Hollow-atom probing of surfaces
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Coster-Kronig transitions in hollow atoms

High resolution KLL-Auger spectra emerging from collisions of H-like and metastable He-like C, N, and O on a B-doped Si(100) surface are presented. In combination with high resolution electron spectroscopy, Hartree-Fock calculations allow us to successfully identify KLL-Auger electrons arising from specific states that form a part of the auto-ionization cascade as the multiply excited projectiles deexcite. We find strong evidence for Coster-Kronig transitions taking place in the hollow atoms which give rise to missing peaks in the Auger spectra. A cascade model of the last deexcitation steps of the highly charged ions based on the atomic structure data of the previous chapter provides detailed insight into the time scales involved.
6.1 Introduction

In the previous chapters it was found that the various peaks at the lower energy side of the KLL spectra could be identified as Auger electrons emitted from 1s 2l^2 3l^2-3 hollow atom configurations. However, their relative intensities could not be explained in a straightforward way by assuming a statistical distribution of the L-electrons over the available 2s^2, 2s2p and 2p^2 states. In this chapter, we investigate in more detail the various decay paths of the states involved with a special emphasis on Coster-Kronig transitions. In order to do this, high resolution electron energy spectra of hydrogen-like C^5+, N^6+, and O^7+ and of helium-like (1s2s core) C^4+, N^5+, and O^6+ metastables colliding with the Si(100) target are discussed. In the metastable ions, part of the possible 2l^2 states are excluded from the decay, giving rise to possible differences between the Auger spectra obtained from hydrogenic and helium-like ions. These differences allow us to track the sequence of the Al cascade and to identify distinct states populated prior to the emission of the K-Auger electron. The shape of the spectra is strongly influenced by the presence or absence of Coster-Kronig transitions in the particular hollow atom under consideration.

6.2 Experimental results

Figures 6.1(a) – (c) show K-Auger spectra measured during collisions of 250 eV C^4+/5+, N^5+/6+, and O^6+/7+ with a Si(100) surface. An improved quality in the relevant parts of the spectra was obtained by using an energy window in which the step length between successive points was decreased and the measuring time was increased yielding better statistics. All spectra are characterized by the presence of a broad structure with sharp peaks superimposed on it. This broad underlying structure, the relative importance of which increases with increasing collision energies, has previously been identified as arising from electrons emitted by the projectiles from inside the top few surface layers of the target while the narrow peaks are assigned to electrons that are mainly emitted above the surface.

Measurements of the strong peaks in hydrogenic nitrogen and oxygen as a function of the emission angle show that the two sharp peaks at 347 eV and 358 eV in nitrogen and at 464 eV and 478 eV in oxygen (figures 6.1(b) and 6.1(c)) exhibit a Doppler shift in accordance with ions moving along the incident direction (see chapter 4). The narrow width of these peaks is an indication of specific initial configurations in contrast to the broad (subsurface) structure which contains contributions from a whole variety of initial configurations.184

Comparison of calculated KLL energies of C, N, and O 1s 2l^2 3l^2-3 hollow atoms (listed in table 5.3 in the previous chapter) with the measured
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spectra indicates that the two low energy peaks in the various spectra arise from initial states \(1s2s^2^3S\) and \(1s(2s2p^3\text{P})\) \(^3\text{P}\) respectively (for brevity we will omit in the following the \(3l\) electrons from the notation and label the configurations as \(1s2l^l\)). Regarding the peak assignment Andrå \textit{et al}.\textsuperscript{105} have come to a similar conclusion regarding the first KLL Auger peak. The second peak however they assign – different from their earlier tentative suggestion\textsuperscript{106} – to a configuration with 3 \(L\)-electrons. Regarding intensities some striking differences can be observed when one compares the spectra from hydrogenic projectiles with their He-like counterparts. For metastable projectiles the contribution of the two low-energy peaks compared to the total intensity is much larger than for H-like ones. For the initial (\(1s2s\)) configuration in the metastables the formation of a \(1s2s^2\) or \(1s2s2p\) configuration is much more probable than of \(1s2p^2\) which would need an \(s\rightarrow p\) transition of the initial \(2s\) electron. In the H-like spectra a significant contribution can be expected from \(1s2p^2\) states, which contribute to the higher energy part of the KLL-Auger spectrum. In the hydrogenic C and N spectra peaks arising from \(1s2p^3\) configurations \((1s(2p^3\text{D})\) \(^3\text{D}\) at resp. 265 and 369 eV) are indeed observed, but calculations show that at these energies also \(n_L > 2\) configurations contribute. This prohibits a clear separation of the \(2p^2\) peaks from other contributions.

\textbf{Figure 6.1:} Electron energy spectra arising from collisions of 250 eV \((\psi = 15^\circ, \theta = 90^\circ)\) hydrogenic (upper spectra) and helium-like (lower spectra) carbon \((a)\), nitrogen \((b)\), and oxygen \((c)\) on Si(100). In the relevant parts of the spectra the sampling time per channel is increased to improve the statistics.
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For oxygen there is certainly no evidence for a $2p^2$ ($1s\ (2p^2\ 1D)^2\ D$ at 490 eV) contribution, although it is reasonable to assume that all the states arising from $1s2l^2$ parent configurations are populated. The absence of the $2p^2$ peaks implies the presence of a mechanism in $O(1s\ 2l^2)$ hollow atoms that inhibits the ‘depopulation’ of the $2p^2$ configurations via KLL-Auger decay.

