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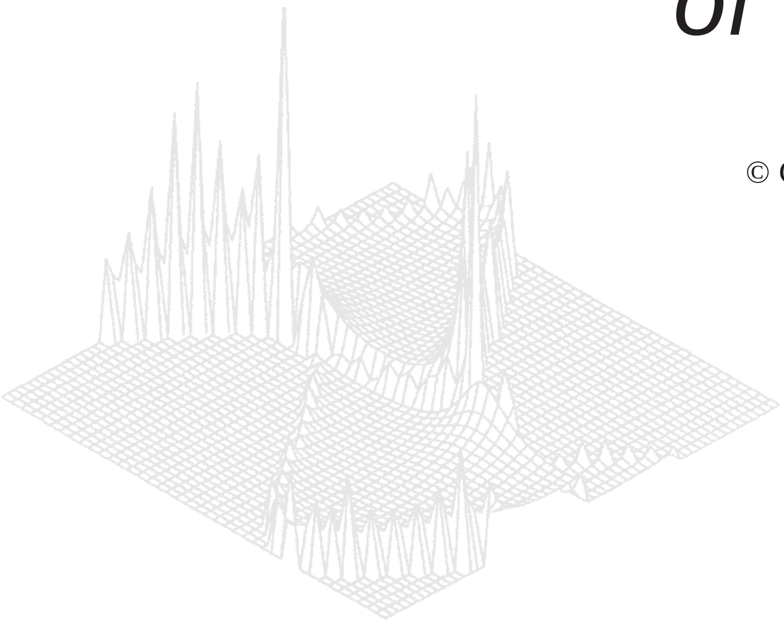

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Electron Recapture near Thresholds*

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Abstract

Electron recapture following photon or electron-impact ionisation near thresholds attracts considerable interest. A comparison is made of the information gained from studies utilising different methods of observation including ion yields, (e, 2e) coincidence, and photo-electron spectroscopy, to increase understanding of the electron recapture process.

1. Introduction

Recapture of a slow electron into an atom following inner-shell ionisation by electron or photon impact is attracting considerable attention as improved experimental and computational techniques enable better resolved and deeper probes of near-threshold processes. Experimental techniques such as charge state analysis of the residual ion, observations of near-threshold Auger transitions via (e, 2e) measurements and studies of near-threshold and resonant photo-electron spectra have only just begun to unravel the complex mix of interactions that occur near inner-shell ionisation thresholds. The detailed data obtained via these techniques are analysed in this paper to reveal an electron recapture mechanism that is consistent with observations. The work has stimulated the advancement of calculations from semi-classical two-step models to fully quantum-mechanical descriptions of the process.

Many studies of recapture have focussed on features observed in ion yield data near thresholds and from observations of post-collision interaction (PCI) effects in Auger electron spectra very close to the emission threshold. In this region the presence of a near-zero-energy electron introduces new avenues for correlation effects that emphasise the quantum nature of near-threshold processes. PCI-induced recapture will not affect the Auger transition intensity but can make investigations of, for example, the applicability of the Wannier threshold law near innershell thresholds (Kamm *et al.* 1994) difficult by altering the fragmentation process of two electrons in the field of the ion. It is therefore important that an accurate understanding of recapture processes is attained. A description of the post-collision interaction will be given first, and the emergence

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of data providing evidence of recapture processes will be discussed. Some of the difficulties associated with further disentanglement of the near-threshold data will be described.

