Measurements of state-selective electron capture by slow multiply charged ions in specified ground or metastable states

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Abstract

The technique of double translational energy spectroscopy (DTES) has been used in this laboratory to study state-selective electron capture by slow state-prepared ions in collisions with a variety of targets including atomic hydrogen. Measurements are described involving one-electron capture by C^{2+} ^1S ground state and C^{2+} ^3P metastable ions, N^{2+} ^2P ground state ions and O^{2+} ^3P ground state ions in the range $0.8 - 6$ keV. Use of DTES overcomes the difficult problem of interpretation inherent in the many previous measurements carried out with ion beams containing unknown fractions of metastable ions.

1. INTRODUCTION

A detailed understanding of one-electron capture processes of the type

$$X^{q+} + Y \rightarrow X^{(q-1)+}(n, l) + Y^+(n', l')$$
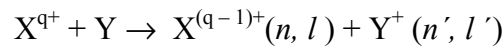
leading to product ions in specified excited states is directly relevant to the accurate modelling of the behaviour of edge plasmas in fusion devices. At velocities $v < 1$ au, it is well known that, in processes with moderate exothermicity, electron capture may take place very effectively through a limited number of pseudocrossings of the adiabatic potential energy curves describing the initial and final molecular systems. In many such processes, experimental measurements have provided both identification and a quantitative assessment of the main excited product channels. Since accurate calculations are difficult, particularly for partially ionized primary ions, where a number of curve crossings may be important, reliable experimental data are of particular value in determining the range of validity of the approximations used in the theoretical models.

In this laboratory we have used the well-established technique of translational energy spectroscopy (TES) to obtain detailed information on state-selective electron capture in many different processes. In the TES approach, the X^{q+} primary ion beam of well defined energy T_1 is passed through the target gas and the kinetic energy T_2 of the forward scattered $X^{(q-1)+}$ ions formed as products of single collisions is then measured. The difference in kinetic energy ΔT is then given by

$$\Delta T = T_2 - T_1 = \Delta E \qquad - \Delta K$$

where ΔK is a small recoil correction of the target. Provided that the ratio $\Delta E/T_1 \ll 1$ and the scattering is confined to small angles, the measured change in translational energy $\Delta T \approx \Delta E$. The relative importance of collision product channels characterised by particular values of ΔE may then be assessed from a careful analysis of the energy change spectra subject to the limitations of the available energy resolution.

The TES approach has been extremely successful in providing definitive data for many different processes including collisions in atomic hydrogen. However, in many processes, TES studies have revealed the presence of collision channels associated with metastable ions in addition to ground state ions in the primary ion beam (cf. review by Gilbody [1]). For example, in the case of one-electron capture in C^{2+} - H(1s) collisions, our TES measurements [2] identified collision product channels associated with both ground state C^{2+} $(2s^2)$ ^1S and metastable C^{2+} $(2s2p)$ $^3P^o$ primary ions. In the range 2 – 8 keV, between 60% and 65% of the observed C^+ product yield arose from channels associated with C^{2+} $^3P^o$ metastable primary ions. In such cases, a detailed quantitative analysis is precluded unless the metastable content of the beam can be specified. These TES measurements also indicate that many previous measurements of total electron capture cross sections carried out with ion beams containing unknown fractions of metastable ions must be interpreted with caution. Indeed, in some cases, large discrepancies between total cross sections measured in different laboratories seem likely to be due to the use of beams containing different and unknown fractions of metastable ions.

In the modelling of edge plasmas in fusion devices, there is a need for data on electron capture by both ground state and metastable species. An attractive solution to this difficult problem is provided, in principle, by the use of the technique of double translational energy spectroscopy (DTES). In this approach, primary ions in a particular ground or metastable state are prepared by electron capture collisions in a suitable gas target and then selected and identified by TES. The selected ions in well defined states are then used as primary ions in a second stage of TES to study electron capture in the target gas of interest without any ambiguities in the interpretation of the collision product channels. The feasibility of DTES was first demonstrated by Huber *et al* [3] in 1984, but was not seriously applied until the recent series of measurements carried out in this laboratory. To date, we have studied one-electron capture by C^{2+} ^1S ground state and C^{2+} ^3P metastable ions in He, Ne, Ar, H_2, N_2 and O_2 [4, 5] by N^{2+} ^2P ground state ions in He, Ne, Ar and H_2 [6, 7] and by O^{2+} ^3P ground state ions in He, Ne and Ar [8]. Recently, we have also succeeded in carrying out DTES measurements in atomic hydrogen for one-electron capture by C^{2+} ^1S ground state and C^{2+} ^3P metastable ions [9], by N^{2+} ^2P ground state ions [10] and by O^{2+} ^3P ground state ions [11]. Unlike our previous TES measurements, which employed a tungsten tube furnace to provide a target of highly dissociated hydrogen, we have used a specially developed aluminium target cell fed with highly dissociated hydrogen from a microwave-driven discharge source. All the measurements to date have been carried out within the range 0.8 – 6 keV. In this review, we shall describe the results obtained for a few representative processes.

2. EXPERIMENTAL APPROACH

A schematic diagram of the basic DTES apparatus is shown in figure 1. In order to provide a state-prepared beam of X^{2+} ions, an intense beam of X^{3+} ions is first extracted from an ECR ion source. This beam is focused, momentum analysed by a double focusing magnet and then enters the electrostatic lens system L1 of the double translational energy spectrometer. After focusing and deceleration by L1, the beam passes though the hemispherical electrostatic energy analyser EA1 at an energy of 40q eV (where q = 3). The emerging energy resolved beam of intensity about 0.2 nA and with an energy spread corresponding to about 1 eV FWHM , is accelerated by lens L2 to an energy of qV_{01} eV. It then enters the first target cell T1 containing helium where the gas pressure is adjusted to maximise the transmitted yield of X^{2+} ions formed by electron capture collisions.

The X^{2+} products emerging from T1 are decelerated and focused by the lens system L3 before entering the hemispherical analyser EA2. Application of an appropriate positive bias

