Spectral line shape and angular momentum

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Abstract. Data have been obtained for ejection of valence shell 4p and 3d electrons in krypton and the \( ^{1}t_{2} \) and \( ^{2}a_{1} \) orbitals in methane. Measurements, with kinematics both on and off the Bethe ridge, examine how the spectral shapes change for fixed energies of 1015 eV for the incident electron, 880 eV for scattered and 120 eV for ejected electron and angular momentum changes. The studied interactions are activated by excitation and ionization of inner shell (-d) electrons and concern complex electron correlations. The triple differential cross sections for the Bethe ridge conditions within the experimental accuracy are similar to the values predicted by the Distorted Wave Impulse Approximation and Born Approximation calculations but need further consideration of electron correlation effects.

1. Introduction

This paper is part of studies of atomic spin-dependent interactions which are activated by excitation and ionization of inner shell (-d) electrons and concern complex electron correlations. Substantial improvement of instrumentation for production and detection of electron spin are encouraging the study of Auger processes with the emission of a recoiled ion and two electrons, one fast and one slow, as functions of angular momentum. Fig. 1 is a representation of the electron scattering geometry where \( E_{i} \) are the energies and \( k_{i} \) are the momentum vectors of the incident (0), scattered (s) and ejected (e) electrons, for recoil and binary peaks scattering mechanisms with momenta \( k_{0} - k_{e} = k_{s} \) and energy \( |k_{0} - k_{s}|^2 = 2E_{e} \). Also shown are typical coplanar TDCS (triple differential cross sections) for ionisation of the 4p orbital of krypton (details in caption). Other studies in helium of auto-ionization and direct ionisation processes, and post-collision-interaction effects of \( ^{1}D \) and \( ^{1}P \) states, are reported separately.

Figure 1. (left) Electron scattering (E, k, \( \theta_{i} \)) kinematics for incident, scattered and ejected (0, s, e) electrons and (right) coplanar TDCS (triple differential cross sections) for ionisation of the 4p orbital.
of krypton with $E_0 = 1014$ eV, $E_a = 880$ eV and $E_e = 120$ eV. The values of $\theta_s$ are indicated in the figure and $\theta_s = 20^\circ$ correspond to the Bethe ridge condition.

Further interpretation of this collision process is obtained by considering second order effects which indicate that auto-ionization profiles tend to be more symmetric at backward angles, i.e. in the recoil direction. The second order terms describe elastic scattering of the electron by the nucleus, coupling between degenerate states and successive interactions of the scattered particle with each electron. Fair agreement of the measured data is modelled by different potentials influencing the scattered electrons wave function in the ionising, excitation and resonance amplitudes.[1, 2, 3]

2. Krypton

Angular distributions of the Auger lines in krypton are shown in Fig. 2 for $E_0$ of 1014 eV and $E_{A0}$ of 50 eV to 59 eV. Fig. 2 (right) is a 3-dimensional display of the data to aid the visualisation of the angular distributions and Fig. 2 that the $M_3-N_{23}N_{23}$ and $M_4-N_{23}N_{23}$ $^1S_0$ lines at ~51.75 eV and 52.5 eV are isotropic as expected. The respective $^1D_2$, $^1P_0$ and $^1P_2$ lines all display intensity variations with angle. In particular, the $M_3-N_{23}N_{23}$ $^1P_0, 1$ and $M_4-N_{23}N_{23}$ $^1D_2$ line intensity dropping to 30% of the maximum value at 90°.

![Figure 2](image)

**Figure 2.** (left). Kr $M_{4,5}N_{23}N_{23}$ Auger lines from 50 to 59 eV in non-coincidence mode with $\theta_s = 90$ deg. (right) The Kr $M_{4,5}N_{23}N_{23}$ Auger lines from 50 to 59 eV, non-coincidence with energy resolution of 0.4 eV showing a compilation of eight data scans for $\theta_s = +60^\circ$ to 120°.