2. Post-collision Interactions

In some respects it is difficult to separate a photon or electron-impact interaction into pre-, during and post-collision regimes and indeed in a fully quantum mechanical sense the distinction is invalid. However, it is often helpful conceptually to delineate reactions in such a way, and in classical models the distinction is readily made. In this sense, the post-collision Coulombic interactions between particles after inner-shell ionisation with associated Auger electron emission can be thought of in the following way. The pre-collision system contains an atom and either a projectile photon or electron that ionises an electron from an inner shell of the atom. The ejected electron has a given energy, called the excess energy, which may be close to zero. During the collision the atom relaxes by dropping an electron from an outer orbital into the inner-shell vacancy and the additional energy (characteristic of the particular re-arrangement that takes place) made available by the relaxation process is transferred to an 'Auger' electron that is emitted from the atom. In the post-collision state an ejected electron from the initial inner-shell ionisation (assumed here to have lower energy than the Auger electron) sees a singly-charged ion until it is passed by the Auger electron. The slow electron then sees a doubly-charged ion and slows in the stronger potential. The Auger electron initially sees a doubly-charged ion until it passes the slow ejected electron, and the subsequent shielding allows the Auger electron to gain energy.

Calculations predicted the observed Auger PCI effects for photon impact (Niehaus 1977) and experimental data were in good agreement (see e.g. Schmidt *et al.* 1977). Berezhko *et al.* (1978) proposed a theoretical framework for Auger emission based upon a two-step plane wave first Born approximation that contained two assumptions. First, Auger emission was completely independent from the ionising collision and, second, a first Born approximation correctly described the initial ion creation. The model assumed that direct excitation of the final state was negligible and that the intermediate state lifetime was long compared with the time characteristic of the collision process. Reasonable agreement was found with existing data and it was found later (Sheinerman *et al.* 1994) that using different approximations to describe the inner-shell ionisation did not appreciably alter the features resulting from PCI. It is clear however that PCI between the Auger electron and the slow ejected electron violates the assumption in the classical model of complete independence of inner-shell ionisation and Auger emission. This is not surprising, and means for example that the Auger transition anisotropy predicted by Sheinerman *et al.* (1994), and others, cannot be attributed solely to alignment of the intermediate ion state, thus preventing interpretation of the angular distributions in terms of a pure alignment tensor. However, models based upon the two-step approach, including the eikonal model of Sheinerman *et al.,* are in agreement with most aspects of the PCI effects.

The Auger lineshapes measured in near-threshold photon-impact experiments show clearly the energy and momentum transfer between the final state electrons via post-collision interaction. The Auger electrons are shifted towards higher energy and the lineshapes become asymmetric, developing a high-energy tail. Both effects are larger for smaller excess energy (the energy of the slow ejected electron from the inner-shell ionisation). Similar PCI effects were first reported in non-coincidence electron (rather than photon) impact ionisation investigations with near-threshold incident energies by Ohtani *et al.* (1976) for Xe N_{45} Auger transitions. Huster and Mehlhorn (1982) presented experimental data and model calculations for PCI effects following electron impact ionisation based upon the photon impact theory of Niehaus. They recognised that lacking detailed knowledge of the undetected ejected electron energy distribution made a general comparison between theory and experiment difficult.

An (e, 2e) coincidence measurement removes the uncertainty in the energy of the slow ejected electron, so allowing detailed investigations of PCI effects via electron impact ionisation. A review of electron-impact (e, 2e) studies of PCI effects was given by Lohmann (1996). Sheinerman *et al.* (1994) presented calculations of the lineshape distortion and angular distribution of Auger electrons observable in (e, 2e) data after electron impact ionisation. The (e, 2e) data reported by Waterhouse and Williams (1997*a*, 1997*b*) provided detailed confirmation of the PCI effects predicted by Sheinerman *et al.* for a wide range of excess energies for the argon $L_{2,3}M_{2,3}M_{2,3}$ $^1S_0$, $^1D_2$ and $^3P_{0,1,2}$ Auger transitions. At the same time their data provided strong evidence of recapture processes near the inner-shell ionisation limit, and this will be discussed in more detail shortly.