voltage V_{R1} to EA2 and the associated lenses L3 and L4 ensures passage of the X^{2+} ions while rejecting X^{3+} primary ions. The acceptance energy of EA2 is $60(q - 1)$ eV. By adjusting the scanning voltage V_{S1} the translational energy change spectrum obtained from EA2 in this first stage of TES can be displayed and used to select X^{2+} ions in either the ground or metastable state. This is illustrated in figure 2 which shows the energy change spectrum obtained for C^{2+} ions formed by one-electron capture by 15 keV C^{3+} ions in helium. In this case, a beam of either ^1S ground state or ^3P metastable C^{2+} ions could be produced from the ions comprising peaks A or B respectively. Actually, peak A corresponds to the C^{2+} $(1s^2 2s2p)$ ^1P excited product channel but this is known to decay very rapidly (see [4]) to the ^1S ground state before reaching the second target. In contrast, less than 0.1% of the long-lived ^3P metastables in peak B decay in transit to the second target.
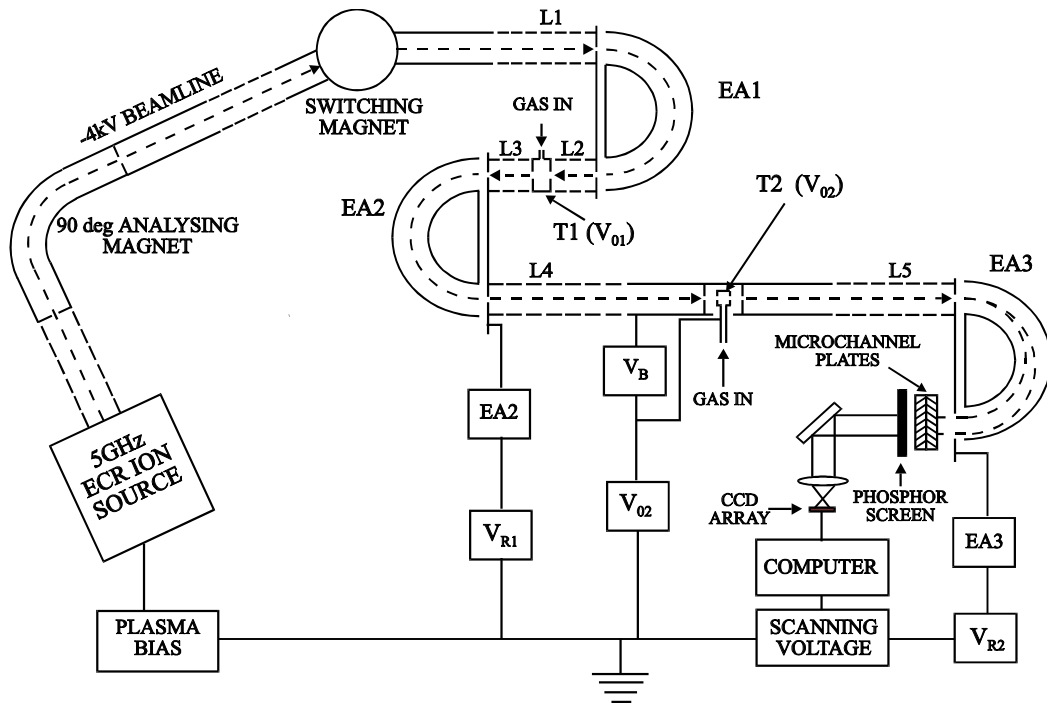

Figure 1. Schematic diagram of the DTES apparatus (from [4]).

A pure beam of either ^1S ground state or ^3P metastable C^{2+} ions emerging from EA2 is accelerated and focused by lens system L4 into the main target gas cell T2. The gas pressure in T2 is low enough to ensure single collision conditions. The forward-scattered C^{2+} products emerging from T2 are decelerated and focused by lens L5 into the final electrostatic analyser EA3. As in the case of electron capture in the target cell T1, appropriate potentials were applied to L5 and EA3 to allow product C^+ ions to enter with an energy of $40(q - 2)$ eV. The energy analysed product C^+ ions from EA3 are counted by a computer controlled position sensitive detector.

Our DTES measurements with N^{2+} and O^{2+} ions were carried out with beams in well-defined states prepared in a similar way. However, unlike C^{2+} ions where yields of both the ground state and metastable species were adequate, only the ground state components of the N^{2+} and O^{2+} beams have usually been intense enough to be able carry out the second stage TES measurements.
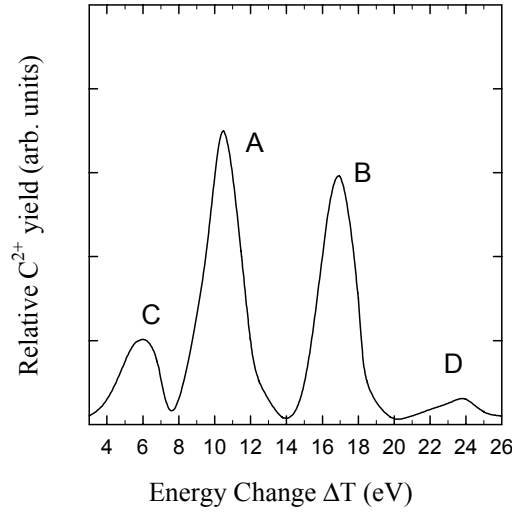
Figure 2. Energy change spectrum of C^{2+} ions formed in one-electron capture by 15 keV C^{3+} ions in helium (from [4]).
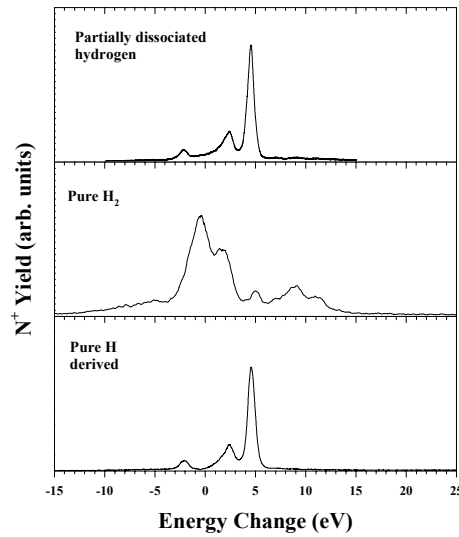

Figure 3. Energy change spectra at 3 keV measured for one-electron capture by pure N^{2+} $^{2}P^{o}$ ions in highly dissociated hydrogen, in pure H_2 and derived (see text) for pure H atoms.

In order to carry out DTES measurements in an atomic hydrogen target, the gas cell T2 in figure 1 is replaced by an aluminium target cell fed by a microwave-driven hydrogen discharge source (see [10]). The tube is held typically at a potential of + 50V with respect to the surrounding region. This voltage labelling ensures that the collisions occurring in the region outside the cell do not contribute to the observed energy change spectrum.

Although highly dissociated hydrogen is injected into the target cell, H_2 molecules are formed by collisions with the cell walls so that the spectra obtained reflects the mixture of H and H_2 present in the cell. Energy change spectra for atomic hydrogen alone can be derived from the measured spectra by subtracting the molecular contribution from the spectra obtained in the 'mixed' target. The accurate subtraction process is facilitated by the ability of the hydrogen source to be rapidly switched from highly dissociated hydrogen to pure H_2.

Typical energy change spectra obtained at 3 keV for one-electron capture by pure $N^{2+}\ ^2P^o$ ground-state ions are shown in figure 3. The spectra for highly dissociated (about 70 %) hydrogen and pure molecular hydrogen can be seen to be very different while the derived spectrum for a pure atomic hydrogen target exhibits clearly defined product channels suitable for quantitative analysis..

Our DTES apparatus does not yet allow absolute measurements of the total one-electron capture cross sections for state-prepared ions. However, in a few measurements with C^{2+} ions it has been possible to use a simple beam attenuation technique to determine the ratios $\sigma(^3P)/\sigma(^1S)$ of the total cross sections for metastable and ground state species. Figure 4 shows the attenuation of a beam of pure metastable or ground state C^{2+} ions in helium as the target thickness μ is increased so that the total recorded beam intensity follows the simple relation $I = I_0\,e^{-\mu\sigma}$. Analysis [4] of plots of this type in helium, neon and argon at 4 keV, provide ratios $\sigma(^3P)/\sigma(^1S) = 11.5 \pm 3.0,\ 3.1 \pm 0.2$ and 3.5 ± 0.3 respectively. These observations indicate the need for cautious interpretation of any measurements of cross sections carried out with ion beams of unknown metastable content.

