spectrometer source pressure of $2 \cdot 10^{-4}$ Torr gave the data shown in figure 8. The region below 16 eV appears to have two components with onset potentials that differ by about 1 eV. This is to be expected if either the sampled oxygen includes metastable a $^1\Delta_g$ oxygen, or if the latter were produced in the mass spectrometer source. For the present experiment, the source process dominated.

Conclusions

Reducing the pressure differential between a plasma reactor and an attached mass spectrometer enables direct detection of metastable species produced in the plasma if these have long life-times and sufficient internal energy. Detection of lower energy, but still long-lived, metastable species and other plasma products is also simplified, such measurements may be relevant in considering the role of energetic neutral species in the plasma processing of surfaces.

References

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