3. Evidence for Recapture

(3a) Ion Detection

Experimental evidence for recapture was first provided in photo-ionisation ion-yield data from van der Wiel *et al.* (1976). They noted the combined Ar^{2+} and Ar^{3+} yield could not account for all of the electron energy loss yield within a few eV of the L_2 threshold and proposed a ‘shake-down’ mechanism that would produce additional Ar^+, which at that time could not be experimentally detected. Hayaishi *et al.* (1984) reported excess Ar^+ yields up to a few eV above the argon 2p threshold, and concluded this could only be due to a capture process. They carried their analysis further (Hayaishi *et al.* 1988) with photoion-threshold electron coincidence studies. The imposition of coincidence detection significantly simplified the observed ion spectrum and allowed study of the photon-energy dependence of the recapture phenomena. Hayaishi *et al.* observed a ‘PCI’ effect in the coincidence ion signal above threshold and argued that, rather than an unlikely shake-off process (Meyer *et al.* 1991), a two-step Auger emission–autoionisation process would better account for the formation of Ar^{2+} and Ar^{3+} below the 2p threshold. For this to occur, the initial excited states must undergo shake-up to states above the double ionisation threshold, from where autoionisation could occur via valence multiplet Auger decay.

Further evidence for recapture above threshold was provided by Eberhardt *et al.* (1988) in the photo-ionisation Ar^{2+} and Ar^{3+} yields near the 2p threshold. They observed a steady variation in the ion branching ratio, which they ascribed to PCI effects in the Auger decay of the 2p hole. By applying the semi-classical model of Russek and Mehlhorn (1986) they were able to predict the variation of the recapture probability near threshold. Better agreement was obtained by Tulkki *et al.* (1990) with a quantum-mechanical model that predicted the recapture probability as a function of the excess energy of the slow photo-electron, assuming that the probability of recapture for a zero-energy electron was unity. Following similar coincidence studies Levin *et al.* (1990) suggested that recapture induced by post-collision interaction was a suitable link between below threshold resonant excitation to bound np levels with subsequent Rydberg shake-off, and above-threshold energy-dependent shake-off and double-Auger effects.

Pre-edge production of higher-charge-state ions was investigated further by Doppelfeld *et al.* (1993) with observations near the Ar K edge. They observed a gradual, rather than abrupt change in the relative ion abundance near the ionisation limit, in common with the earlier work just discussed. Again above threshold this was attributed to recapture of the 'free' photoelectron by PCI with the faster Auger electron. The phenomenon of pre-edge photo-ionisation was investigated in more detail by von Busch *et al.* (1996).

Convincing evidence of recapture was reported by Samson *et al.* (1996), again for photo-ionisation near the Ar $L_{2,3}$ ionisation threshold. In this work the recapture model of Tulkki *et al.* (1990) was extended to higher excess energies and an approximate relation between the recapture probability $P(E_{\rm ex})$ and the energy $E_{\rm ex}$ of the slow photo-electron ejected in the initial inner-shell ionisation was found to be

$$P(E_{\rm ex}) = 1 - \exp(-\Gamma/E_{\rm ex}),$$

where Γ is the linewidth of the Auger transition. Reasonable agreement was obtained with observed Ar^{2+} and Ar^{3+} ion yield spectra, however the model was not applied closer than $0{\cdot}25$ eV above threshold due to computational difficulties.

Esser *et al.* (1997) examined the role of PCI-induced recapture in the fragmentation of small molecules. They observed a gradual increase in the total ion charge of OCS and CS_2 fragments detected from a few eV below the sulphur 1s ionisation threshold to around 6 eV beyond the threshold. Their data were in agreement with observations of analogous processes in argon K shell ionisation. Recapture effects were shown by Hansen *et al.* (1998) to enhance the yield of H^+ ions in the first few eV above the chlorine K edge in photo-ionisation of HCl, which is isoelectronic with argon. They included a correction for recapture 'cascades' (for example when determining the partial yield of Cl^{4+}, the additional yield of Cl^{4+} from electron recapture by Cl^{5+} and the loss of Cl^{4+} by electron recapture to become Cl^{3+} is included). They also found the Cl photo-electron could be recaptured by the H^+ fragment, an effect that cannot be described with a conventional 'atomic-PCI' model because the fragment orbital is not localised.