3. RESULTS AND DISCUSSION

3.1. DTES measurements with C^{2+} ions

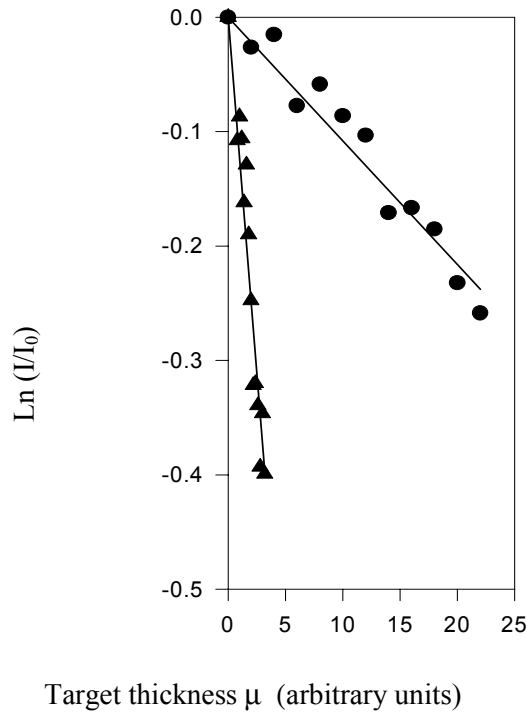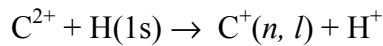As already noted, our previous TES studies [2] of the electron capture process

$$C^{2+} + H(1s) \rightarrow C^+(n,\ l) + H^+$$

Figure 4. Attenuation by one-electron capture collisions in helium of pure ground state $C^{2+}\ ^1S$ (●) and pure metastable $C^{2+}\ ^3P$ (▲) ion beams at 4 keV as the target thickness μ is increased (from [4]).

were carried out with ion beams of unknown metastable content and the observed energy change spectra exhibited channels associated with both $C^{2+}(2s^2)^1S$ ground state and $C^{2+}(2s2p)^3P^o$ metastable primary ions. Our recent DTES measurements [9] carried out at 6 keV, remove the ambiguity of interpretation of the earlier measurements and allow the relative importance of the product channels to be determined for both $C^{2+}\ ^1S$ ground state and $C^{2+}\ ^3P^o$ primary ions. Figure 5 shows the energy change spectra observed for each of these selected ions in a highly dissociated hydrogen target, in a pure H_2 target and the derived spectra for a pure H atom target after the molecular contributions have been subtracted.

In figure 5 we include for comparison, relative cross sections for specific product channels based on our calculations [9], using an impact parameter semi-classical treatment and a molecular expansion including a common translation factor, and those of Gu *et al* [12] which considered only the case of $C^{2+}\ ^1S$ ions. To facilitate this comparison, the maximum calculated partial cross sections have been normalised to the maximum observed peak in the energy spectra. In the $C^{2+}\ ^1S$ - H case, the observed dominance of the G2 channel is confirmed by theory, and there is reasonable accord between experiment and theory for relative magnitudes of the exothermic channels G1 and G2. This is also true in the case of the two endothermic channels G4 and G5 but observed channels G3 and G6 are smaller than the calculated values.
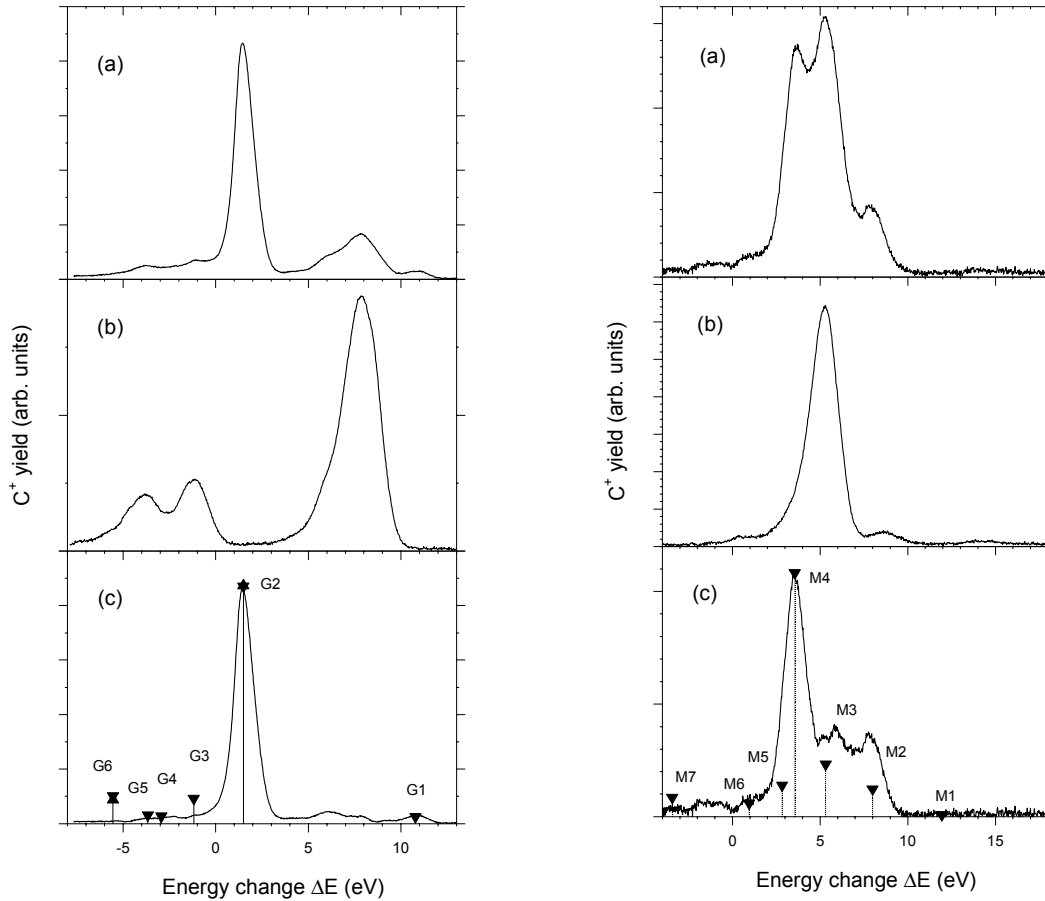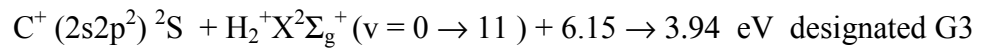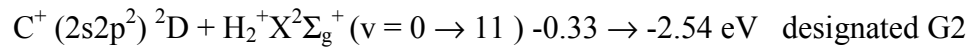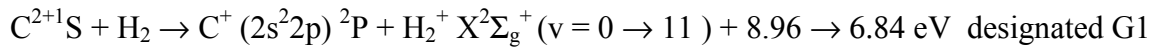

Figure 5. Energy change spectra (from [9]) for one-electron capture by 6 keV $C^{2+\ 1}S$ ions (left hand block) and by $C^{2+\ 3}P^o$ ions (right hand block) in (a) highly dissociated hydrogen, (b) in pure H_2 and (c) derived for pure H. In (c) relative values ($\blacktriangledown$) and($\blacktriangle$) are based on calculations [9] and [12] respectively. Collision product channels designated G and M are identified in table 1.