6.3 Coster-Kronig transitions and rate equations

So far we only have considered KLL-Auger transitions from the hollow atom $1s\ 2l^2\ 3l^Z-3$ configurations. From the atomic structure calculations of the previous chapter the conclusion was drawn that the Z-3 M-electrons can be regarded as mere spectator electrons. Their main influence on the KLL-Auger spectra is an overall shift of the KLL-Auger peak energies due to screening effects. Furthermore the KLL-Auger transition rates are not influenced by the presence of the M-electrons. However, for the hollow atom configurations another decay channel is available, i.e. LLM-Coster-Kronig transitions which will in the first place be discussed in the following.

LLM-Coster-Kronig transitions are particular Auger transitions in which a rearrangement of L-electrons leads to the emission of an M-electron, e.g. $1s\ 2p^2\ 3l^Z-3$ to $1s\ 2s2p\ 3l^Z-4 + e^-$. Assuming that the binding energy of the outermost M-electron is of the order of the target work function ($W_d(Si)\approx 5\ eV$) the rearrangement of the L-electrons has to yield at least this amount of energy in order to allow for a Coster-Kronig transition. Inspection of the calculated KLL-Auger energies for oxygen listed in table 5.3 of the previous chapter shows that this condition is fulfilled for nearly all rearrangements. This is however not evidently true for nitrogen and carbon hollow atoms. Therefore the following discussion will be focussed on oxygen.

In figure 6.2 a diagram showing all possible decay channels for $1s\ 2l^2\ 3l^Z-3$ configurations is displayed. We assume that Coster-Kronig transitions conserve the total electron spin of the $1s\ 2l^2$ core, i.e. spin flips are not allowed.
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From the diagram it is readily seen that Coster-Kronig transitions lead on the one hand to an indirect contribution of the metastable states with $1s\, (2p^2 3P)\, ^2P$ [D] core to the KLL-Auger spectra for limited observation times and on the other hand to a transfer of KLL-Auger intensity from high to low energy peaks. Because of spin conservation, the metastable states with $1s2p^2\, 4P$ [b] core can only decay to the metastable states with $1s2s2p^4P$ [a] core which further can only decay via KLL-Auger emission. The latter is not observed for short observation times. Therefore the metastable states with a $1s\, 2l^2\, ^4P$ core are not considered at all.

Since Coster Kronig transitions are at least an order of magnitude faster than KLL-Auger transitions\cite{footnote} it can be anticipated that the influence of the LLM-Coster-Kronig transitions on the KLL-Auger spectra, i.e. on the relative peak intensities, will be strong. A more quantitative study of the deexcitation dynamics of the $1s\, 2l^2\, 3l^2-3l$ configurations is facilitated by translating the transition diagram given in figure 6.2 into a set of rate equations:

\begin{align}
\dot{n}_F &= -(\Gamma_F + \Gamma_{FC}) \cdot n_F , \\ 
\dot{n}_E &= -(\Gamma_E + \Gamma_{EC}) \cdot n_E , \\ 
\dot{n}_D &= -(\Gamma_D + \Gamma_{DB}) \cdot n_D , \\ 
\dot{n}_C &= -(\Gamma_C + \Gamma_{CA}) \cdot n_C + \Gamma_{FC} \cdot n_F + \Gamma_{EC} \cdot n_E , \end{align}

Figure 6.3: Solutions of the rate equations for the deexcitation of the $O^{14+}$ projectile. The time dependent population of the various states is shown in the left panel, the corresponding peak intensities in the right panel. The KLL-Auger rates are taken from table 5.2 of chapter 5 and all Coster-Kronig rates are taken to be $3 \times 10^{15}$ s$^{-1}$. At an observation time of 200 fs (marked by the vertical line in the right panel) agreement with the measured peak intensities is obtained.
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\[ \dot{n}_B = -\Gamma_B \cdot n_B + \Gamma_{DB} \cdot n_D, \]
\[ \dot{n}_A = -\Gamma_A \cdot n_A + \Gamma_{CA} \cdot n_C. \]

Figure 6.4: Solutions of the rate equations for the deexcitation of the O\(^{6+}\) projectile. As in the O\(^{7+}\) case, agreement with the experimental peak intensities is obtained at 300 fs.

\[ n_i(0) = (2S_i + 1)(2L_i + 1) \]

where \( S_i \) and \( L_i \) denote the total spin and total orbital angular momentum of a particular 1s 2l\(^2\) core state \( i \). Since the same coupling scheme for the M-electrons applies to all 1s 2l\(^2\) core states the relative statistical weights of the core states are not altered by adding Z-3 M-electrons.

