

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

Tsveta Miteva,^{*,†} Nikolai V. Kryzhevoi,[‡] Nicolas Sisourat,[†] Christophe Nicolas,[¶]
Wandared Pokapanich,[§] Thanit Saisopa,^{||} Prayoon Songsiriritthigul,^{||} Yuttakarn
Rattanachai,[⊥] Andreas Dreuw,[#] Jan Wenzel,[#] Jérôme Palaudoux,[†] Gunnar
Öhrwall,[@] Ralph Püttner,[△] Lorenz S. Cederbaum,[‡] Jean-Pascal Rueff,^{†,¶} and
Denis Céolin^{*,¶}

[†]*Sorbonne Université, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement,
UMR 7614, F-75005 Paris, France*

[‡]*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im
Neuenheimer Feld 229, D-69120 Heidelberg, Germany*

[¶]*Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, F-91192 Gif-sur-Yvette Cedex,
France*

[§]*Faculty of Science, Nakhon Phanom University, Nakhon Phanom 48000, Thailand*

^{||}*School of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000,
Thailand*

[⊥]*Department of Applied Physics, Faculty of Sciences and Liberal Arts, Rajamangala
University of Technology Isan, Nakhon Ratchasima 30000, Thailand*

[#]*Interdisciplinary Center for Scientific Computing, Ruprecht-Karls University, Im
Neuenheimer Feld 205A, D-69120 Heidelberg, Germany*

[@]*MAX IV Laboratory, Lund University, P.O. Box 118, SE-22100 Lund, Sweden*

[△]*Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195, Berlin, Germany*

E-mail: tsveta.miteva@upmc.fr; denis.ceolin@synchrotron-soleil.fr

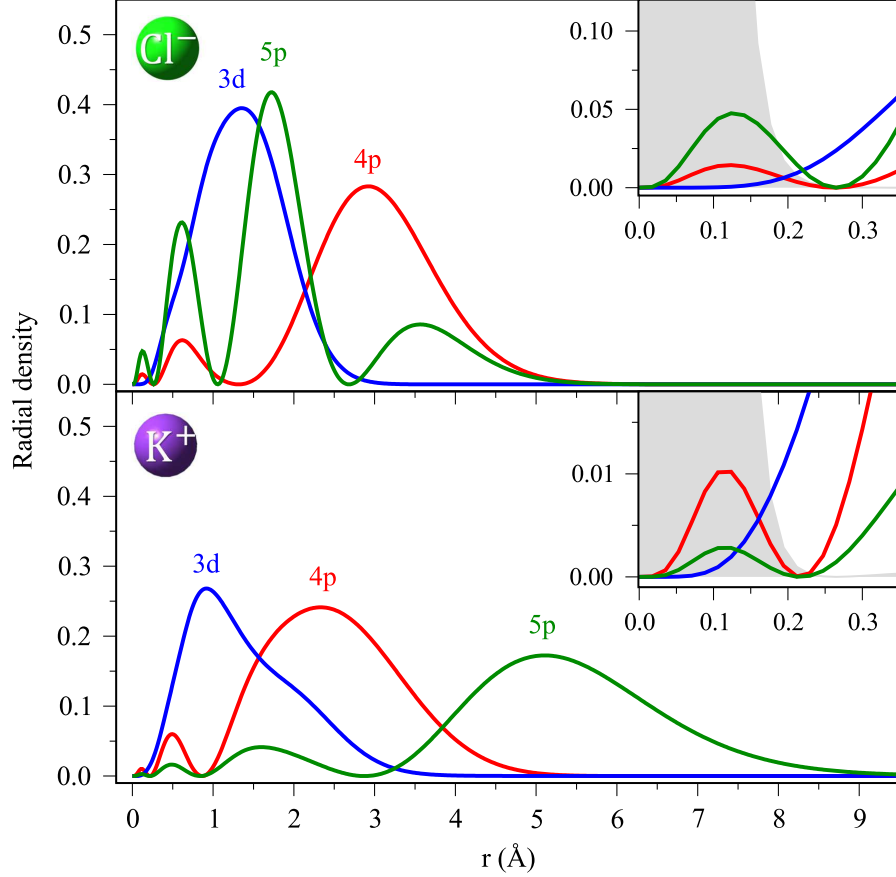


Figure 1: Radial density distributions of the singly-occupied natural orbital occupied by the excited electron corresponding to the $1s^{-1}4p$, $1s^{-1}3d$ and $1s^{-1}5p$ core excitations in K^+ (lower panel) and Cl^- (upper panel). The insets show the region of distances relevant for the overlap with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