TABLE 1. MEASURED YIELDS OF ELECTRON CAPTURE CHANNELS IN ATOMIC HYDROGEN FOR 6 KEV C^{2+} ^1S IONS (DESIGNATED BY G) AND FOR C^{2+} ^3P IONS (DESIGNATED BY M) COMPARED WITH CALCULATED VALUES [9].
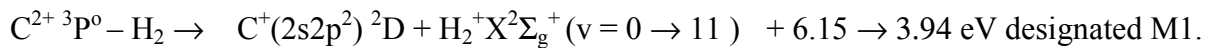
Peak	Product Channels	Energy Defect ΔE (eV)	Percentage of total yield	
			Measurement	Calculation
G1	$C^+ (2s^2 2p)$ $^2P^o$ $+ H^+$	10.78	3.5	2.2
G2	$C^+ (2s2p^2)$ ^2D $+ H^+$	1.49	88	75.9
G3	$C^+ (2s2p^2)$ ^2S $+ H^+$	-1.18	4	8.0
G4	$C^+ (2s2p^2)$ ^2P $+ H^+$	-2.94	2	2.4
G5	$C^+ (2s^2 3s)$ ^2S $+ H^+$	-3.66	1.5	2.7
G6	$C^+ (2s^2 3p)$ $^2P^o$ $+ H^+$	-5.54	1	8.8
M1	$C^+ (2s2p^2)$ ^4P $+ H^+$	11.95	0.5	0.5
M2	$C^+ (2s2p^2)$ ^2D $+ H^+$	7.99	18	7.1
M3	$C^+ (2s2p^2)$ ^2S $+ H^+$	5.32	20.5	13.5
M4	$C^+ (2s2p^2)$ ^2P $+ H^+$	3.56	46	62.5
M5	$C^+ (2s^2 3s)$ ^2S $+ H^+$	2.83	6	8.1
M6	$C^+ (2s^2 3p)$ $^2P^o$ $+ H^+$	0.95	4	3.5
M7	$C^+ (2s^2 3d)$ ^2D $+ H^+$	-0.78	3	0.0
M8	$C^+ (2s2p3s)$ ^4P $+ H^+$	-3.43	2	4.8

In the C^{2+} $^3P^o$ - H spectrum, the dominant channel M4 is correctly predicted by theory, but there are differences between experimental and calculated relative values for all the channels.

Figure 6 shows the energy change spectra obtained [5] for one-electron capture by 4 keV C^{2+} ions in collisions with H_2. The spectrum obtained using a beam of C^{2+} ions with unknown metastable content obtained directly from our ECR ion source exhibits the same main features observed in the TES measurements of Unterreiter et al [13]. Our DTES spectra in figure 6 exhibit evidence of H_2^+ being formed in vibrationally excited states and we show the position of channels up to $v = 11$. For C^{2+} ^1S ground state ions, electron capture involves only the three product channels:

$$C^{2+1}S + H_2 \rightarrow C^+ (2s^2 2p)\ ^2P + H_2^+\ X^2\Sigma_g^+ (v = 0 \rightarrow 11\ ) + 8.96 \rightarrow 6.84\ eV\ \text{ designated G1}$$

$$C^+ (2s2p^2)\ ^2D + H_2^+ X^2\Sigma_g^+ (v = 0 \rightarrow 11\ ) \text{-}0.33 \rightarrow \text{-}2.54\ eV\ \text{ designated G2}$$

$$C^+ (2s2p^2)\ ^2S + H_2^+ X^2\Sigma_g^+ (v = 0 \rightarrow 11\ ) + 6.15 \rightarrow 3.94\ eV\ \text{ designated G3}$$

The electron capture process for C^{2+} $^3P^o$ ions is highly selective with only one significant channel

$$C^{2+}\ ^3P^o - H_2 \rightarrow\ \ C^+(2s2p^2)\ ^2D + H_2^+ X^2\Sigma_g^+ (v = 0 \rightarrow 11\ )\ \ + 6.15 \rightarrow 3.94\ eV\ \text{designated M1}.$$

The well separated G and M collision product channels in the DTES spectra allows us to confirm the absence of the spin - forbidden product channel $C^+ (2s2p^2)$ ^4P + H_2^+ $X^2\Sigma_g^+$ (v). It is also worth noting that the asymmetry evident in the observed peaks reflect the influence of the Franck-Condon factors for $H_2 X^1\Sigma_g^+ (v = 0) \rightarrow H_2^+ X^2\Sigma_g^+ (v)$ transitions on the probability for electron capture into a particular level. The positions of the maxima in G2, G3 and M1 can be seen to be close to $v = 2$ where the Franck-Condon factor is known to have a maximum value [14]. However, the maximum in peak G1 is closer to $v = 5$. Recently,

calculations by Errea *et al* [27] have predicted a maximum in the vibrational distribution after capture in $C^{2+}\,{}^3P^o$ – H_2 collisions near v = 3 at 4 keV.

We have calculated a reaction window (see [15]) for one-electron capture in $C^{2+}\,{}^1S$ – H_2 collisions based on the dependence of the single crossing Landau-Zener cross section for a series of crossings in the range covered by the energy change spectra. The calculated reaction window extends from ΔE = 3.0 to 7.4 eV. However, in figure 6, it can be seen that such a window can only accommodate the products in the higher vibrationally excited states within peak G1 while the products within peaks G2 and G3 lie completely outside this window.

Energy change spectra obtained for C^{2+} - He collisions [4] are shown in figure 7. Here, results obtained using a C^{2+} ion beam of unknown metastable content derived directly from our ECR ion source may be compared with DTES spectra for pure $C^{2+}\,{}^1S$ ground state and pure $C^{2+}\,{}^3P$ metastable ions. In the case of ground state $C^{2+}\,{}^1S$ ions, the two exothermic peaks G1 and G2, surprisingly, both arise from collisions with an unidentified trace impurity species.
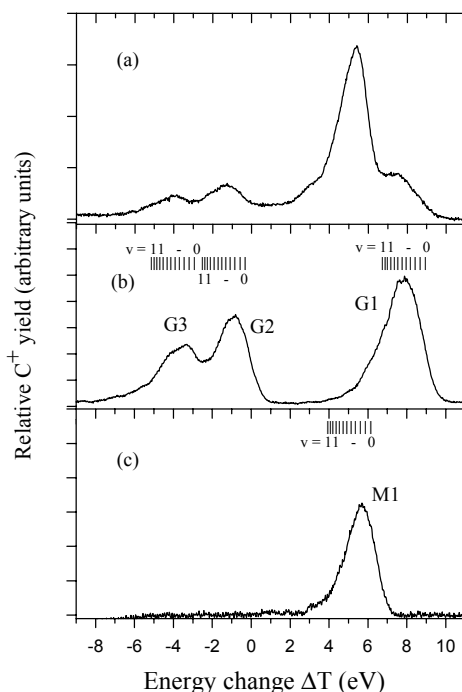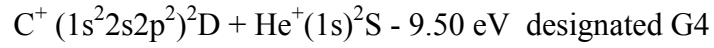

Figure 6. Energy change spectra for one-electron capture in 4 keV C^{2+}- H_2 collisions (from [5]). The spectrum (a) for C^{2+} ions of unknown metastable content obtained directly from the ion source is compared with the DTES measurements (b) for pure $C^{2+}\,{}^1S$ ground state ions and (c) for pure $C^{2+}\,{}^3P$ metastable ions. Positions of product channels corresponding to the formation of vibrationally excited $H_2^+\,X^2\Sigma_g^+(v)$ which accompany the $C^+(n, l)$ products are shown for v = 0 to 11.

