

Multi-atom Resonance in Simple Binary Molecules -Comparison between Solid and Aqueous Solution-

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1 Introduction

Multi-atom resonance (MAR) by X-ray irradiation is a phenomenon where intensity of photoelectrons (or Auger electrons, fluorescence X-rays) from an atom is changed by the resonant core-level excitation of the neighboring atom. The MAR phenomenon was firstly reported in photoelectron spectra for MnO [1]. On the other hand, MAR was not observed in C $K\alpha$ X-ray emission for TiNbC at the Ti $L_{2,3}$ resonance [2]. Although some experimental and theoretical studies have been reported after that, the uncertainty still remains as to whether MAR really happens or not.

In the present study, we re-investigated the existence of MAR by measuring the X-ray emission for simple binary molecules of alkali metal halide and alkali-earth metal halides. In order to make the existence of MAR more clearly, we particularly focused on comparison between solid and aqueous solution for the same molecule.

2 Experiment

The experiments were performed at the BL-27A soft X-ray station, Photon Factory. We used the specially designed X-ray fluorescence system [3], in which fluorescence X-ray absorption fine structure (XAFS) in soft X-ray region can be measured for both solid and liquid samples. The X-rays were irradiated from the bottom of the sample at the angle of 0.8° . The fluorescence X-ray was detected with Si drift detector that was located perpendicularly under the sample. The photon flux was normalized by the drain current of aluminium mesh located in front of the sample.

For solid sample, the reagent was mixed with cellulose powder and pulverized using a mortar. The concentration of the sample was 1wt%. Then, it was pressed into a pellet at a pressure of 3 ton/cm². For aqueous solution sample, the reagent was simply dissolved in pure water at a concentration of 1 wt%. The solution was put into a vessel, whose bottom was made of 4 μ m mylar film.

3 Results and Discussion

3.1 MAR for CaCl₂

Fig. 1 shows the intensity of the fluorescence X-rays for CaCl₂ as a function of the X-ray energy around the Ca K -edge. In Fig.1(a), the intensity of

the Ca $K\alpha$ X-rays was plotted, so the plots represent general XAFS spectra. The peak at 4045 eV originates from the resonant excitation from the Ca $1s$ to the unoccupied Ca $4p^*$ orbitals [3]. The intensity of the Cl $K\alpha$ X-rays was plotted in Fig.1(b). For solid sample shown as filled circles, the intensity was unexpectedly decreased around the Ca $1s \rightarrow 4p^*$ resonance. Since the concentration of CaCl₂ was so low (1%) that the effect of self-absorption of the incident and fluorescence X-rays can be neglected. Therefore, the observed decrease in the Cl $K\alpha$ intensity is considered to be caused by the Ca $1s \rightarrow 4p^*$ resonance excitation in the neighboring Ca atom. On the other hand, the decrease in the Cl $K\alpha$ intensity is not observed for aqueous solution. This is simply because the CaCl₂ was dissociated to Ca²⁺ and Cl⁻ ions, so few Cl atoms existed around a Ca atom.

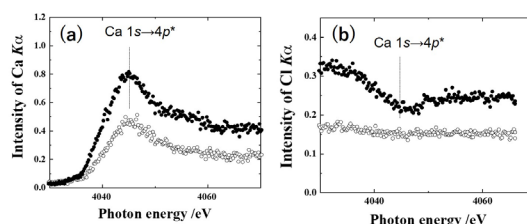


Fig. 1: Photon-energy dependencies of the intensity of Ca $K\alpha$ (a) and Cl $K\alpha$ (b) for 1% CaCl₂. Filled and open circles represent solid and aqueous solution,

3.2 MAR for KCl

Fig. 2 shows the photon-energy dependencies of fluorescence X-rays around the K K -edge for KCl. The peak at 3615 eV is attributed to the K $1s \rightarrow K$

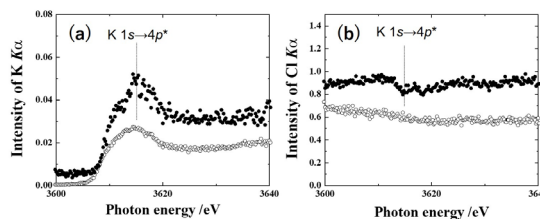


Fig. 2: Photon-energy dependencies of the intensity of K $K\alpha$ (a) and Cl $K\alpha$ (b) for 1% KCl. Filled and open circles represent solid and aqueous solution, respectively.