(3b) Photoelectron Observations

Schmidt (1992) discussed advances in photo-ionisation studies using synchrotron radiation and suggested that near threshold PCI-induced energy exchanges might be so large that the slow photoelectron would be recaptured by the ion into a bound orbital. Schmidt proposed that a suitable recapture mechanism would provide a natural link between inner-shell ionisation followed by Auger decay and outer-shell ionisation with simultaneous excitation. The challenge was to obtain well-resolved data spanning the ionisation threshold, and then to search for indications of recapture effects.

An elegant non-coincidence photon impact experiment by Čubric *et al.* (1993) was the first to address the challenge. They recorded electron energy-loss data from Xe around the 4d ionisation threshold. The incident photon energy was increased in small steps and the electron spectra were sequentially recorded and presented a two-dimensional view of Auger electron energy and incident photon energy. The data showed the PCI region above threshold, a shake-modified resonant Auger emission area below threshold and the quasi-continuum region in-between. In a small energy range just above threshold the slow photoelectron could lose enough energy via PCI to be recaptured by the ion. Within the region where recapture could occur two pathways to the same final state were identified, one direct and another involving the PCI-induced recapture event. The two pathways would not be distinguishable and given sufficient resolution it was thought that interference effects would be observed in the form of discrete structure, particularly on the high-energy side of the Auger line.

The boundary region was again studied in detail by de Gouw *et al.* (1995), with the aim of developing a model to explain how PCI phenomena above threshold evolved into the resonance Auger effect below threshold. They presented a time-dependent semi-classical model based upon the trajectory of a Rydberg electron moving in the Coulomb potential of the core ion. The model was in reasonable agreement with their data. Below threshold the trajectory of the Rydberg electron contained a turning point thus indicating the possibility of recapture but this was not explicitly discussed. Consequently, the Rydberg electron would be at the same radius R twice in its trajectory, once when receding from the ion and once when returning. In both instances the subsequently emitted Auger electron would suffer an identical PCI effect, leading to interference in the Auger electron lineshape. The model then implies that for excess energies below threshold the Auger lineshape would contain oscillatory structure on the high-energy side of the lineshape. Their model indicated that further below threshold the interference tends to make the Auger lineshape appear almost Lorentzian, but with low amplitude oscillations extending on the high energy side of the lineshape. However, their energy resolution was insufficient to resolve such structure and they noted deficiencies in the model, including the lack of quantisation of the final state.

In spectator (or resonant) Auger emission just below threshold the photoelectron remains bound to the residual ion core in a 'spectator' nd orbital, while in diagram Auger processes the photoelectron enters the continuum. Armen *et al.* (1997) examined suppression of the Xe $\mathrm{L_3M_{4,5}M_{4,5}}$ diagram Auger intensity observed for excess energies up to about 4 eV above threshold, and found that the observed near-threshold intensity was actually due to PCI-induced photo-electron recapture into large-n bound spectator nd orbitals. The possibility of interference effects was not explored but the necessity of coincidence experiments to partition the observed near-threshold intensity into spectator and diagram contributions was noted, as was the inherent difficulty of observing the boundary region.

The question of what happens to the recaptured electron was discussed at about the same time by Samson *et al.* (1996) who noted that contrary to the observation of a finite $\mathrm{Ar^{2+}}$ yield at the $\mathrm{L_3}$ threshold, if all zero-energy electrons were recaptured at the threshold, no $\mathrm{Ar^{2+}}$ would be observed. To account for the finite $\mathrm{Ar^{2+}}$ yield they reasoned that electrons could be recaptured into high-lying

Rydberg states forming Ar^{+*} and that some of the states would subsequently autoionise back into the Ar^{2+} continuum. They found that about 33% of the recaptured electrons remain captured and a similar fraction, about 26%, remains captured at the L_2 threshold. They also calculated that about 15% of electrons recaptured by Ar^{3+} remain captured, compared with only about 5% permanently recaptured by Ar^{4+}. Recently Lu *et al.* (1998) examined the role of recapture in production of the Ar $(^1D)6d$ final state, thought to be the only suitable candidate for the two-step autoionisation model proposed by Hayaishi *et al.* (1988) discussed earlier. They found that inclusion of a recapture contribution was essential for a proper description of the production of near-zero-energy electrons in the decay of all Ar $2p^{-1}$ ns and nd resonances.

