Studies of Collision Mechanisms in Electron Capture by Slow Multiply Charged Ions

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Abstract. We review measurements based on translational energy spectroscopy which are being used to identify and assess the relative importance of the various collision mechanisms involved in one-electron capture by slow multiply charged ions in collisions with simple atoms and molecules.

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 ion trap operation and design, to many astrophysical phenomena and to fusion devices. Ion sources of the EBIS and ECR type have made it possible to carry out experimental studies with a wide range of multiply charged ions in collisions with both atoms and molecules. However, measurements at energies below 1 keV amu⁻¹ are still comparatively sparse and often exhibit large unexplained discrepancies while the range of validity of many theoretical models is uncertain.

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 $\Delta T$ is then given by

$$\Delta T = T_2 - T_1 = \Delta E - \Delta K$$
where $\Delta K$ is a small recoil correction of the target. Provided 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 $\Delta E$ 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 and is complementary to methods based on photon emission spectroscopy (PES). The TES approach can reveal 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]). A detailed quantitative analysis is then precluded unless the metastable content of the beam can be specified. However, such TES studies do show that 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. There is also a need for data on electron capture by both ground state and metastable species. For these reasons, in recent years we have also used 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. These state prepared ions are then used as primary ions in a second stage of TES.

**FIGURE 1.** Schematic diagram of the Belfast single and double translational energy spectrometers.
In 1983 we first demonstrated the feasibility of carrying out TES measurements in atomic hydrogen by using a tungsten tube furnace as a target cell and this technique has subsequently been used in many other laboratories. More recently we have used a specially developed aluminium target cell fed with highly dissociated hydrogen from a microwave-driven discharge source. In this way we have been able to carry out DTES measurements in atomic hydrogen for the first time.

In this review, we shall describe the results of measurements using TES and DTES for a few representative processes involving atoms and simple molecules which illustrate the current degree of understanding of the collision mechanisms involved in one-electron capture by multiply charged ions.

**DTES measurements in atomic hydrogen**

Our previous TES studies [2] of the electron capture process

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

were carried out with ion beams of unknown metastable content and the observed energy change spectra exhibited channels associated with both \(\text{C}^{2+}(2s^2)^1S\) ground state and \(\text{C}^{2+}(2s2p)^3P^o\) metastable primary ions of which the latter were dominant. Our more recent DTES measurements [3] 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 \(\text{C}^{2+}\) and \(\text{C}^{2+}\) primary ions.

![Figure 2](image_url)

**Figure 2.** Energy change spectra (from [9]) for one-electron capture by 6 keV \(\text{C}^{2+}\) ions (left hand block) and \(\text{C}^{2+}\) ions (right hand block) in (a) highly dissociated hydrogen, (b) in pure \(\text{H}_2\) and (c) derived for pure \(\text{H}\). In (c) relative values (\(^*\)) and(\(\triangle\)) are based on calculations [3] and [4] respectively.
Figure 2 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. We include for comparison, relative cross sections for specific product channels based on our calculations [3], using an impact parameter semi-classical treatment and a molecular expansion including a common translation factor, and those of Gu \textit{et al} [4] 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. In the C\(^{2+}\) 3P\(^0\) - 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.

In another example of the use of DTES, we consider O\(^{2+}\) - H(1s) collisions where 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\(^3\)) 1D metastable ions in addition to O\(^{2+}\) (2s\(^2\)2p\(^5\)) 3S ground state ions in the primary ion beams.

Figure 3 shows our DTES energy change spectrum [5] 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\(^+\) (2s2p\(^3\))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\(^+\) (2s2p\(^3\))2p 4P product channel.

\[
\text{O}^{2+} (2s^22p^3) 3S + \text{H}(1s) \rightarrow \text{O}^+ (2s2p^3)2p 4P + \text{H}^+ + 6.64 \text{ eV}
\]

\[
\begin{array}{c}
\text{O}^+ \text{ yield (arb. units)} \\
\text{Mixed beam} \\
\text{Pure ground state O}^{2+} 3P \text{ beam}
\end{array}
\]

\textbf{Figure 3.} Energy change spectra 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.
Our measurements confirm the low energy quantal calculations by Butler et al [6] which predict that only the $\text{O}^+ (2s2p^3)2p^4\text{P}$ product channel should be significant for $\text{O}^+ \text{S}^3$ ground state ion impact.

**Collisions of He$^{2+}$ ions with Simple Molecules**

In 1995 our TES studies [7] of He$^{2+}$ - H$_2$ collisions (Figure 4) provided the first direct evidence of the great importance of highly selective dissociative excitation mechanisms in the one-electron capture process at low energies.

![Figure 4](image.jpg)

*Figure 4. Energy change spectra for one-electron capture by 0.5 and 2 keV amu$^{-1}$ He$^{2+}$ ions in H$_2$.*

At 0.5 keV, the dominant collision channel (Peak B) can be seen to correspond to dissociative electron capture accompanied by the formation of H atoms in the n = 2 states (mainly 2p) and this has been supported by PES measurements [8] in Groningen. In the non-dissociative capture channels (Peaks A and C) He$^+$ ions are formed in either the n = 2 or n = 3 states and account for only about 1% of the total at 0.5 keV amu$^{-1}$ and 25% at 2.0 keV amu$^{-1}$. Peak D arises from water vapour as a trace contaminant. Recently, calculations have been carried out by the Madrid group [9] which confirm importance of this dissociative excitation process in one-electron capture but quantitative agreement with experiment is not very good. There are also serious unexplained discrepancies between experimentally measured total cross sections for this system at low energy.