The rate equations can be solved analytically (see appendix C). Inserting the solutions into equation 5.7 derived in chapter 5 yields the corresponding Auger intensities. The KLL-Auger rates are taken from table 5.2 and Coster-Kronig rates have been taken as a configuration average of \(3 \times 10^{15} \text{s}^{-1}\). For O\(^{6+}\) all states with a 1s 2p\(^2\) core, i.e. states labeled D, E, and F, are removed from transition diagram figure 6.2 and correspondingly from the set of rate equations 6.1 - 6.6.

Figures 6.3 and 6.4 show populations and KLL Auger intensities for O\(^{7+}\) and metastable O\(^{6+}\) respectively. For O\(^{7+}\) it is clearly seen that the Coster-Kronig transitions effectively depopulate states D, E, and F having a 1s 2p\(^2\)
core and states with a metastable \( 1s(2s2p^1P)^2 \) configuration. Consequently, the final states of the Coster-Kronig transitions gain population, leading to a strong increase of the corresponding KLL-Auger emission. For observation times larger than \( \approx 2 \) fs, the final states \( A \) and \( B \) dominate the Auger spectrum. For times larger than 200 fs, the ratio \( A : B \) saturates at a value 1.6 for \( O^{7+} \) and at 1.3 for \( O^{6+} \).

Within the uncertainties due to background subtraction, these values agree remarkably well with the observed ratios. Figure 6.5 shows the background subtracted \( O^{7+} \) and \( O^{6+} \) spectra together with simulated curves for \( T = 200 \) fs.

### 6.4 Discussion

For \( C^{5+} \) and \( N^{6+} \), the energy difference between the \( 1s(2p^2 \, ^1D)^2 \, ^2D \) configuration and \( 1s(2s2p \, ^1P)^2 \, ^2P \) configuration is only 3 to 4 eV. In view of the 5 eV workfunction of the Si target, this is too small an energy difference for the proposed LLM Coster-Kronig transitions to proceed. Therefore, the only possible Coster-Kronig transitions in C and N are those from \( 1s(2p^2 \, ^1S)^2 \, ^2S \) to \( 1s(2s2p \, ^1P)^2 \, ^2P \) and from \( 1s(2s2p \, ^1P)^2 \, ^2P \) to \( 1s(2s^2 \, ^1S)^2 \, ^2S \). In reality the stepwise variation in the occurrence of Coster-Kronig transitions in O as opposed to C and N is a smoother one from C via N to O due to the possibility that the emitted electrons can for instance also be emitted into unoccupied states of the conduction band. The efficiency of such a mechanism might
however be too small to allow for large Coster-Kronig rates for C and N. Such an effect is indeed observed in the spectra of figure 6.1. In the spectra, the differences between the distributions obtained from hydrogenic ions and helium-like ions spectra vanish going from C to O.

The fact that the O$^{7+}$ and O$^{6+}$ spectra are reproduced for the same values of the observation time $T > 200$ fs and the Coster-Kronig rate ($3 \times 10^{15}$ s) can be taken as a strong hint that Coster-Kronig transitions do play an important role in the rearrangement of the various O 1s 2$l^2$ substates prior to KLL-Auger emission.

The left panels of figures 6.3 and 6.4 show that virtually all projectiles initially in a 1s 2$l^2$ 3$l^5$ configuration have decayed after about 200 fs. During this time, the O$^{7+}$ and O$^{6+}$ projectiles ($v_L = 0.14$ Å/fs) have travelled about 28 Å in a direction perpendicular to the target (note that according to the overbarrier model (equation 2.12) the initial electron capture of these ions takes place about $8 - 10$ Å in front of the Si surface). Whereas the maximum population of states A and B is reached after only 5 fs, corresponding to a vertical travel distance of 0.7 Å, the deexcitation of the 1s 2$l^2$ 3$l^5$ configurations is completed much later, at least after the surface has been reached.

Since observance of Auger electrons emitted from within the solid is limited to shallow depths of a few angstroms we conclude that the observed KLL-Auger electron emission stems from projectiles which are reflected at the surface. Evidence for emission from reflected projectiles at even higher projectile energies has already been reported by Köhrbrück et al. The assumption that the KLL-Auger emission is due to projectiles which stay above the surface also explains why the relative peak intensities stay constant when lowering the projectile energy. The complete deexcitation of the 1s 2$l^2$ 3$l^5$ configurations is observed for each low enough projectile energy.

The only mechanism which limits the observation time in case of emission from reflected projectiles is the filling of the projectile L-shell. As soon as a third L-electron is captured, emission from configurations with a 1s 2$l^2$ core stops. Under the present conditions the filling of the projectile L-shell is not very effective. If the L-shell filling would be considerably more rapid than the K-Auger decay a significant fraction of KLL-Auger electrons would be expected from configurations with more than 2 L-electrons. Inside a metal many electrons are available and the L-shell apart from being filled by LMM-Auger transitions might also be filled by direct inner shell capture as proposed by Folkerts and Morgenstern. The filling of the L-shell as a function of LMM/LVV Auger rates, direct capture rates and KLL Auger rates is the subject of a model which is presented in the next chapter.