$4p^*$ resonance [4]. The results were similar to those for CaCl₂. For the intensity plots of Cl $K\alpha$ X-rays (Fig.

2(b)), the intensity of the solid sample was reduced around the $K\ 1s \rightarrow 4p^*$ resonance. But the intensity was constant for aqueous solution.

3.3 MAR for SrCl_2

The former two results were MAR in chlorine (anion) induced by the resonant excitation in the neighboring cation. In order to check whether the MAR in cation induced by the counter anion happens or not, we next investigated the MAR in SrCl_2 following the Cl K -edge resonant excitation. Fig. 3 shows the intensity of the Cl $K\alpha$ and Sr $L\alpha$ fluorescence X-rays as a function of the X-ray energy around the Cl K -edge for SrCl_2 . Deduced from the reported Cl K -edge XAFS spectra for alkali chlorides, the peak at 2825 eV is considered to originate from the Cl $1s \rightarrow 4p^*$ resonance [5]. In Fig. 3(b), the intensity of the Sr $L\alpha$ X-rays was reduced around the Cl $1s \rightarrow 4p^*$ resonance for solid. But the intensity was not changed for aqueous solution.

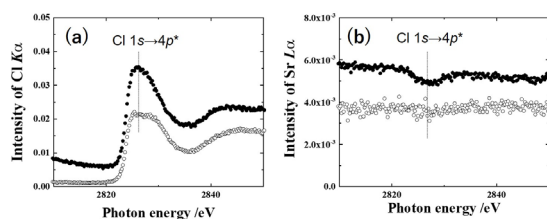


Fig. 3: Photon-energy dependencies of the intensity of Cl $K\alpha$ (a) and Sr $L\alpha$ (b) for 1% SrCl_2 . Filled and open circles represent solid and aqueous solution,

3.4 Possible mechanism of MAR

Resonant X-ray (or photoelectron, Auger electron) emission from a single atom is well established phenomenon. A typical example of X-ray emission from a single atom following resonant core-level excitation is shown in the upper part of Fig. 4, which is called “resonant x-ray emission” (or resonant x-ray Raman scattering). In this case, the intensity changes of X-ray emission can be simply explained by the changes in the inner-shell photoionization cross section (σ_A) of the atom. On the other hand, X-ray emission following the core-level resonant excitation in the neighboring atom is schematically shown in the lower part of Fig. 4. In this case, the intensity of X-ray (or photoelectron, Auger electron) emission from an atom “A” is perturbed by the changes in the inner-shell photoionization cross section of the neighboring atom “B”. As described above, MAR was firstly observed in photoemission from MnO where O $1s$ photoelectron emission was enhanced by the resonant excitation at the Mn L_3 -edge [1]. They interpreted this phenomenon in terms of the extension of resonant photoemission theory in a single atom to the interatomic case. As to the intensity, the reverse phenomena were observed in the present study, i.e., the intensity of X-ray emission from an atom was reduced at the

resonance excitation in the neighboring atom. Considering that the probability of X-ray emission after core-level ionization is determined by the fluorescence yield depending only on the atomic number, we consider that the intensity of the X-ray emission was changed not by the changes in the X-ray emission probability, but by the changes in the inner-shell ionization cross section itself.

Generally, the photoionization cross section of an atom “A” (σ_A) by X-ray irradiation is independently defined for the atom even for a molecule “A-B”. However, at the energy of the core-to-valence

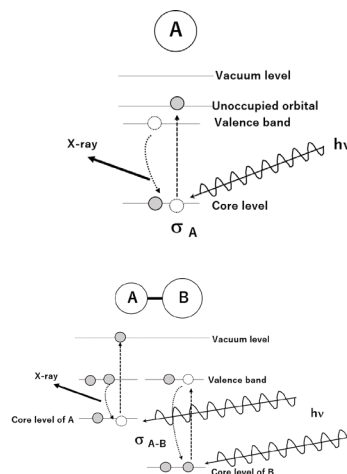


Fig. 4: Schematic diagrams of single-atom resonance (upper figure) and multi-atom resonance (lower figure) for X-ray emission.

resonance of the atom “A”, σ_A drastically increases, which coherently induces the reduction of σ_B . This means that we have to newly consider the photoionization cross section of a molecule, σ_{A-B} , at the resonance energy of one of the atoms.

Further theoretical study is needed to interpret the present results for MAR. Considering that the present phenomenon gives information about the atomic species of neighboring atoms, the phenomena will be applied to a method for structural analysis, which compensates the conventional synchrotron-based methods such as EXAFS and XANES.

References

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