The all-seeing eye of resonant Auger electron spectroscopy: a study on aqueous KCl

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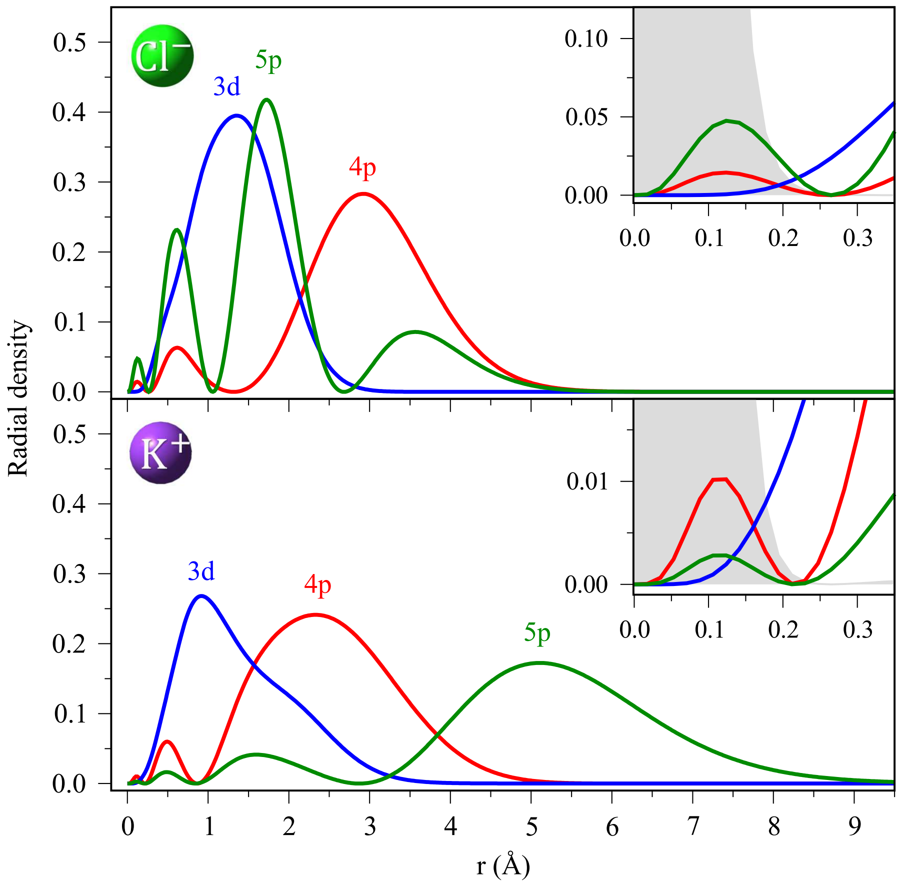

Figure 1: Radial density distributions of the singly-occupied natural orbital occupied by the excited electron corresponding to the $1s^{-1}4p$, $1s^{-1}3d$ and $1s^{-1}5p$ core excitations in K^+ (lower panel) and Cl^- (upper panel). The insets show the region of distances relevant for the overlap with the 1s core orbital whose radial density is shown as a grey shaded area.

In what follows we give a tentative explanation of the difference in the radial density distributions of the $1s^{-1}4p$ and $1s^{-1}5p$ states in K^+ and Cl^-. In the case of K^+, the excited electron mainly sees a $2/r$ potential. In addition, it sees a short range potential coming from the pointlike nucleus and the screening electrons. The latter one normally leads to a quantum defect different from 0. Beside this one has Rydberg series with an infinite number of states. However, in case of Cl- the outer electron does not see a Coulomb potential and the short-range potential becomes dominant. As a result we see the unusual behaviour, like e.g. a finite number of bound states (here obviously 4p). In contrast to this 3d and 5p are in the continuum.

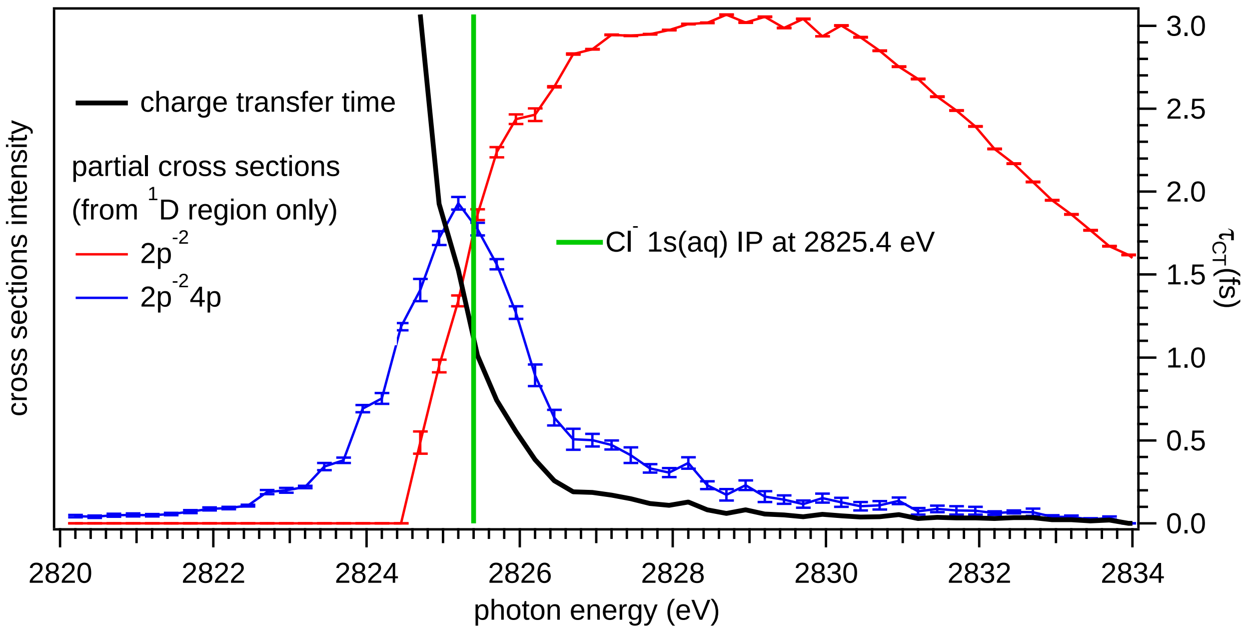

Figure 2: Partial cross sections and charge transfer time extracted from Fig. **??**. The blue and red curves are obtained by integrating the area of the $2p^{-2}$ and $2p^{-2}4p$ final states (^{1}D state region only) at each photon energy step. From these curves we determine the charge transfer time τ_{CT} according to the formula $\tau_{\mathrm{CT}} = \tau l/d$, with τ being the Cl 1s core-hole lifetime and l/d being the intensity ratio of the localized ($2p^{-2}$ 4p) and delocalized ($2p^{-2}$) states at a given excitation energy.[1] The green line defines the $\mathrm{Cl}^-_{\mathrm{aq}}$(1s) ionization potential.

References

(1) Föhlisch, A.; Feulner, P.; Hennies, F.; Fink, A.; Menzel, D.; Sanchez-Portal, D.; Echenique, P. M.; Wurth, W. *Nature* **2005**, *436*, 373.