These peaks account for 29% of the total product signal in spite of the fact that the background pressure in the collision region was about 100 times lower than the helium target gas pressure. Only the following two G channels, which are both endothermic, arise from collisions with He:

$$C^{2+}\,{}^1S + He \rightarrow C^+ (1s^2 2s^2 2p)^2P + He^+ (1s)^2S - 0.20 \text{ eV designated G3}$$

44

$$C^+ (1s^2 2s 2p^2)^2D + He^+(1s)^2S - 9.50 \text{ eV} \quad \text{designated G4}$$

The dominant contribution to the C^+ product ion yield arises from the G3 channel while the much smaller contribution from G4 channel involves core electron rearrangement.

In the case of C^{2+} ^3P metastable ions, electron capture occurs mainly via the exothermic channel

$$C^{2+\ 3}P + He \rightarrow \quad C^+ (1s^2 2s^2 2p)^2P + He^+(1s)^2S + 6.28 \text{ eV} \quad \text{designated M1}$$
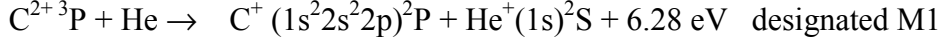
A minor peak is associated with the channel

$$C^{2+\ 3}P + He \rightarrow \quad C^+ (1s^2 2s 2p^2)^4P + He^+(1s)^2S + 0.95 \text{ eV} \quad \text{designated M2.}$$

Our DTES studies of electron capture in C^{2+} - He collisions resolve some ambiguities in previous TES measurements carried out with primary beams of unknown metastable content. For example, the peak G2 at 2.8 eV, which corresponds to a trace contaminant, was also observed by Lee e*t al* [16] who suggested that it might be associated with 'metastable' $C^{2+}(2p^2)$ ^3P ions in the primary beam, although (see [4]) this state has a lifetime of only 7.7×10^{-10} s.
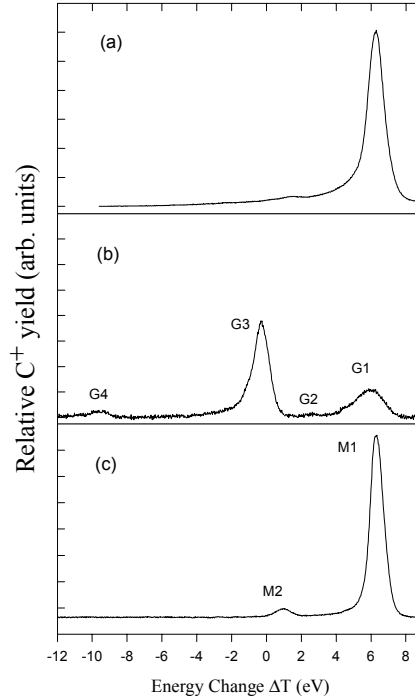

Figure 7. *Energy change spectra for one-electron capture in 4 keV C^{2+}-He collisions (from [4]). The spectrum (a) for C^{2+} ions of unknown metastable content obtained directly from the ion source is compared with the DTES measurements (b) for pure C^{2+} ground state ions and (c) for pure C^{2+} ^3P metastable ions.*

We have also carried out DTES studies of one-electron capture by C^{2+} ions in Ne, Ar [4], N_2 and O_2 [5] which allow the relative importance of the product channels for C^{2+} ^1S ground state and C^{2+} $^3P^o$ primary ions to be determined unambiguously for the first time. Figure 8 shows energy change spectra for C^{2+}- Ar collisions at 4 keV. The spectrum shown
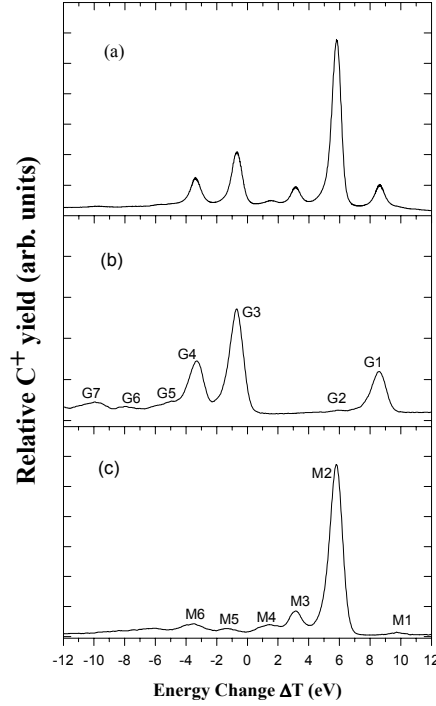

Figure 8. Energy change spectra for one-electron capture in 4 keV C^{2+}- Ar collisions (from [4]). The spectrum (a) for C^{2+} ions of unknown metastable content obtained directly from the ion source is compared with the DTES measurements in (b) for pure C^{2+} ground state ions and (c) for pure C^{2+} ^3P metastable ions.

for an ion beam of unknown metastable content direct from the ion source contains unresolvable contributions associated with one-electron capture by both ground and metastable C^{2+} ions. However, these contributions are clearly identified as peaks G1 – G7 and M1 – M6 in the DTES spectra. A detailed discussion of the channels corresponding to these peaks has been given by Greenwood *et al* [4]. The main peaks G3 in the C^{2+} ^1S ground state spectrum and M2 in the C^{2+} $^3P^o$ metastable spectrum both arise from the product channel C^+ ($2s\,2p^2$) ^2D + Ar^+ ($3s^23p^5$) ^2P which involve energy defects of –0.67 eV and + 5.82 eV respectively

3.2 DTES measurements with N^{2+} ions

Recently, we have carried out DTES measurements [10] of the process

$$N^{2+} + H(1s) \rightarrow N^+(n,\ l) + H^+$$
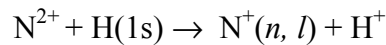
at energies within the range 0.8 – 6.0 keV using a beam of pure ground-state $N^{2+}(2s^22p)$ $^2P^o$ primary ions. These new measurements allow comparison with current theoretical predictions and a re-evaluation of previous TES measurements [17] of this process carried out in this laboratory with ion beams containing an unknown fraction of metastable $N^{2+}(2s2p^2)$ ^4P ions.

