Molecular Inner-Shell Spectroscopy: Electronic Structure and Intermolecular Interaction

Department of Photo-Molecular Science
Division of Photo-Molecular Science III

KOSUGI, Nobuhiro	Professor
YAMANE, Hiroyuki	Assistant Professor
NAGASAKA, Masanari	Assistant Professor
KIMBERG, Victor	Post-Doctoral Fellow
NAKANE, Junko	Secretary

In order to reveal electronic structure and intermolecular interaction of molecular solids, liquids, and clusters, we are developing and improving soft X-ray spectrometers for resonant Auger spectroscopy (RAS) and inelastic soft X-ray emission spectroscopy (XES). We are also developing and improving an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

1. Charge-Transfer- to-Solvent States of Aqueous Chloride Ions Revealed by Cl^- 2p Resonant Auger Spectroscopy[1)]

Charge transfer-to-solvent (CTTS) excited states of 2 mol/l NaCl and 3 mol/l LiCl aqueous solutions are revealed through soft X-ray electron spectroscopy. The excitation of the Cl 2p core electrons to the CTTS states is hardly visible in soft X-ray absorption spectroscopy. In this work it is clearly shown that the CTTS states can be detected by measuring RAS following the Cl 2p excitation to the CTTS state. During the resonance Auger decay emitting an Auger electron the CTTS electron behaves like a spectator; in the Auger final state with valence double holes, the CTTS electron gets strongly bound by a singly charged state and definitely observable.

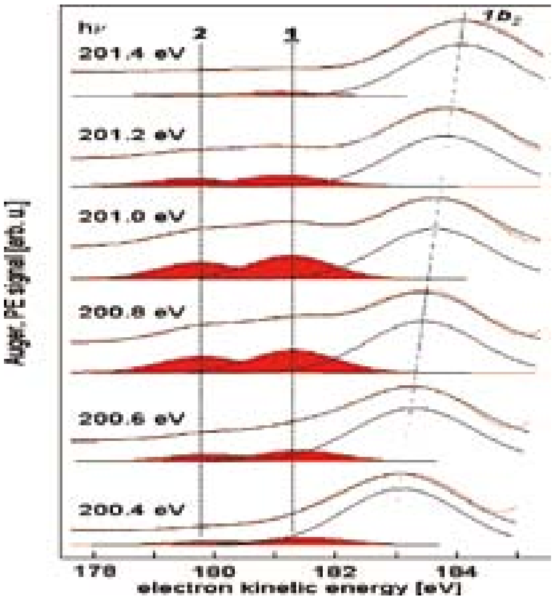

Figure 1. Photon energy dependence of electron kinetic energy spectra of resonant Auger electrons from the Cl 2p CTTS states in aqueous Cl^- ions and non-resonant photoelectrons from the liquid water $1b_2$ level.

The observed results are satisfactorily reproduced by *ab initio* calculations of four different cluster models to simulate about 2 mol/l NaCl and LiCl aqueous solutions, that is, 1 alkali halide and about 30 water molecules in a volume of $(10\ \text{Å})^3$. The initial guess of these geometries was chosen from a stable cluster of 30 H_2O molecules composed of five- and four-member water rings, where the center water molecule of this cluster was exchanged to either Cl or Na/Li. We chose two local minima for $LiCl{+}29{\cdot}H_2O$ and a local minimum for $NaCl{+}29{\cdot}H_2O$ and for $NaCl{+}31{\cdot}H_2O$. In these clusters Cl^- is stabilized by five or six nearest-neighbor H_2O molecules. The theoretical method for the Cl 2p ionized states (to describe photoionization) and Cl 3p doubly ionized states (to describe Auger decay) is also an all-electron ab initio approach taking into account Cl 2p and Cl 3p holes explicitly, using the GSCF3 code. The energy levels corresponding to CTTS electrons bound by single and double hole states, which are optimized within the static exchange (STEX) method, simulate the experimental results quite well.

As shown in Figure 1, we also have observed the small negative photon-energy dependence of the lowest spectator Auger electron, which indicates localized character of the lowest CTTS electron. Similar negative photon-energy dependence of the resonant Auger electron energy has been observed in molecular solid[2)] and DNA,[3)] and discussed in terms of localization and delocalization of the excitonic features.

The present liquid-jet experiments and *ab initio* calculations highlight the potential of combination of resonant inner-shell excitations with liquid photoelectron spectroscopy to explicitly characterize CTTS electron dynamics in aqueous solutions.