In what follows we give a simple 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 originating from the point-like nucleus and the screening electrons. The influence of the latter can be described by a quantum defect $\delta \neq 0$, which is almost constant for the entire infinite Rydberg series. However, in case of Cl^- the outer electron does not experience a Coulomb potential and the short range potential becomes dominant. As a result of the absence of the Coulomb potential we see a different behavior in the properties of the states, like e.g. only a finite number of bound states (here obviously $4p$)¹. In contrast to this, the $3d$ and $5p$ are not bound.

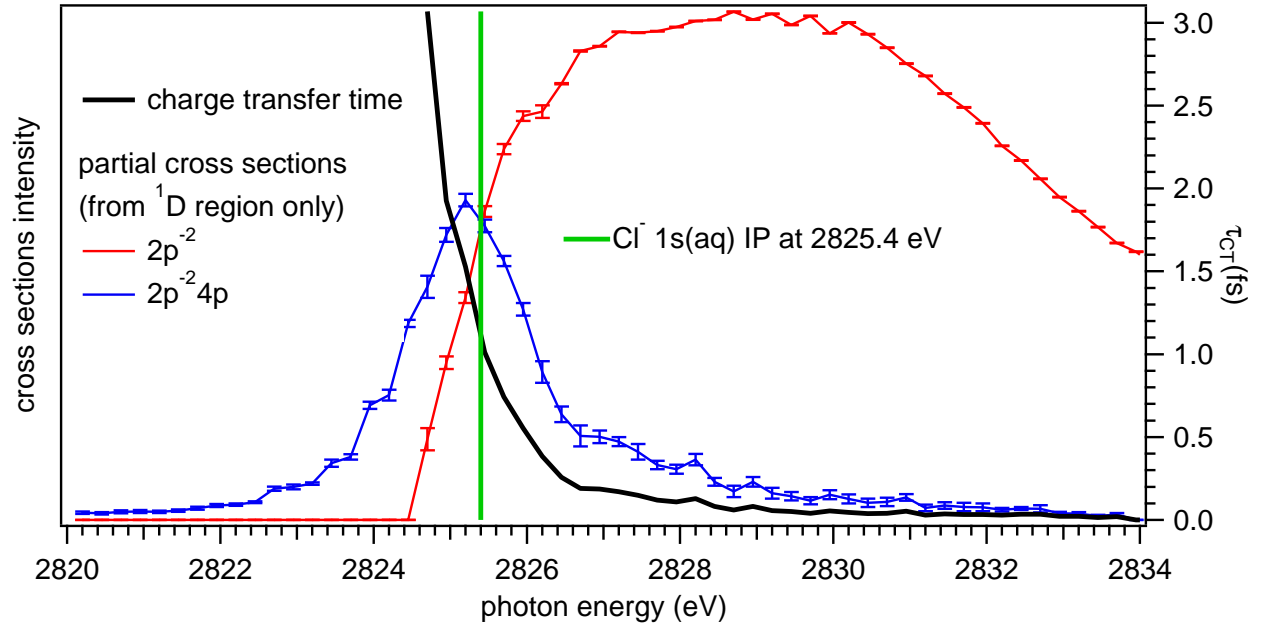


Figure 2: Partial cross sections and charge transfer time extracted from Fig. 3. The blue and red curves are obtained by integrating the area of the $2p^{-2}$ and $2p^{-2}4p$ final states (1D state region only) at each photon energy step. From these curves we determine the charge transfer time τ_{CT} according to the formula $\tau_{CT} = \tau_c l/d$, with τ_c 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.² The green line defines the $Cl_{aq}^{-}(1s)$ ionization potential.

References

- (1) Buckman, S. J.; Clark, C. W. *Rev. Mod. Phys.* **1994**, *66*, 539–655.
- (2) Föhlisch, A.; Feulner, P.; Hennies, F.; Fink, A.; Menzel, D.; Sanchez-Portal, D.; Echenique, P. M.; Wurth, W. *Nature* **2005**, *436*, 373.