Figure 9 shows energy change spectra obtained for one-electron capture by 6 keV N^{2+} ions in atomic hydrogen. The 'mixed' beam spectrum for N^{2+} ions obtained directly from the ion source containing an unknown fraction of metastable ions may be compared with the spectrum obtained using a state-prepared pure N^{2+} ^2P ground-state beam. In this case, the 'mixed' beam and pure ground state spectra are very similar evidently because collision product channels with not greatly different energy defects provide the dominant contributions to both.
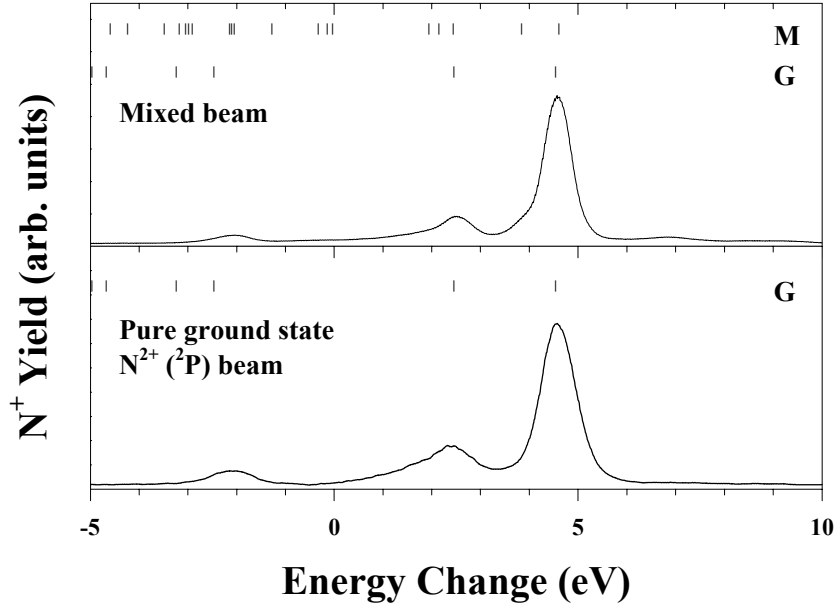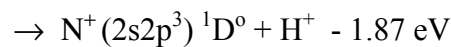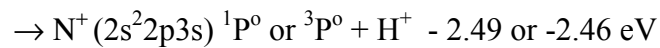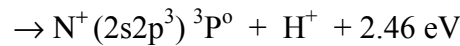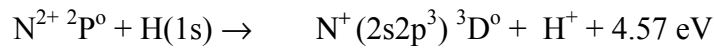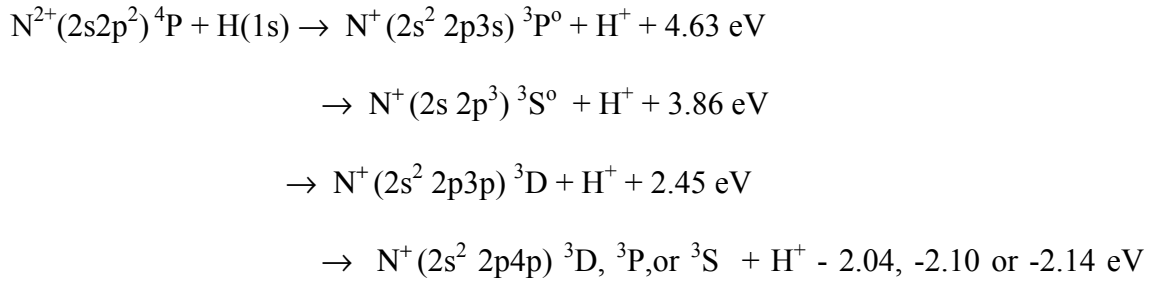

Figure 9. Energy change spectra (from [10]) obtained for one-electron capture by 6 keV N^{2+} ions in atomic hydrogen. The 'mixed' beam spectrum for N^{2+} ions obtained with ions containing an unknown fraction of metastable ions is compared with the DTES spectrum obtained using a pure N^{2+} $^2P^o$ ground-state beam. Positions of possible product channels corresponding to ground-state primary ions (G) and metastable primary ions (M) are also shown.

In the case of ground-state primary ions, the three main product channels can be identified as:

$$N^{2+}\,^2P^o + H(1s) \rightarrow \quad N^+\,(2s2p^3)\,^3D^o + H^+ + 4.57\ eV$$

$$\rightarrow N^+\,(2s2p^3)\,^3P^o + H^+ + 2.46\ eV$$

$$\rightarrow N^+\,(2s^2 2p3s)\,^1P^o\ or\ ^3P^o + H^+ - 2.49\ or\ -2.46\ eV$$

$$\rightarrow N^+\,(2s2p^3)\,^1D^o + H^+ - 1.87\ eV$$

of which the two exothermic channels (which involve core excitation) are dominant.

In the case of metastable primary ions, the channels which seem most likely to contribute to the observed 'mixed' beam spectrum are:

$$N^{2+}(2s2p^2)\,^4P + H(1s) \rightarrow N^+(2s^2\,2p3s)\,^3P^o + H^+ + 4.63\ eV$$

$$\rightarrow N^+(2s\,2p^3)\,^3S^o + H^+ + 3.86\ eV$$

$$\rightarrow N^+(2s^2\,2p3p)\,^3D + H^+ + 2.45\ eV$$

$$\rightarrow N^+(2s^2\,2p4p)\,^3D,\,^3P,\text{or}\,^3S + H^+ - 2.04,\ -2.10\ \text{or}\ -2.14\ eV$$

The close similarity between the 'mixed' beam and pure ground-state energy change spectra using DTES confirms the results of our earlier TES measurements [17] in the range 0.6 – 8.0 keV using N^{2+} beams which contained an admixture of metastable ions. In those measurements, changes in the metastable fraction were found to have no detectable effect on the measured total electron capture cross sections leading us to conclude that the total cross sections for ground and metastable ions N^{2+} in atomic hydrogen were not greatly different. In view of the lack of dependence of these total cross sections on the metastable content of the primary beam, we have normalised the DTES data obtained at different energies (table 2) to our previously measured total electron capture cross sections [17]. The latter values are in good agreement with measurements by Seim *et al* [18] and by Phaneuf *et al* [19] in the energy ranges of overlap.

TABLE 2. CROSS SECTIONS FOR FORMATION OF $N^+\,^3D^O$, $^3P^O$ AND ($^1P^O + ^3P^O + ^1D^O$) IN $N^{2+}\,^2P^O$ – H(1S) COLLISIONS [10].

Energy (keV)	Cross sections ($10^{-16}\ cm^2$)		
	$N^+\,^3D^O$	$N^+\,^3P^O$	$N^+(^1P^O + ^3P^O + ^1D^O)$
0.8	3.19 ± 0.26	0.32 ± 0.26	-
1.2	2.97 ± 0.36	0.40 ± 0.37	-
1.5	3.16 ± 0.31	0.30 ± 0.31	-
3.0	3.80 ± 0.63	0.88 ± 0.51	0.15 ± 0.68
6.0	3.53 ± 0.53	1.70 ± 0.45	0.43 ± 0.62