Individual TDCS for the 4p orbital of krypton indicate, for two sets of kinematical conditions, that the scattering angle is moved from below the Bethe ridge angle to several degrees above it. All the amplitudes are scaled to 1.0 for the Bethe ridge condition, and the individual data sets are normalised to one another by the total singles count. Other data (not shown) with $E_0 = 958$ eV, $E_a = 880$ eV, $E_e = 64$ eV and $\theta_s = 6^\circ$ to $\theta_s = 21^\circ$ show a Bethe ridge at $\theta_s = 15^\circ$. The characteristic double-peak structure of the binary lobe expected for the 4p state appears for the scattered electron angle equal to the Bethe ridge condition. Similarly, data for $E_0 = 1014$ eV, $E_a = 880$ eV, $E_e = 120$ eV and $\theta_s = 11^\circ$ to $\theta_s = 26^\circ$ show the Bethe ridge at $\theta_s = 20^\circ$. The characteristic 4p double-peak structure of the binary lobes is measured for the scattered electron angle equal to the Bethe ridge condition indicating equal intensity of the two lobes. Measurements for the inner d-orbital with $E_0 = 1027$ eV, $E_a = 880$ eV, $E_e = 53$ eV and $\theta_s = 10^\circ$ and the momentum transfer is $\pm K = 1.59$ au showed the coincidence count rate was higher than on the Bethe ridge conditions where $\theta_s = 12.5^\circ$. Discrepancies between inner shell measurements and the DWBA (Distorted Wave Born Approximation) [2, 3] probably occur as a result of the effect of PCI (Post Collision Interaction) [2, 3] on the Auger line shapes when the Auger and
ejected electrons have equal energies. Krypton exhibits a large recoil structure symmetric about $K$, with the recoil-to-binary peak ratio of 0.95 ± 0.12 smaller than argon. This effect is most likely due to ionisation from a ‘d’ state and the lower binding energies of the 3d $3/2$ (95.04 eV) and 3d $5/2$ (93.79 eV) states respectively. The physical mechanism is an enhanced interaction between the ejected electron and the residual ion as expected from an inner shell, particularly when the ejected electron energy is less than the binding energy of 94 eV for the 3d electron. The TDCS values predicted by the DWBA models using an ion potential with and without the Gamow factor are clearly in agreement with the measured data while any differences between their predictions cannot be discerned. Better statistics and data near 0° or 180° are not accessible in the present apparatus.

3. Methane
The valence shell structure of methane shows tetrahedral symmetry with the ground state electronic configuration of $(1a_1)^2(2a_2)^2(1t_2)^2(1t_3)^2$ where the $2a_1$ (23.1 eV) and $1t_2$ (14.2 eV) are valence orbitals. With ionisation of the triply degenerate $1t_2$ state the geometry of the ground state of CH$_4^+$ becomes almost square planar and the $1t_2$ orbital is much more sensitive to the molecular geometry and symmetry. However, if the impulse approximation is valid, neither the rotational nor the vibrational states are expected to be significant as shown here. Contributions of the H(1s) atomic orbitals to the $1t_2$ molecular orbital momentum distribution cancel, due to the tetrahedral symmetry of the CH$_4$ molecule (for instance $1t_3$, $a_{1s} = -a_{2s}$ and the vanishing of the cross product. This simplification does not occur for the $2a_1$ state. The present data show the (e, 2e) technique is sensitive to such details of the wave function and to the symmetry of the molecule.

![Figure 3](image-url)

The TDCS of the $1t_2$ orbital of methane for $E_0 = 1014$ eV is shown in Fig 3 for several scattered electron angles. The experimental conditions were $E_s = 880$ eV, $E_e = 120$ eV and the Bethe ridge conditions have $\theta_s = 20^\circ$. A double lobed structure is observed similar to the 4p orbital of krypton. At the Bethe ridge angle, the peak at 65° is approximately half the amplitude of the peak at 90°. As the scattered electron angle is moved away from the Bethe Ridge angle, toward smaller angles, the intensities of the two peaks decrease as does the relative intensity of the 65° peak. The distribution changes to a single peak with a tail at lower ejected electron angles. This is similar to the observations of the 4p peak in krypton at $E_0 = 958$ eV. As the scattered electron angle increases above the Bethe
ridge angle, the intensity of the two peaks decrease at roughly the same rate, and the centre position of the smaller peak moves toward lower scattering angles. The double peaks of the binary region are much better maintained, relative to those observed in argon and krypton, as the scattered electron angle moves through the Bethe ridge condition.

The TDCS of the 1t$_2$ orbital of methane for $E_0 = 1514$ eV is shown for several scattered electron angles. The experimental conditions were $E_s = 1380$ eV, $E_e = 120$ eV, with the Bethe ridge condition $\theta_s = 16^\circ$. The distribution shows a single Gaussian shaped peak with a distinct tail at lower ejected electron angles. The peak observed at $65^\circ$ has reduced intensity and its centre position has increased to $80^\circ$ leaving a tail in the distribution rather than a distinct peak seen at lower incident energies.

Figure 4. Coplanar TDCS for ionisation of the 1t$_2$ and 2a$_1$ orbitals of methane. $E_0 = 1514$ eV (left) and $E_0 = 1523$ eV (right) with $E_s = 1380$ eV and $E_e = 120$ eV. The values of $\theta_s$ are inset and $\theta_e = 16^\circ$ corresponds to the Bethe Ridge location.