2. Exchange Interaction of Rydberg Electrons bound by Singly and Doubly Charged States in Small Kr Clusters[4)]

Similarly to the CTTS electron in aqueous solutions, the Rydberg electron in atomic van der Waals clusters is characterized by means of soft X-ray inner-shell spectroscopy. The Rydberg electron from neutral species is more strongly bound and more clearly observed than the CTTS electron from Cl^-.

Singly charged ion cores created by photoionization of atomic clusters are stabilized by the induced polarization (PL) interaction of the surrounding atoms, showing characteristic redshifts of the ionization energy. On the other hand, the photoexcitation creates Rydberg electrons bound by singly charged ion cores, as schematically shown in Figure 2(a). The photoexcitation energy sometimes shows blueshifts due to larger exchange (EX) interaction of a Rydberg electron with electrons of the surrounding atoms. Following the photoexcitation, the resonant Auger decay creates doubly charged ion cores with the Rydberg electron as a spectator. The doubly charged state can have four times larger PL interaction than the singly charged state. On the other hand, the EX interaction of Rydberg electrons is dependent on overlap of the wavefunctions, indicating that shrink of the Rydberg orbital in the doubly charged state increases more or less EX interaction.

Furthermore, small Kr clusters show surface site (‘corner,’ ‘edge,’ and ‘face’) dependent redshifts in ionization energy in X-ray photoelectron spectroscopy (XPS)[5)] and surface site dependent blueshifts and redshifts in excitation energy in x-ray absorption spectroscopy (XAS).[6)] In the present work, surface site dependent EX and PL interactions of small Kr clusters with an average size of Kr_{15} are investigated in doubly charged ion cores by resonant Auger spectroscopy (RAS), and compared by those in singly ionized core obtained by XAS.

Figure 2(b) shows XAS of Kr clusters at the Kr $3d_{5/2}$ edge. Several surface sites show different energy shifts at the 5p and 6p Rydberg states. The 5p electron has the largest EX interaction of the Rydberg states, because the radius of the 5p Rydberg orbital is close to the inter-atomic distance in Kr clusters and the higher Rydberg electron is more diluted in the cluster with decreasing overlap with the surroundings. It is also noted that the EX interaction is almost proportional to the nearest coordination number at the surface site.

Figure 2(c) shows RAS of Kr clusters in the $4s^{-1}4p^{-1}5p$ and $4p^{-2}6p$ regions after the ‘edge’ site excitation of the $3d_{5/2}{}^{-1}5p$ transition (91.37 eV). The EX interaction of the Rydberg electron in doubly charged ion core can be evaluated from the energy shift of RAS assuming the PL effect of the doubly charged ion is four times larger than that of the singly charged ion. Thus, we have found that the EX interaction of the Rydberg electron is greatly enhanced in the doubly charged ion core due to sudden shrink of the Rydberg orbital; the EX interaction of the 6p Rydberg electron with the doubly charged ion core is almost the same as EX of the 5p Rydberg with the singly charged ion core.

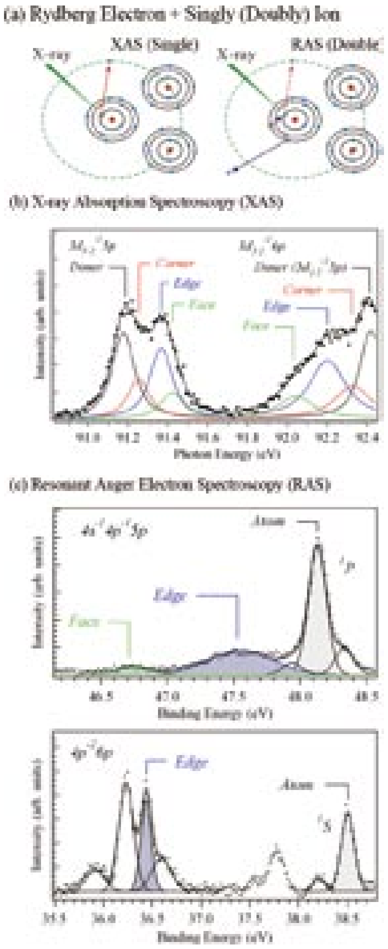

Figure 2. (a) Singly charged ion core and Rydberg electron as revealed by XAS. Doubly charged ion core and Rydberg electron as revealed by RAS. (b) Kr $3d_{5/2}$ XAS spectra of small Kr clusters in the $3d_{5/2}{}^{-1}5p$ and $3d_{5/2}{}^{-1}6p$ region. (c) RAS spectra of small Kr clusters in the $4s^{-1}4p^{-1}5p$ and $4p^{-2}6p$ region after the ‘edge’ site excitation of the $3d_{5/2}{}^{-1}5p$ transition (91.37 eV).

References

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