In figure 10, these cross sections for $N^+\,^3D^o$, $^3P^o$ and $N^+(^1P^O + ^3P^O + ^1D^O)$ formation can be seen to be in good accord with the values obtained in our previous TES measurements [17]. However, it is important to note that, in the lower resolution measurements of [17], the small peak comprising the $N^+(^1P^o + ^3P^o + ^1D^o)$ contributions from endothermic channels were incorrectly identified as due to the $N^+(^1D^o)$ product channel alone. In addition, the measurements of [17] also recorded at and above 6 keV very small contributions from a $N^+(2s^22p3p)\,^3P$ product channel corresponding to $\Delta E = -5.17$ eV; these are absent in the higher resolution DTES measurements. Figure10 also includes cross sections for the main $^3D^o$ product channel calculated by Bienstock *et al* [20] using a molecular approach which extends earlier theoretical work by Heil *et al* [21]. These calculations predict the $^3D^o$ product channel is the only significant electron capture channel at the energies considered and are therefore at variance with experiment. More recent quantal calculations carried out by Herrero *et al* [22], in which molecular states were obtained using *ab initio* SCF-CI methods, correctly predict contributions from channels other than the dominant $^3D^o$ product channel.
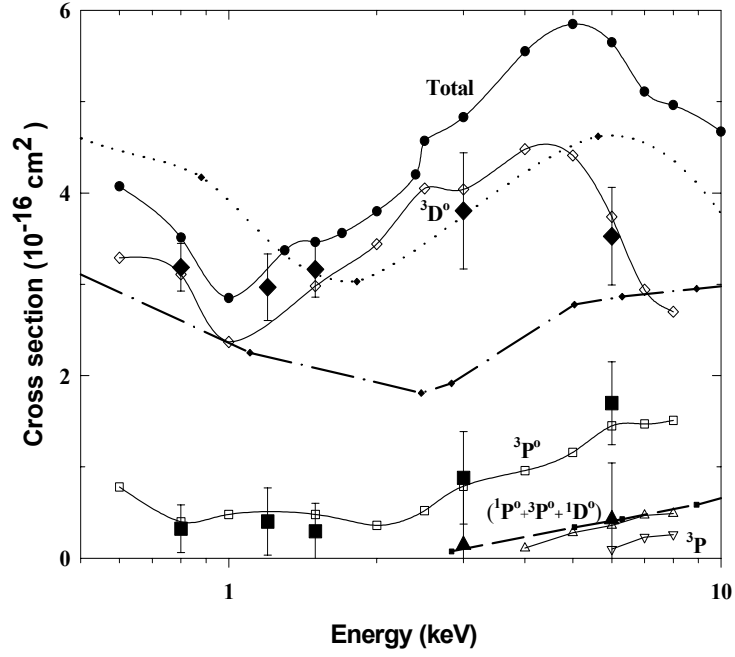
Figure 10. Cross sections for one-electron capture by N^{2+} ions in atomic hydrogen leading to specified $N^+(n, l)$ products. DTES measurements [10] with pure ground-state N^{2+} $^2P^o$ ions, ◆,$^3D^o$; ■, $^3P^o$;▲, ($^1D^o + {}^1P^o + {}^3P^o$). Previous TES measurements [17] using an N^{2+} beam containing an unknown fraction of metastable ions, ●, total; ◊ ,$^3D^o$; □, $^3P^o$; Δ, ($^3P^o + {}^1P^o + {}^1D^o$); ∇, ^3P. Theory by Bienstock et al [20], · · · · · · · ·, $^3D^o$. Theory by Herrero et al [22], — · — · ,$^3D^o$; — — —, $^3P^o$.

However, in the energy range shown in figure 10, their calculated cross sections for the $^3D^o$ and $^3P^o$ channels are not in very satisfactory agreement with the experimental values.

Although our measurements have shown that cross sections for one-electron capture in N^{2+} - H collisions at keV energies are insensitive to the metastable content of the ion beams used, this is certainly not the case for collisions with H_2. We have carried out DTES studies of one-electron capture by N^{2+} $^2P^o$ ground state ions in collisions with H_2 at energies within the range1.75 - 8 keV [7] which resolve discrepancies and serious ambiguities in previous measurements carried out with N^{2+} beams containing unknown fractions of metastable ions. At the energies considered, both non-dissociative and dissociative electron capture channels of the type

$$N^{2+} + H_2 \rightarrow N^+ (n, l) + H_2^+ (\Sigma)$$

$$\rightarrow N^+ (n, l) + H^+ + H(n',l')$$
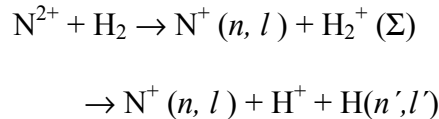
are found to be significant. In figure 11, which shows DTES data obtained at 6 keV, the pure ground state and 'mixed' N^{2+} beam energy change spectra can be seen to be very different.
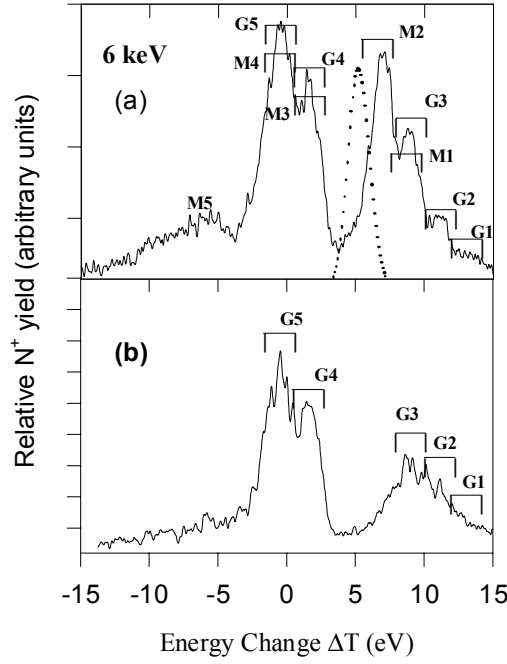
Figure 11. Energy change spectra for one-electron capture in 6 keV N^{2+}- H_2 collisions (from [7]). The spectrum in (a) for N^{2+} ions of unknown metastable content obtained directly from the ion source is compared with the DTES measurements in (b) for pure N^{2+} $^2P^o$ ground state ions. Peaks designated G and M correspond to primary ions in the respective $^2P^0$ ground state and ^4P metastable states. A calculated Landau-Zener reaction window is shown by a dotted line.

While the pure ground state spectrum can be interpreted unambiguously, the prominent peak M2 around 7 eV in the mixed beam spectrum illustrates the strong influence of an unknown admixture of metastable ions. In addition, the long endothermic tail, which is less prominent in the pure ground state spectrum, extends back to about -15 eV and makes a significant contribution to the total N^+ signal. This includes many contributing channels including dissociative one-electron capture via the H_2^+ $A^2\Sigma_u^+$ repulsive state. The G and M channels shown in Figure 11 are identified in table 3. While a full quantitative analysis of the G peaks in our energy change spectra obtained with pure ground N^{2+} ions is precluded by insufficient energy resolution, the peaks (G1+G2+G3), G4 and G5 account for about 37%, 18% and 32% respectively of the total N^+ yield at 8.0 keV and about 31%, 18% and 35% of the total at 6.0 keV. The substantial differences between the pure ground state and mixed beam energy change spectra indicate that interpretations of previous TES measurements and, indeed total cross section measurements, in terms of an assumed 100% ground state primary ion beam are invalid. For example, the energy change spectrum published by Rajgara *et al* [23] at 1.75 keV is considerably different from both our mixed beam spectrum (with a likely different metastable content) and our pure ground state spectrum. Their spectrum, unlike ours, shows no evidence of collision channels in the range -2 to 1 eV. In addition, while they do observe a peak near 7 eV (which our measurements clearly show corresponds to the metastable channel M2) they wrongly attribute this to a ground state primary ion channel. The DTES data are also at variance with our earlier TES measurements (McCullough *et al* [24]) at 8 keV where no channels associated with metastable primary ions were observed.

TABLE 3. COLLISION PRODUCT CHANNELS FOR ONE-ELECTRON CAPTURE IN N^{2+} - H_2 COLLISIONS. PEAKS DESIGNATED G AND M (FIGURE 11) CORRESPOND TO PRIMARY IONS IN THE RESPECTIVE $^2P^o$ GROUND STATE AND ^4P METASTABLE STATES. THE ENERGY DEFECTS SHOWN ALLOW FOR VIBRATIONAL EXCITATION OF H_2^+($v = 0 \rightarrow$ D.L) WHERE D.L IS THE DISSOCIATION LIMIT