The TDCS of the 2a$_1$ orbital of methane for $E_0 = 1523$ eV in Fig.4 for several scattered electron angles and $E_s = 1380$ eV, $E_e = 120$ eV, with the Bethe ridge condition $\theta_s = 16^\circ$. The single Gaussian-like angular distribution, as well as the shape and position of the measured angular distribution, remains unchanged with scattered electron angle. However, the intensity of the distribution increases rapidly from lower scattered electron angles to the Bethe ridge condition and then decreases more slowly as the scattered electron angle is further increased. Other data show the double peaked structure of the 1t$_2$ angular distribution is maintained for $E_0 = 1014$ eV as the scattered electron angle is increased from the Bethe ridge condition. The relative heights of the distributions on either side of the Bethe ridge condition are also similar for the corresponding angles either side of the Bethe ridge condition. The relative heights are similar on either side of the Bethe ridge condition for 2a$_1$ the distributions with $E_0 = 1023$ eV, see Fig 3. (right).

The data corresponding to the ~1500 eV measurements shows a greater variation in the intensity of the angular distributions as the scattered electron angle is changed. The 1t$_2$ measurements with $E_0 = 1514$ eV, Fig. 4 (left) shows a Gaussian peak with a tail toward the lower scattered electron angles as discussed earlier. The slope of the Bethe surface is greater for scattered electron angles greater than the Bethe ridge condition than it is for scattered electron angles less than the Bethe ridge condition. The 2a$_1$ distribution in Fig. 4 (right) shows a steeper slope for the Bethe surface at angles greater than the Bethe ridge condition than for those angles corresponding to the angles lower than the Bethe ridge condition. The 2a$_1$ angular distribution shows a Gaussian angular distribution, with a slight tail toward the higher ejected electron angles. The slope of the Bethe surface is greater for lower scattered electron angles, than those greater than the Bethe ridge condition.
4. Bethe Surface

Coincidence measurements of the 4p valence shell of krypton and the 1t\textsubscript{2} and 2a\textsubscript{1} vibrational states of methane were made in the region of the Bethe ridge. The scattered electron angle was used as the free parameter, with all the energies kept constant and the scattered electron detected over the entire angular range.

A comparison of the angular distributions for krypton and methane and fitted to Gaussian distributions and Bethe surfaces from the different kinematics indicates the relative triple differential cross sections have an approximately Gaussian relationship in peak heights as the scattered electron angle is varied. The argon 3p distribution is peaked at the Bethe ridge angle, with a steeper slope of the Bethe surface on the lower scattered electron angles than those scattered electron angles greater than the Bethe ridge condition. The methane measurements follow a similar pattern to argon (not shown). The distributions are approximately Gaussian in shape, with the peak in the distribution occurring at the Bethe ridge angle. The methane 1t\textsubscript{2} measurement with \(E_0 = 1014\) eV shows a more gentle slope in the Gaussian distribution on the lower scattered electron angles than those scattered electron angles above the Bethe ridge condition. The methane 1t\textsubscript{2} distribution with \(E_0 = 1514\) eV has a smaller half-width than the corresponding distribution at 1014 eV, however the slope of the Bethe surface was again less steep for lower scattered electron angles than those greater than the Bethe ridge condition. The 2a\textsubscript{1} measurement with \(E_0 = 1023\) eV displays a similar distribution to the 2t\textsubscript{1} distribution with \(E_0 = 1014\) eV, however the half-width of the distribution is less than the 1t\textsubscript{2} distribution. The 2a\textsubscript{1} distribution with \(E_0 = 1523\) eV is very similar to the 2a\textsubscript{1} distribution with \(E_0 = 1023\) eV for scattered electron angles less than the Bethe ridge condition. For scattered electron angles greater than the Bethe ridge condition the slope of the Bethe surface is higher.

The distribution for krypton is approximately Gaussian, however the peak in the distribution is approximately 3° and 5° lower in scattered electron angle than the Bethe ridge angle for the 958 eV and 1014 eV measurements respectively. For scattered electron angles greater than the Bethe ridge condition, the distribution is similar to those observed for methane at equivalent kinematics. If one compares the individual TDCS, the shape is as expected, in contrast with the methane measurements while the intensity is significantly greater at lower scattered electron angles. The effect is most probably a “target” effect. Many classical photoionisation “single particle” phenomena such as Cooper minima, with delayed onset and shape resonances are observed in the 4d partial cross section, and coupled to other subshells via interchannel coupling. Further studies of the “multielectron” or “collective” nature are in progress.

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5. References

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