Armen and Levin (1997) provided a fully quantum-mechanical model that described the PCI-induced recapture of photoelectrons near threshold within the framework of radiation-less resonant Raman scattering. The excitation of final double-vacancy states is enabled by resonant creation and decay of virtual intermediate states related to the inner-shell hole. An escape probability distribution is predicted that is consistent with semi-classical models and different from that of Tulkki *et al.* (1990). They found that the ionisation threshold must be exceeded by an energy proportional to $\Gamma^{2/3}$ before the escape mechanism dominates, effectively delaying the onset of double ionisation. For example, in Ar K-shell ionisation the escape probability does not exceed 50% until $1{\cdot}35$ eV above the nominal ionisation threshold, and for Xe L_3 ionisation the delay energy was calculated to be about $3{\cdot}70$ eV. The model predicted the branching ratio between diagram and spectator Auger decay, and the yield of zero-kinetic-energy electrons near threshold that exhibited a $\Gamma^{2/3}$ dependence. It is important to note the model is in quite good agreement with experimental data, even though it does not consider PCI or cascade Auger effects.

(3c) Two-electron Evidence

Lohmann's (1996) review discussed the interference of two outgoing electrons from Auger transitions for kinematics with near-threshold excess energy. Early data from Sandner and Volkel (1984) and Lohmann (1991) contained hints of interference effects, and although uncertain, the interference was thought to be due to interaction of the Auger process with direct double ionisation. For argon, electrons ejected in the double ionisation process have a continuum of energies and form a continuous background under the Auger transitions. The background also contains discrete contributions from valence satellite states due to outer-shell ionisation with simultaneous excitation, identified as belonging to the $3s^2 3p^4 (^1D) nd\,^2S$ ($n = 3, 4, 5$) group and observed for example by McCarthy and Vos (1999, present issue p. 363). It was difficult to quantify the interference because the measurements did not extend far beyond the observed Auger transitions to better characterise the background, and data were sparse.

A significant experimental advance allowed Waterhouse and Williams (1997*a*, 1997*b*) to quantify the interference and determine its energy and angle dependence via (e, 2e) coincidence observations of Auger transitions around the Ar $L_{2,3}$ threshold. They used a data display method not unlike that employed by Čubric *et al.* (1993). The data covered the PCI region above threshold, the quasi-continuum region at threshold, and the region below threshold. An important feature accessed by this technique was overlap of the $L_{2,3}$ threshold Auger signal with the valence satellite states described earlier. A most intriguing aspect of these data was a clear demonstration of energy-dependent interference features in all of the observed $L_{2,3}M_{2,3}M_{2,3}$ transitions near the $L_{2,3}$ threshold.

Further analysis (Waterhouse and Williams 1997*b*) showed the amount of interference was independent of the separation energy of the 'background' signal. Interaction with the double ionisation process as suggested in earlier works therefore did not cause the interference. Instead, the interference exhibited a strong dependence on the excess energy of the slow electron ejected during the inner-shell ionisation, and a rapid increase in the magnitude of the interference occurred below about 4 eV excess energy. This was consistent with the recapture limit proposed by Samson *et al.* (1996) and they proposed the interference was related to a PCI-induced recapture process, whereby the slow ejected electron was recaptured into high-lying Rydberg states forming Ar^{+*}. Electrons recaptured into states with $n < 6$ tend to autoionise, but for states with $n < 6$ around 33% remain captured, as described earlier. For argon, electrons may be permanently recaptured into the $3s^2 3p^4(^1D)nd^2S$ $(n = 3, 4, 5)$ states, which are precisely those identified as satellite states in valence ionisation processes. Interference with the satellite-state ionisation process then seems to provide a consistent picture of what happens to the recaptured electrons following PCI events. A novel experiment to confirm this interpretation is in progress.

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