Peak	Collision product channels	Energy defect (eV)
G1	$N^+ 2s^2 2p^2$ (^3P) + H_2^+ (X $^2\Sigma_g^+$ v =0 $\rightarrow$ D.L)	11.51 $\rightarrow$ 14.16
G2	$N^+ 2s^2 2p^2$ (^1D) + H_2^+ (X $^2\Sigma_g^+$ v =0 $\rightarrow$ D.L)	9.61 $\rightarrow$ 12.26
G3	$N^+ 2s^2 2p^2$ (^1S) + H_2^+ (X $^2\Sigma_g^+$ v =0 $\rightarrow$ D.L)	7.46 $\rightarrow$ 10.11
G4	$N^+ 2s2p^3$ (^3D) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	0.07 $\rightarrow$ 2.72
G5	$N^+ 2s2p^3$ (^3P) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	-2.03 $\rightarrow$ 0.62
M1	$N^+ 2s2p^3$ (^3D) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	7.12 $\rightarrow$ 9.77
M2	$N^+ 2s2p^3$ (^3P) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	5.02 $\rightarrow$ 7.67
M3	$N^+ 2s^2 2p3s$ (^3P) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	0.10 $\rightarrow$ 2.75
M3	$N^+ 2s2p^3$ (^3S) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	-0.67 $\rightarrow$ 1.98
M3	$N^+ 2s^2 2p^2$ (^3P) + [H_2^+ ($A^2\Sigma_u^+$) $\rightarrow$ H^+ +H]	3.0 $\pm$ 2.0
M4	$N^+ 2s2p3p$ (^3P) + H_2^+ (X $^2\Sigma_g^+$ v = 0 $\rightarrow$ D.L)	-2.09 $\rightarrow$ 0.56
M4	$N^+ 2s2p^2$ (^5S) + [H_2^+ ($A^2\Sigma_u^+$) $\rightarrow$ H^+ +H]	-3.0 $\pm$ 2.0

Since there are no detailed theoretical studies of the N^{2+} - H_2 system, we have calculated Landau-Zener windows (see McCullough *et al* [15] for N^{2+} $^2P^o$ impact as shown in figure 11. These windows are found to be seen to be centred on energies which shift from about 4.5 eV at 1.75 keV to about 5.2 eV at 8 keV. As in the case shown in figure 11, the main observed collision channels are not well described by these reaction windows.

We have also carried out DTES studies of one-electron capture in collisions of N^{2+} with He, Ne and Ar [6] which also provide a more detailed and reliable assessment of the main collision product channels than has been possible in previous studies.

3.3 DTES measurements with O^{2+} ions

The interpretation of previous total electron capture cross sections and TES measurements with O^{2+} ions has been complicated by the possible presence of O^{2+} ($2s^2 2p^2$) ^1D and O^{2+} ($2s^2 2p^2$) ^1S metastable ions in addition to O^{2+} ($2s^2 2p^2$) ^3S ground state ions in the primary ion beams. For example, our previous TES studies [25] of one-electron capture in O^{2+}- H(1s) collisions at energies in the range 2 – 8 keV, revealed two peaks in the energy change spectra.. The main peak, which accounts for about 70% of the total O^+ yield could be identified with the ground state primary ion channel

$$O^{2+} (2s^2 2p^2) \ ^3S \ + H(1s) \rightarrow \ O^+ (2s2p^3)2p \ ^4P + H^+ + 6.64 \ eV$$
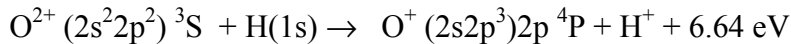
but the available energy resolution could not exclude a possible small contribution from O^{2+} ^1S metastable primary ion channel

$$O^{2+} (2s^2 2p^2) \ ^1S \ + H(1s) \rightarrow \ O^+ (2s2p^3)2p \ ^2D + H^+ + 6.29 \ eV$$
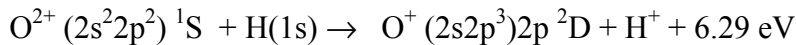
The second smaller peak in the observed spectra was correlated with the O^{2+} ^1D metastable primary ion channel

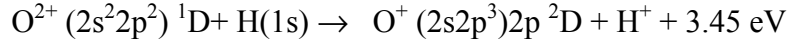$$O^{2+} (2s^2 2p^2) \; {}^1D + H(1s) \rightarrow \; O^+ (2s 2p^3) 2p \; {}^2D + H^+ + 3.45 \text{ eV}$$

Figure 12 shows a DTES energy change spectrum [11] obtained at 6 keV for a beam of pure O^{2+} ^3S ground state ions compared with a 'mixed' beam spectrum measured for O^{2+} ions of unknown metastable content direct from the ion source. In the 'mixed' beam spectrum, the O^+ $(2s 2p^3) 2p$ ^2D contribution in the smaller of the two peaks arising from electron capture by O^{2+} ^1D metastable ions can be clearly seen while, in the pure O^{2+} ^3S spectrum, the single peak corresponds to the O^+ $(2s 2p^3) 2p$ ^4P product channel. These measurements confirm the low energy quantal calculations by Butler $et\ al$ [26] which predict that only the O^+ $(2s 2p^3) 2p$ ^4P product channel should be significant for O^{2+} ^3S ground state ion impact.

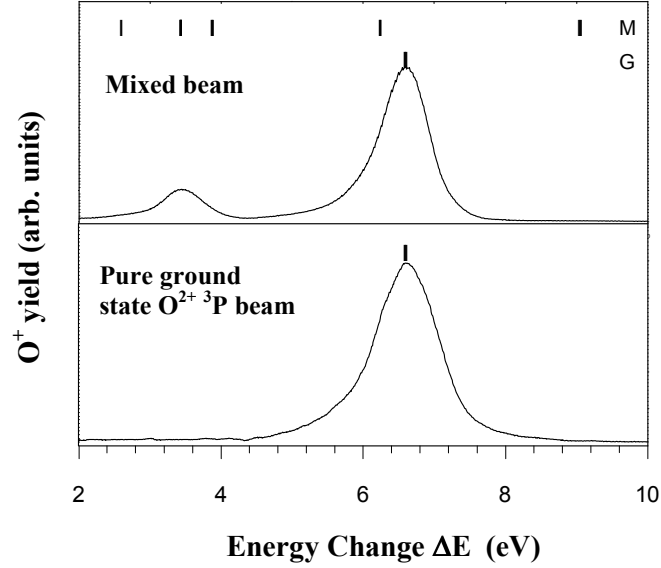*Figure 12. Energy change spectra (from [11]) for one-electron capture in O^{2+} - H(1s) collisions (a) by a beam of O^{2+} ions of unknown metastable content obtained directly from the ion source and (b) by pure O^{2+} ^3S ground state ions prepared by DTES. Possible product channels associated with O^{2+} ^1D metastable ions and O^{2+} ^3S ground state ions are indicated as M and G respectively.*

We have also carried out preliminary DTES studies of one-electron capture by O^{2+} ions in He, Ne and Ar [8]. Only in the case of the measurements in He has it so far been possible to obtain energy change spectra for O^{2+} ^1D metastable ions as well as O^{2+} ^3S ground state ions. However, the measurements again demonstrate the advantages of DTES over previous TES measurements where peak assignments have been in doubt.

4. CONCLUSION

Our measurements with state-prepared C^{2+}, N^{2+} and O^{2+} have demonstrated that DTES is a powerful technique capable of providing detailed information on state-selective electron capture without the ambiguities of interpretation associated with previous measurements carried out with ion beams of unknown metastable content. DTES measurements in several atomic and molecular gases of fusion interest and in atomic hydrogen have been made. Our apparatus does not yet provide absolute cross sections for each selected ground or metastable species but the collision product channels can be identified unambiguously and their relative

importance determined. The data provide a much more reliable assessment of the range of validity of a number of theoretical predictions than has been possible previously and help to resolve some of the serious discrepancies in both TES measurements and in total cross sections obtained previously in different laboratories.

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