Our subsequent TES studies [10] of one-electron capture by 0.2 – 1 keV amu$^{-1}$ He$^{2+}$ ions in CO have also confirmed the dominant role of processes involving dissociative electron capture at low energies. The contribution from many unresolved dissociative electron capture channels associated with He$^+(1s)$ formation accounts for about 99% of the total cross section at the lowest energy considered. In addition, for the first time, excited product channels in non-dissociative one-electron capture were identified. The He$^+(n = 2) + \text{CO}^+ [X^2\Sigma^+]$ formation channel is the most important of these channels. This accounts for about 40% of the total cross section at 1 keV amu$^{-1}$ although the contribution falls to about 1% at 0.2 keV amu$^{-1}$.

Very recently [11] we have also confirmed that dissociative excitation channels also increase in relative importance with decreasing energy in the case of He$^{2+}$ ions in H$_2$O and in CH$_4$. Figure 5 shows energy change spectra for one-electron capture by 0.25 – 2 keV amu$^{-1}$ He$^{2+}$ ions in H$_2$O.
Figure 5. Energy change spectra for one-electron capture by 0.25 - 2 keV amu\(^{-1}\) He\(^{2+}\) ions in H\(_2\)O. 

In this case the broad exothermic peak associated with He\(^{+}\)(n = 1) formation is likely to involve mainly transfer dissociative ionization channels.

**Collisions of H and He-like ions of C, N and O with H atoms**

Recently [12,13] we have used TES in conjunction with an aluminium target cell fed by highly dissociated hydrogen from a microwave discharge source to study one-electron capture by H and He-like ions of C, N and O at energies below 1 keV amu\(^{-1}\). In all cases it is found that, as the impact energy decreases, electron capture becomes more selective until only a single product \(n\) channel is significant. This is illustrated by the results shown in Figure 6 for N\(^{5+}\) in H.

**Figure 6**: One-electron capture into the \(n = 4\) and \(n = 3\) states of N\(^{4+}\) by N\(^{5+}\) ions in atomic hydrogen shown as a fraction of the total electron capture cross section. Experiment: ●, our work; Δ, Dijkkamp *et al* [14]. Theory: — —, Shimakura and Kimura [15]; ———, Bendahman *et al* [16].
There are large discrepancies between previously measured total cross sections for this case so here we show our measured yields of \( N^{4+} \) product ions in the \( n = 4 \) and \( n = 3 \) states expressed as a fraction of the total electron capture cross section. Our data are in good accord with the higher energy PES measurements of Dijkkamp et al [14]. Theoretical estimates of the \( N^{5+} - H(1s) \) one-electron capture process by Bendahman et al [16] based on a molecular orbital expansion method and by Shimakura and Kimura [15] based on both quantum mechanical and semiclassical molecular-orbital expansion methods extend down to the low energies considered here. Their predicted relative yields of both the \( n = 4 \) and \( n = 3 \) states are included in figure 6. The theoretical values of Bendahman et al [16] can be seen to be in somewhat better accord with the low energy experimental values for \( n = 4 \) capture but, in the case of \( n = 3 \) capture, their predicted yields are significantly smaller than those calculated by Shimakura and Kimura [15]. However, neither theory satisfactorily describes the very rapid decrease in the \( n = 3 \) state yields observed at low energies in the present work. The main product channel in this and the other cases studied are quite well predicted by reaction windows based on a simple Landau-Zener approach.

### Collisions of H and He-like ions of C, N and O with \( H_2 \)

Our TES measurements [13] for one-electron capture by H and He-like ions of C, N and O in collisions with \( H_2 \) at energies below 1 keV amu\(^{-1}\) have revealed striking differences in behaviour. The results for \( N^{5+} \) in \( H_2 \) the energy change spectra for which are shown in Figure 7, are of special interest. At the highest energy of 857 eV amu\(^{-1}\), three main peaks centred on energy defects of about 8, 24 and 42 eV are apparent. The largest of these corresponds to the non-dissociative capture process

\[
N^{5+}(1s^2)^1S + H_2(1\Sigma_g^+) \rightarrow N^{4+}((1s^2)^23s,3p,3d) + H_2^+(v = 10 - 0) + (20.4 - 25.9) \text{ eV}
\]

which involves capture into the three \( N^{4+}(3s,3p,3d) \) sublevels together with some evidence of vibrational excitation of the \( H_2^+ \) product ion. The second largest peak in the spectrum at 857 eV amu\(^{-1}\) can be identified with a similar process

\[
N^{5+}(1s^2)^1S + H_2(1\Sigma_g^+) \rightarrow N^{4+}(1s^2)^24s,4p,4d,4f) + H_2^+(v = 10 - 0) + (3.78 - 7.29) \text{ eV}
\]

involving electron capture into the \( N^{4+}(4s,4p,4d,4f) \) sublevels. The third peak in the spectrum at 857 eV amu\(^{-1}\), which involves the largest energy defects, contains possible contributions from a number of incompletely resolved processes leading to \( N^{4+}(n = 2) \) production. The main contribution appears to be due to the dissociative electron capture process

\[
N^{5+}(1s^2)^1S + H_2(1\Sigma_g^+) \rightarrow N^{4+} (n = 2) + H^+ + H(2l) + (36.87 - 61.61) \text{ eV}
\]

but contributions from

\[
N^{5+}(1s^2)^1S + H_2(1\Sigma_g^+) \rightarrow N^{4+} (n = 2) + H^+ + H^+ + e + (34.15 - 49.66) \text{ eV}
\]

also appear likely.

At impact energies below 857 eV amu\(^{-1}\), the peaks corresponding to \( N^{4+}(n = 3) \) and \( N^{4+}(n = 3) \) formation remain as major features of the energy change spectra. However, additional collision mechanisms leading to \( N^{4+}(n = 2) \) production become apparent. In particular, at our lowest energy of 214 eV amu\(^{-1}\), the dominant peak (centred on an
energy defect of about 28 eV) can be correlated with the autoionizing double capture channels

\[
N^5+(1s^2 1S) + H_2(1\Sigma^+) \rightarrow N^3+(***) + H^+ + H^+ \\
\rightarrow N^4+(1s^2 2p) + H^+ + H^+ + e + (24.15 - 39.66) \text{ eV} \\
\rightarrow N^4+(1s^2 2s) + H^+ + H^+ + e + (34.15 - 49.66) \text{ eV}
\]

of which 2p formation is dominant. However, it will be noted that due to the overlap in the energy defects of the various channels, a clear quantitative assessment is impossible.

These results are in contrast with the situation in He\(^{2+} - H_2\) where we found that dissociative excitation was the main electron capture mechanism at low energies. The most surprising feature is the dominant role at the lower energies of the two-electron
capture autoionizing mechanism leading to $N^{4+}(n = 2)$ production. In order to compare our TES measurements with other relevant data, we have normalised our observed relative $N^{4+}$ yields to total cross sections we measured using a simple beam attenuation technique. This procedure was adopted because of large discrepancies between previously published total cross sections. Cross sections obtained in this way for $N^{4+}(n = 2)$, $N^{4+}(n = 3)$ and $N^{4+}(n = 4)$ formation are compared in Figure 8 with PES measurements [17,18,19] of the KVI Groningen group and some theoretical estimates. Unlike the PES data, our TES measurements have been able to record the substantial contribution of the $N^{4+}(n = 2)$ products to the total one-electron capture cross section. The preliminary theoretical estimate [20] by the Madrid group of cross sections for autoionizing double capture leading to $N^{4+}(n = 2)$ formation can be seen to be much smaller and in poor agreement with our measured cross sections.

Our TES measurements over the same energy range for one-electron capture by both $O^{6+}$ and $C^{4+}$ ions in $H_2$ are very different from the case of $N^{5+}$ in $H_2$. In both cases non-dissociative electron capture is found to be the main collision mechanism.

In the case of electron capture by the hydrogen-like C, N and O ions in $H_2$ there are also significant differences. For $O^{7+}$ in $H_2$ non-dissociative and dissociative capture are found to be of about equal importance but for $N^{6+}$ in $H_2$ there is no evidence of dissociative electron capture. In contrast, for $C^{5+}$ in $H_2$ dissociative electron capture is substantial and increases in relative importance with decreasing energy when evidence of a two-electron autoionizing capture mechanism also appears. We also find that, in the absence of detailed theoretical calculations, the main product channels observed in our measurements on $H_2$ are not well predicted by reaction windows based on a simple Landau-Zener approach.

Conclusions

Translational Energy Spectroscopy (TES) continues to be an important technique for identifying and assessing the relative importance of the main collision mechanisms leading to state selective electron capture in collisions with atoms and simple molecules. However, it is often difficult to normalize these data because of unexplained discrepancies in previously published total cross sections.

We have also shown that DTES can be used to carry out measurements with state-prepared ion beams - even in atomic hydrogen targets - to obtain data for ground and metastable primary ions. It avoids the errors and ambiguities in the interpretation of previous measurements carried out with beams containing unknown fractions of metastable ions.

In the case of collisions with $H_2$ and other simple molecules below 1 keV amu$^{-1}$, we have found striking differences in the relative importance of contributions from non-dissociative and dissociative capture as well as from two-electron capture into autoionizing states. We have also observed discrepancies with theoretical predictions and with some previous measurements based on photon emission spectroscopy.

Our TES measurements in atomic hydrogen below 1 keV amu$^{-1}$ show that, as the impact energy decreases, electron capture becomes more selective until only a single $n$ product channel is significant. These product main channels are well described by reaction windows calculated using a simple Landau-Zener approach. However, the
same approach applied to the more complex energy change spectra observed in H$_2$ is much less successful.

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